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Checking kinetic modeling enhancement of the catalyzed BTBE synthesis reaction through Hansen solubility parameters

Uso de los parámetros de solubilidad de Hansen como mejora del modelo cinético de la reacción catalizada de síntesis de BTBE

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CONTENTS

SUMMARY

The prediction of reaction rates of the BTBE synthesis reaction is enhanced by including the reaction medium effect in the kinetic model, as demonstrated in a previous study based on experimental kinetic data. The Hildebrand solubility parameter was used to predict such interaction. The aim of the present work is to check if the use of the Hansen solubility parameters presents an advantage over Hildebrand solubility parameters in the kinetic modelling of the studied reaction, because it is based on a more accurate description of intra- and intermolecular forces.

Several estimation methods will be considered to find Hansen solubility parameters. The method which provides the best accurate results, will be used to find Hansen solubility parameters of BTBE. Different tests are carried out to check if Hansen solubility parameters depend significantly on temperature. At this point, the kinetic equation obtained from the previous work and other kinetic equations will be tested to find the best results that describe the kinetics of the BTBE synthesis.

1. INTRODUCTION

The reaction between isobutylene (IB) and 1-butanol (BuOH) in the presence of Amberlyst^{TM} 35 as the catalyst produces butyl *tert*-butyl ether (BTBE) (Fig. 1). BTBE can replace methyl (MTBE) and ethyl *tert*-butyl ether (ETBE) as oxygenate in gasoline blending to better enhance the octane number, among other properties. Until now, the production of BTBE was not raised because 1-butanol is expensive, but at present becomes more affordable from the increasing biomass use.

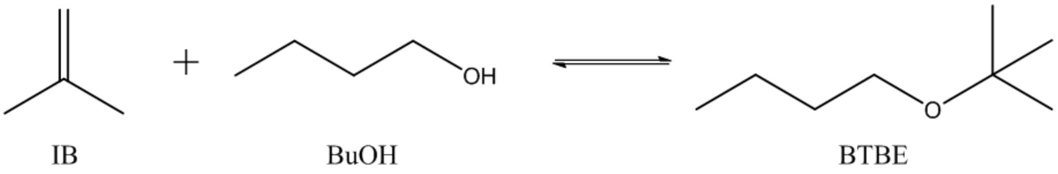

Figure 1. BTBE synthesis reaction.

Only a few literature references can be found focused on BTBE synthesis. A previous rigorous study was carried out to study the kinetics of the BTBE synthesis reaction [1]. The experimental procedure was done at 303-356 K and 1.5-2.0 MPa in the liquid phase in two different reactors (batch and fixed-bed). Initial BuOH/IB molar ratio varied between 1:1 and 2:1. The reaction rates of the mixture of Isobutylene and 1-butanol it is very slow, so to improve the reaction rates a catalyst is added to the mixture. Considering some physicochemical characteristics such as the pre-treatment requirements, thermal stability, acidity, and reaction development, macroporous ion exchange resins are the most efficient catalysts for this type of organic synthesis.

Amberlyst^{TM} 35, manufactured by DuPont, has been proved to produce high velocity rates. It is a sulfonic macroreticular styrene divinylbenzene resin (Fig. 2) with different pore levels (macro-, meso- and microporous). In *Appendix 1* the main properties of this catalyst are listed.

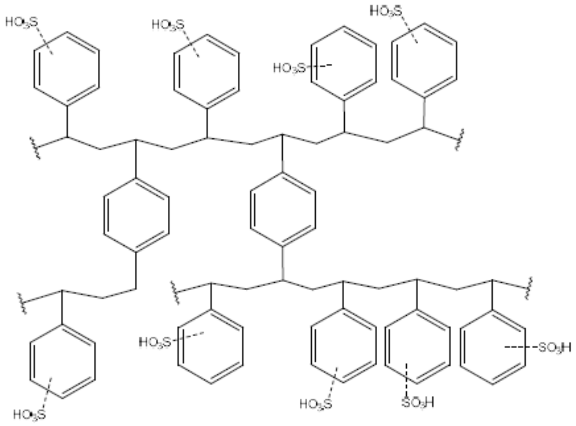

Figure 2. Structure of Amberlyst^{TM} 35.

One of the main characteristics of this catalyst is that the resin swells depending on the reaction medium. That means changes in accessibility to active centres and distance between them as the reaction proceeds (Fig. 3). Therefore, catalytic activity is affected along with conversion which it involves reaction medium effect has to be included in the kinetic model.

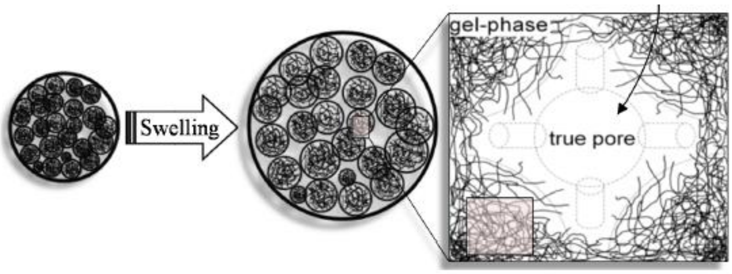

Figure 3. Catalyst swelling.

1.1 Kinetic Model

The best kinetic model searched among a large number of kinetic equations resulting from the systematic combination of possible elementary reactions, absorbed species, and rate-determining step, is the kinetic model for reactions catalysed by solids obtained from Langmuir-Hinselwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) formalism. The Eley-Rideal mechanism describes a reaction between a reactant which has chemisorbed and another one directly from the fluid phase. The mechanism proposed to describe the BTBE synthesis consists of the following steps (Fig. 4) [2]:

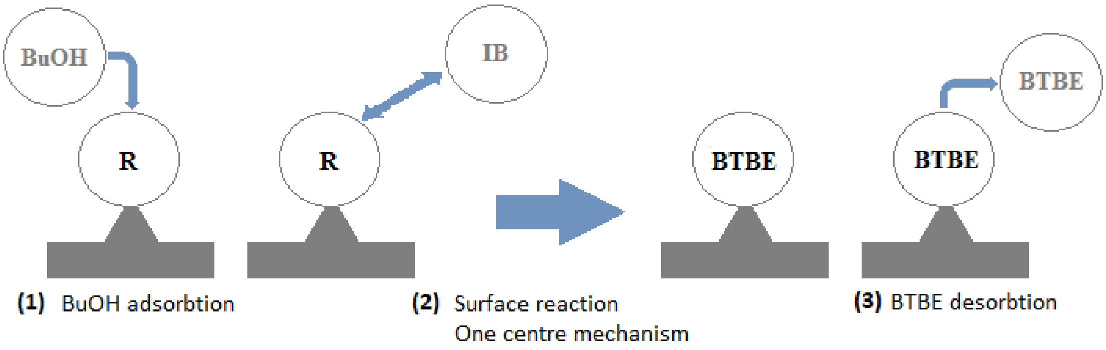

Figure 4. Elemental steps of BTBE synthesis through Eley-Rideal mechanism [2].

1) One molecule of 1-butanol adsorbs on a resin active site.
2) It reacts with one molecule of isobutylene from the solution to form one molecule of adsorbed BTBE.
3) The newly formed BTBE molecule desorbs.

The rate-limiting step of the overall reaction process is the surface reaction step.

Hyperbolic expressions are obtained, whose general form is (Yang and Hougen, 1950) [3]:

$$\begin{Bmatrix} reaction \\ rate \end{Bmatrix} = \begin{Bmatrix} kinetic \\ term \end{Bmatrix} \frac{\{driving\ force\}}{\{adsorption\ term\}^n} \qquad (1.1)$$

where n is the number of active centres that take part in rate determining step of the reaction.

Due the effect of the catalyst on the reaction rate, the interaction between the resin and the medium should be included:

$$\begin{Bmatrix} reaction \\ rate \end{Bmatrix} = \begin{Bmatrix} kinetic \\ term \end{Bmatrix} \frac{\{driving\ force\}}{\{adsorption\ term\}^n} \begin{Bmatrix} resin - medium \\ interaction \end{Bmatrix} \qquad (1)$$

The kinetic model proposed in the previous experimental work [1]:

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

$$\begin{Bmatrix} \boldsymbol{kinetic} \\ \boldsymbol{term} \end{Bmatrix} = k' \left[\frac{mol}{g\ h}\right] = exp\left[(0.320 \pm 0.006) - (9.17 \pm 0.04) \cdot 10^3 \left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$\{\boldsymbol{driving\ force}\} = \left(a_{IB}\ a_{BuOH} - \frac{a_{BTBE}}{K_{Eq}}\right)$$

$$\{\boldsymbol{adsorption\ term}\}^{\boldsymbol{n}} = a_{BuOH} + K_{BTBE} a_{BTBE}$$

$$\begin{Bmatrix} \boldsymbol{resin - medium} \\ \boldsymbol{interaction} \end{Bmatrix} = exp\left(\frac{\bar{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$$

where: k’ is the kinetic coefficient. aIB, aBuOH and aBTBE are activities of the three main components of BTBE synthesis. UNIFAC-Dortmund activities were used instead of concentrations due to high non-ideality of the reacting mixtures [31]. K_{eq} is the chemical equilibrium constant for the synthesis of BTBE. K_{BTBE} is the adsorption equilibrium constant. $\bar{V}_M$ is the molar volume of the mixture. ϕ_P^2 is the catalyst porosity in the swollen-state that is considered: 0.513. R is the constant of ideal gases considered: 8.31J/(mol·K). T is the temperature. δ_M is the solubility parameter of the medium δ_P is the solubility parameter of the resin.

The interaction term between the resin and the reaction medium is based on the difference between the solubility parameter of the medium (δ_M) and solubility parameter of the resin (δ_P). The SI units for the solubility parameter are $MPa^{1/2}$.

1.2 Hildebrand solubility parameter

The solubility parameter is a numerical value that indicates the relative solubility capacity of a specific solvent by means of the strength of molecular interaction between solvent molecules [4]. So the solubility parameter reflects the cohesive energy of species.

The term solubility parameter was first used by Hildebrand and Scott [5, 6]. It has been shown as a useful factor in the determination and prediction of the fundamental properties of material such as solubility and swelling of polymers by solvents and/or being an effective tool for selecting a favourable solvent for main applications such as [7]: solvent selection, drug permeation to skin, gas capture tablet film coating, etc. [8-12]. The use of the solubility parameter for the selection of solvents is based on the well-known rule of chemistry: “like dissolves like” [13]. Thus, if the intermolecular forces between the molecules of the solvent and between the molecules of a solute are of a similar strength, the solvent is usually a good solvent for this solute.

In the previous work [1], the Hildebrand solubility parameter was used estimate the medium solubility parameter to describe the interaction between the catalyst and the reaction medium.

Hildebrand solubility parameter (δ_{Hil}) can be evaluated by various methods: heat vaporization (ΔH_V)-temperature data, group contribution, solubility measurement, osmotic pressure, swelling, intrinsic viscosity, etc. [14, 15]. The most common method is using the cohesive energy. Hildebrand solubility parameter (δ_{Hil}) [5], is defined as the square root of the cohesive energy density:

$$\delta_{Hil} = \sqrt{\frac{E_{coh}}{V_i}} \qquad (3)$$

where V_i is the molar volume of the pure solvent i and E_{coh} is the cohesive energy given by equation (5):

$$E_{coh} = \Delta H_{vap,i} - RT \qquad (4)$$

where $\Delta H_{vap,i}$ is the enthalpy of vaporization of the compound i, R is the universal gas constant, and T is the absolute temperature. Thus, the Hildebrand solubility parameter for liquid-phase individual compounds, δ, at a given temperature, T, can be estimated by the following equation:

$$\delta_i = \sqrt{\frac{\Delta H_{vap,i} - RT}{V_i}} \qquad (5)$$

The medium solubility parameter at a given temperature is estimated as the Hildebrand solubility parameter for liquid-phase mixtures, δ_M. For a liquid mixture, it can be calculated as follows:

$$\delta_M = \sum_i \Phi_i \, \delta_i \qquad (6)$$

where Φ_i is the volume fraction of compound i. If additive volumes are considered, volume fractions can be calculated as:

$$\Phi_i = \frac{x_j \frac{M_j}{\rho_j}}{\sum_k x_k \frac{M_k}{\rho_k}} \qquad (7)$$

where x_j, Mj, ρj are the molar fraction, molecular mass and density of compound j.

The Hildebrand solubility parameter was considered in the previous kinetic study [1] to find the best kinetic equation that describes the experimental reaction rates among a large number of candidate models. As a general conclusion, the best ranked models included the resin-medium interaction term. Fig. 5 shows the comparison between experimental and calculated values for the best kinetic model.

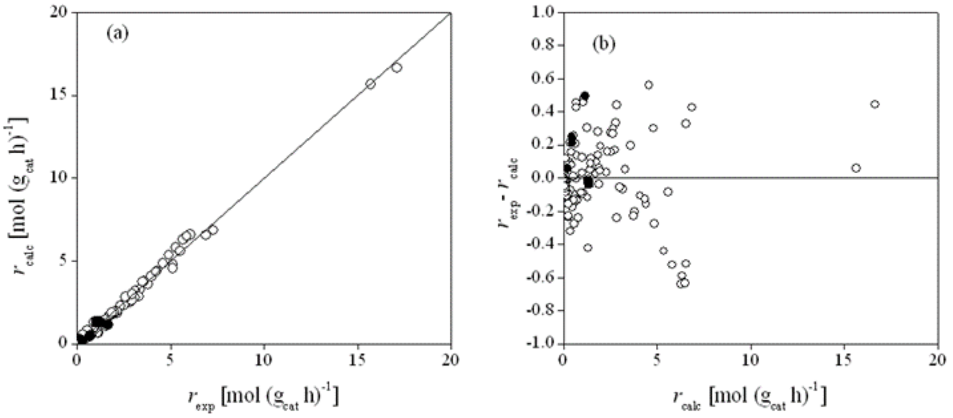

Figure 5. Fit of the proposed kinetic equation as the best kinetic model in a previous work [1].

The kinetic model proposed fits pretty good to experimental data. But, the question raised is if a better kinetic equation could be obtained using an alternative method to estimate the solubility parameter δ_M.

At first, Hildebrand solubility parameter appears to be a good description of the intermolecular interactions for pure liquids. But for many liquids and polymers, Hildebrand solubility parameters may be not enough to describe the solubility behaviour. In the Hildenbrand solubility parameter, only dispersion forces between structural units are taken into account. But the cohesive energy is not only dependent of dispersion forces, it is also dependent of the interaction between polar groups and on hydrogen bounding. For that reason, Hildebrand parameters can be useful for non-polar, non-hydrogen-bonding solvents, but it could be not enough descriptive for liquids with polar and hydrogen-bonding interactions. In mixtures of dissimilar components in contact with a solid catalyst, interactions are expected to be more complex and, therefore, more effects should be considered. The Hansen solubility parameter is based on a more accurate description of intra- and intermolecular forces and, for that reason, it is expected to better predict such interactions.

1.3 Hansen solubility parameter

The basis of Hansen solubility parameter is that the total cohesive energy (E_{coh}) of a liquid consists of three major intermolecular interactions [16]:

$$E_{coh} = E_D + E_P + E_H \qquad (8)$$

Dispersion forces, (E_D):

Dispersion forces are derived from atomic forces and are also considered a type of Van der Waals interactions. As molecules are built up from atoms, all molecules contain those types of attractive forces.

Polar forces, (E_P):

Polar forces are derived from molecular dipolar interactions. These are inherently molecular interactions and are found in most molecules.

Hydrogen bond forces, (E_H):

Hydrogen bonding can be called an electron exchange parameter. It accounts for molecular interaction due to hydrogen bonds.

The square of the Hildebrand solubility parameter is obtained as the sum of the squares of Hansen components, each being the ratio of the type of forces and the molar volume:

$$\frac{E_{coh}}{V} = \left(\frac{E_D}{V}\right) + \left(\frac{E_P}{V}\right) + \left(\frac{E_H}{V}\right) \qquad (9)$$

Equation 10 describes the relation between the Hansen solubility parameter, δ_t, and its three solubility parameters contributions, δ_D, δ_P, and δ_H.

$$\delta_t^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad (10)$$

The unit of solubility parameters in the SI system of units is ($MPa^{1/2}$). As a consequence, the Hansen solubility parameter can be seen through a geometric image in a 3D space, where it is the vector with components δ_D, δ_P, and δ_H to form the Hansen space (Fig. 6).

In practice, two different compounds are more likely to dissolve into each other not just because the present a similar modulus of the Hansen solubility parameter, but also because their vectors are very close in the Hansen space.

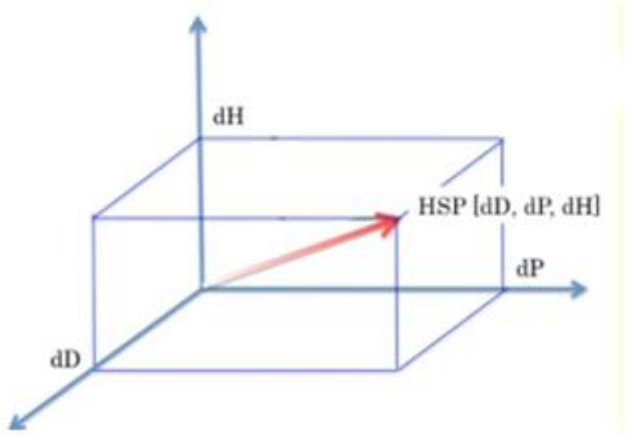

Figure 6. Hansen space [40].

So, comparing the Hildebrand solubility model and Hansen solubility model the difference between them is appreciable.

Hildebrand solubility model (Figure 7) consider that those solvents within a range ± 2 $MPa^{1/2}$ of the solubility parameter of the polymer, are good solvents and those solvents that the different between its solubility parameter and the solubility parameter of the polymer is more than ± 2 $MPa^{1/2}$ are considered non-solvent.

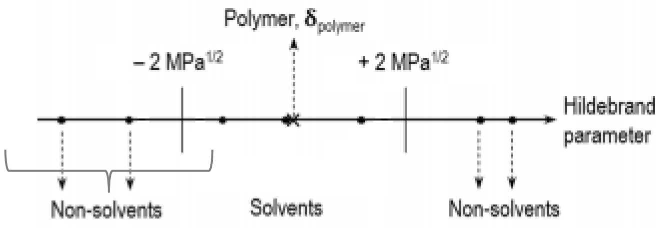

Figure 7. Hildebrand solubility model [41].

On the other hand, if visualized as three dimensional plot, the axes being $2\delta_D$, δ_P and δ_H, the polymers and solvents are represented by points in this space (Figure 8). Those solvents within a sphere radius R = 8 $MPa^{1/2}$ centred at a point corresponding to a polymer are good solvents for that polymer, and those solvents falling outside the sphere are considered non-solvents.

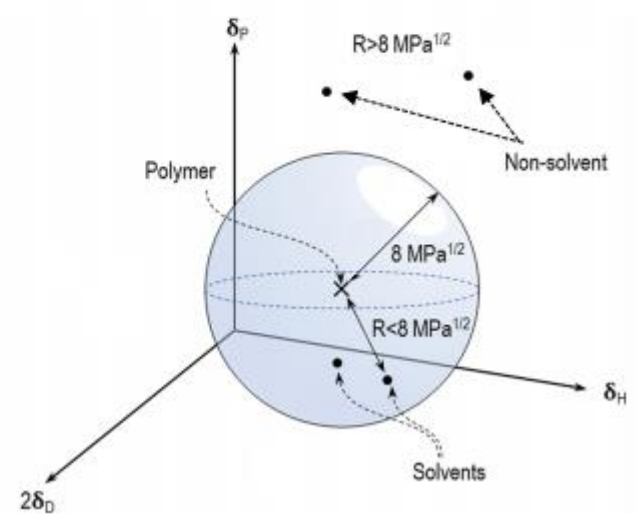

Figure 8. Hansen solubility model [41].

So, for δ_M of BTBE synthesis, the Hansen solubility parameter is expected to better predict compound interactions than the Hildebrand solubility parameter. The procedure to estimate HSPs of the mixture for each point of the reaction mixture and to apply it in the fit of the kinetic model is as follows:

1. First, estimate the Hansen Solubility parameters of each pure component involved in the reaction.
2. Estimate molar volumes for each component at every single temperature and pressure points of the reaction. From HSP's and molar volumes of each component at every single point estimate HSPs of the mixture at each point of the reaction.

3. Fit the proposed kinetic model, (Equation 2), to the experimental reaction rate data using the Hansen solubility parameter in the resin-medium interaction term.
4. Check if the changes in the Hansen solubility parameters taking into account the temperature dependence affects significantly to the fitting.
5. Test different kinetic models check if a better kinetic model exists.

2. OBJECTIVES

The aim of the present work is to check if the use of Hansen solubility parameters presents a distinct advantage over Hildebrand solubility parameters in the kinetic modelling of the studied reaction. The project is divided in different stages:

- Estimation of Hansen solubility parameters of the reaction medium for each experimental point.
- Fitting kinetic equations (proposed and alternatives) to experimental data.
- Check:
    - Does the Hansen solubility parameter improve the fit to experimental data?
    - Which is the best way to quantify interaction?
    - Do the fitted parameters depend significantly on temperature?
    - Would an alternative kinetic equation be better?

3. METHODS

The best method to calculate individual Hansen solubility parameters (HSPs) depends to a great extent on what data are available. Using Hansen Database [16], Hansen solubility parameters of both, 1-butanol and isobutylene are obtained. Nevertheless, for butyl *tert*-butyl ether and other secondary products of the reaction as: isobutane and trans-2-butene, data for estimation are not available, because of a lack of information about this compound. So, several estimation methods are proposed to estimate Hansen solubility parameters of butyl *tert*-butyl ether and the secondary products of the reaction. The method which provides the most similar value to real Hansen solubility parameters of isobutylene and 1-butanol will be the chosen one to estimate HSPs of butyl *tert*-butyl ether and the secondary products of the reaction. They are group contribution methods:

3.1. Stefanis –Panayiotou method.

The molecular structure of each organic compound is described by the use of two kind of functional group: first-order groups (UNIFAC groups) that describe the basic molecular structure of compounds and second- order groups that are based on the conjugation theory and give a physical meaning to the method [17].

This method allows a rough estimate keeping things simple just ignoring the 2nd-order groups. The basic equation that is based this method is:

$$f\ (x) = \sum_i N_i\, C_i + W\ \sum_i M_j\, D_j \qquad \text{(A1)}$$

where C_i is the contribution of the first-order group of type i that appears N_i times in the compound, and D_j is the contribution of the second-order group of type j that appears M times in the compound. For compounds without second-order groups, W is equal to 0 and equal to 1 for compounds with second-order groups.

For many compounds, first-order groups are sufficient, but it can be improved with the introduction of second-order groups based on the ABC framework [38, 39].

The equations for the estimation of Hansen solubility parameters applying Stefanis-Panayiotou method are the following:

$$\delta_D = (\sum_i N_i\, C_i + W\ \sum_i M_j\, D_j + 17.3231)\ [MPa^{1/2}] \qquad \text{(A2)}$$

$$\delta_p = (\sum_i N_i\, C_i + W\ \sum_i M_j\, D_j + 7.3548)\ [MPa^{1/2}] \qquad \text{(A3)}$$

$$\delta_H = (\sum_i N_i\, C_i + W\ \sum_i M_j\, D_j + 7.9793)\ [MPa^{1/2}] \qquad \text{(A4)}$$

If the values of δ_P and δ_H are expected to be low (less than 3 MPa$^{1/2}$), the equations for the estimation of these parameters are the following:

$$\delta_P = (\sum_i N_i\, C_i + W\ \sum_i M_j\, D_j + 2.7467)\ [MPa^{1/2}] \qquad \text{(A5)}$$

$$\delta_H = (\sum_i N_i\, C_i + W\ \sum_i M_j\, D_j + 1.3720)\ [MPa^{1/2}] \qquad \text{(A6)}$$

The first-order group and second-order group contributions to the dispersion partial solubility parameter, δ_d, the polar partial solubility parameter, δ_p, and the hydrogen-bonding partial solubility parameter δ_h, are attached in tables of [17].

The values of the group contribution used of both components (Isobutylene and 1-butanol) are shown in [Table A1 and A2]:

Table A1. Isobutylene group contribution (Stefanis-Panaytou method).

Group contribution	Nº	δ_D	δ_P	δ_H
$-CH_3$	2	-0.9714	-1.6448	-0.7813
$CH_2=C<$	1	-0.4829	-0.7794	-0.8260

Only First-Order groups are used for isobutylene, but δ_p and δ_h are expected to be lower than 3 MPa$^{1/2}$:

$$\delta_D = (\sum_i N_i\, C_i + 17.3231)\ [MPa^{1/2}] \qquad \text{(A2.1)}$$

$$\delta_P = (\sum_i N_i\, C_i + 2.7467)\ [MPa^{1/2}] \qquad \text{(A5.1)}$$

$$\delta_H = (\sum_i N_i\, C_i + 1.3720)\ [MPa^{1/2}] \qquad \text{(A6.1)}$$

Table A2. 1-Butanol group contribution (Stefanis-Panayiotou method).

Group contribution	Nº	δ_D	δ_P	δ_H
$-CH_3$	1	-0.9714	-1.6448	-0.7813
$-CH_2$	3	-0.0269	-0.3045	-0.4119
-OH	1	-0.3462	1.1404	7.1908

Given that only first-order groups are used, and that δ_p and δ_h are expected to be higher than 3 $MPa^{1/2}$, the equations to be used are the following, with W= 0:

$$\delta_D = (\sum_i N_i\, C_i + 17.3231)\ [MPa^{1/2}] \qquad \text{(A2.1)}$$

$$\delta_P = (\sum_i N_i\, C_i + 7.3548)\ [MPa^{1/2}] \qquad \text{(A3.1)}$$

$$\delta_H = (\sum_i N_i\, C_i + 7.9793)\ [MPa^{1/2}] \qquad \text{(A4.1)}$$

3.2. Hoftyzer-Van Krevelen method.

The Hansen solubility parameters of a compound may be predicted using Hoftyzer-Van Krevelen group contributions method. The equation for the estimation of dispersion partial solubility parameters is [18]:

$$\delta_D = \frac{\sum F_{di}}{V} \qquad \text{(B1)}$$

where F_{di} are the group contributions of type *i* to the dispersion component*,* F_d, and *V* is the molar volume.

$$\delta_P = \frac{\sqrt{\sum F_{pi}^{\,2}}}{V} \qquad \text{(B2)}$$

where F_{pi} are the group contributions of type *i* to the polar component*, Fp*.

If the compound has two identical polar groups in a symmetrical position, the polar component is reduced. Then, to take this effect into account, the value calculated by Equation B2 must be multiplied by a symmetry factor of:

- 0.5 for one plane of symmetry

- 0.25 for two planes of symmetry
- 0 for more planes of symmetry

The equation for the estimation of hydrogen-bonding energy is the following:

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \qquad \text{(B3)}$$

where E_{hi} is the hydrogen-bonding energy per structural group *i*.

For molecules with several planes of symmetry, δ_H=0.

The group contributions F_{di}, F_{pi} and E_{hi}, used are presented in [Tables B1 and B2]:

Table B1. Group contribution parameters for isobutylene (Hoftyzer-Van Krevelen method) [18].

Group contribution	Nº	F_d	F_p^2	E_{hi}
$-CH_3$	2	420	0	0
$CH_2=$	1	400	0	0
$=C<$	1	70	0	0

Table B2. Group contribution parameters for 1-butanol (Hoftyzer-Van Krevelen method) [18].

Group contribution	Nº	F_d	F_p^2	E_{hi}
$-CH_3$	1	420	0	0
$-CH_2$	3	270	0	0
-OH	1	210	250000	20000

3.3. Hoy method.

Hoy method is a different group-contribution method to estimate the Hansen solubility parameters. In this method, a system of equations is used. It contains four additive molar functions, a number of auxiliary equations and the final expressions for the component $\delta_{t\ (total)}$ and for the components of δ [19].

In the case of low-molecular liquids (solvents) the system of equations proposed by Hoy is as follows:

Table C1. Additive molar functions for Hoy method [19].

	Low-molecular liquids (solvents)	
Additive molar functions	$F_t = \sum N_i F_{t,I}$	(C1)
	$F_p = \sum N_i F_{p,i}$	(C2)
	$V = \sum N_i V_i$	(C3)
	$\Delta_T = \sum N_i \Delta_{T,i}$	(C4)

where *Ft* is the molar attraction function, *Fp* is its polar component, and *V* is the molar volume. Δ_T is the Lydersen correction for non-ideality [20] which is used in the auxiliary equations [Table C2].

Table C2. Auxiliary equations for Hoy method [19].

	Low-molecular liquids (solvents)	
Auxiliary equations	$\text{Log } \alpha = 3.39 \log(T_b/T_{cr}) - 0{,}1585 - \log V$	(C5)
	$T_b/T_{cr} = 0567 + \Delta_T - (\Delta_T)^2$	(C6)

α: molecular aggregation number, T_b: boiling point, and T_{cr} : critical temperature.

The expressions for δ components are showed in Table C3.

Table C3. Equations to be used in Hoy for estimation of the solubility parameters and its components [42].

	Low-molecular liquids (solvents)	
Expressions for δ and δ-components	$\delta_t = \frac{F_t + B}{V};$	(C7)
	$\delta_p = \delta_t \left(\frac{1}{\alpha} \frac{Fp}{Ft + B}\right)^{1/2}$	(C8)
	$\delta_h = \delta_t \left(\frac{\alpha - 1}{\alpha}\right)^{1/2}$	(C9)
	$\delta_d = (\delta_t^2 - \delta_p^2 - \delta_h^2)^{1/2}$	(C10)

where *B* is the base value. The method of Hoy, is the only method that uses a base value *"B"* in the estimations of δ parameters of low-molecular liquids (solvents). This value, is fixed as 277 and it appears in the estimation of δ_t and δ_p.

The values of the group contribution of both components is shown in Tables C4 and C5:

Table C4. Group contribution parameters for isobutylene (Hoy method) [19].

Group contribution	Nº	F_T	F_p	V	ΔT
$-CH_3$	2	303.5	0	21.55	0.023
$CH_2=$	1	259	67	19.17	0.018
=C<	1	173	63	7.18	0

Table C5. Group contribution parameters for 1-butanol (Hoy method) [19].

Group contribution	Nº	F_T	F_p	V	ΔT
$-CH_3$	1	303.5	0	21.55	0.023
$-CH_2-$	3	269	0	15.55	0.020
-OH	1	675	675	12.45	0.082

3.4. Yamamoto method

The method of Yamamoto is based in different correlations [21]:

- A correlation between the boiling point and latent heat of vaporization.
- Correlation between the square root of molecular weight and boiling point
- Correlation between the latent heat of vaporization with the solubility parameter.

Stating by some considerations Yamamoto's method estimates δ_d using the following equation:

$$\delta_d{}^2 = \delta_{Dvdw} + \delta_{Dfg} \qquad (D1)$$

where:

- δ_{Dvdw} is a value determined only from the molecular weight and the molar volume. All compounds have the scheme (Equation D2) force as a universal interaction force:

$$\delta_{\mathrm{Dvdw}} = (9.0463 * \mathrm{MW0.5} + 28.51)/(\mathrm{Molar\ volume}) = 0.5 \qquad \text{(D2)}$$

- δ_{Dfg} is an interaction based on the polarizability of the functional group.

Both, partial solubility parameters δ_p and δ_h are obtained using a functional group method:

$$\delta_P = \left(\sum_i N_i\, V_i\, \delta_{P,i}\right) / \sum_i Vi \qquad (D3)$$

$$\delta_H = \left(\sum_i N_i\, V_i\, \delta_{H,i}\right) / \sum_i Vi \qquad (D4)$$

where $\delta_{P,i}$ / $\delta_{H,i}$ is the contribution of the polar / hydrogen-bounding group of type *i* that appears N_i times in the compound and V_i is the molar volume of each functional group.

The values of the group contribution of both components are the following:

Table D1. Group contribution parameters for isobutylene (Yamamoto method) [21].

Group contribution	Nº	δ_D	δ_{Dfg}	δ_P	δ_H	Vol	MW
$-CH_3$	2	12.9	7.5	0.7	0.1	28.85	15.034
$CH_2=$	1	11	0	3.2	4.2	26.50	14.026
C:_rrr	1	25.3	24.1	0.1	1.1	10.92	12.01

Table D2. Group contribution parameters for 1-butanol (Yamamoto method) [21].

Group contribution	Nº	δ_D	δ_{Dfg}	δ_P	δ_H	Vol	MW
$-CH_3$	1	12.9	7.5	0.7	0.1	28.85	15.034
CH_2	3	16.4	14.3	1.5	0.9	22.05	14.026
-OH	1	181.4	11.3	16.6	36.6	18.05	17.008

3.5. Temperature dependence of Hansen Solubility parameters

Only very limited attempts have been made to calculate solubility parameters at a temperature higher than 25°C. Recalculation of HSP at higher temperatures are possible, but generally they are not found necessary [16].

HSP values changes with temperature. If temperature raises, then the density decreases so the HSP values decrease. A temperature increase can cause a non-solvent to become a good solvent. The effect depends on temperature increasing from 25°C, and on the thermal expansion coefficient, α. The change of δ_D, δ_P and δ_H with temperature can be estimated using the following equations [16]:

$$\frac{d\delta_D}{dT} = -1.25\alpha\delta_D \qquad (5.1)$$

$$\frac{d\delta_P}{dT} = -0.5\alpha\delta_P \qquad (5.2)$$

$$\frac{d\delta_H}{dT} = -\delta_H(1.22\ x\ 10^{-3} + 0.5\alpha) \qquad (5.3)$$

where α is the thermal expansion coefficient.

An alternative way to relate temperature variations with HSP for polymers has been suggested [22]:

$$\delta = \delta_g + m_i\left(T - T_g\right) \qquad (5.4)$$

where m_i is an empirical constant, and δ_g is the solubility parameter at glass transition temperature T_g.

In this case, HSPs temperature dependence is estimated as follows:

$$\int_{\delta_{D0}}^{\delta_{Df}} \frac{d\delta_D}{\delta_D} = \int_{T_0}^{T_f} -1.25\ \alpha\ dT \qquad (5.5)$$

$$\int_{\delta_{P0}}^{\delta_{Pf}} \frac{d\delta_P}{\delta_P} = \int_{T_0}^{T_f} -0.5\alpha\ dT \qquad (5.6)$$

$$\int_{\delta_{H0}}^{\delta_{Hf}} \frac{d\delta_H}{\delta_H} = \int_{T_0}^{T_f} -(1.22\ x\ 10^{-3} + 0.5\alpha)dT \qquad (5.7)$$

Due the slightly variation of thermal expansion coefficient with temperature and the lack of information for isobutylene and BTBE, thermal expansion coefficient can be considered as constant with temperature variation obtaining the following equations:

$$ln\delta_{Df} = ln\delta_{D0} - 1.25\alpha\delta_D(T_f - T_0) \qquad (5.8)$$

$$ln\delta_{Pf} = ln\delta_{P0} - 0.5\alpha\delta_P(T_f - T_0) \qquad (5.9)$$

$$ln\delta_{Hf} = ln\delta_{H0} - (1.22\ x\ 10^{-3} + 0.5\alpha)\ (T_f - T_0) \qquad (5.10)$$

Values of thermal expansion coefficient are obtained from references 23 and 24.

The next step is to obtain Hansen solubility parameters of mixtures for each reaction medium composition.

3.6. Hansen solubility parameters of mixtures

Hansen solubility parameters (HSP) of mixtures are estimated from Hansen solubility parameters of each compound present in the reaction medium. Obviously, different values can be obtained if the temperature dependence is taken into account.

HSP for mixtures are additive according to the respective volume fraction of its components. Hansen solubility parameters of a liquid-phase mixtures, $\delta_D^M,\ \delta_P^M\ and\ \delta_H^M$, can be calculated as follows:

$$\delta_D^M = \sum_{i=1} \delta_{Di}^{Si}\,\varphi_i = \delta_{D1}^{S1}\varphi_1 + \delta_{D2}^{S2}\varphi_2 + \delta_{D3}^{S3}\varphi_3 \qquad (6.1)$$

$$\delta_P^M = \sum_{i=1} \delta_{Pi}^{Si}\,\varphi_i = \delta_{P1}^{S1}\varphi_1 + \delta_{P2}^{S2}\varphi_2 + \delta_{P3}^{S3}\varphi_3 \qquad (6.2)$$

$$\delta_H^M = \sum_{i=1} \delta_{Hi}^{Si}\,\varphi_i = \delta_{H1}^{S1}\varphi_1 + \delta_{H2}^{S2}\varphi_2 + \delta_{H3}^{S3}\varphi_3 \qquad (6.3)$$

where φ_i is the volume fraction of each reaction species, S_i

Under the assumption that volumes are additive, volume fractions can be calculated as:

$$\Phi_j = \frac{x_j \frac{M_j}{\rho_j}}{\sum_k x_k \frac{M_k}{\rho_k}} \qquad (6.4)$$

where x_j is the molar fraction, M_j is the molar mass and ρ_j is the density of pure compound *j*.

Molar mass divided by density can be expressed as molar volume:

$$\frac{M\ [\cancel{kg}/mol]}{\rho\ [\cancel{kg}/L]} = V_m \left[\frac{L}{mol}\right] \qquad (6.5)$$

$$\Phi_j = \frac{x_j V_{mj}}{\sum_k x_k V_{mk}} \qquad (6.4.1)$$

As the reaction proceeds, molar fractions of each component will change. Molar fraction of BTBE will increase while isobutylene and 1-butanol molar fraction will decrease. Molar fractions are obtained in a previous experimental study [1].

On the other hand, molar volumes can be estimated using Hankinson-Brobst-Thomson method (HBT) [25-28]:

- Hankinson-Brobst-Thomson (HBT) method for the estimation of molar volume:

Molar volume is a function of temperature and pressure. Estimation of the molar volume, V_m, through the Hankinson-Brobst-Thomson (HBT) method can be accomplished by the following expresions [25-27]:

$$V = V_s - c\, ln\frac{\beta+P}{\beta+P_v} \qquad \text{(E1)}$$

$$\frac{\beta}{P_C} = -1 + a\,(1-T_r)^{1/3} + b\,(1-T_r)^{2/3} + \; c\,(1-T_r) + d\,(1-T_r)^{4/3} \quad \text{(E2)}$$

Where:

$a = -9.070217$ $\qquad$ $b = 62.45326$

$c = j + k\,\omega_{SRK}$ $\qquad$ $d = -135.1102$

$e = \exp\,(f + g\,\omega_{SRK} + h\,\omega_{SRK}^2)$ $\qquad$ $f = 4.79594$

$g = 0.250047$ $\qquad$ $h = 1.14188$

$j = 0.0861488$ $\qquad$ $k = 0.034483$

where V_S is the saturated liquid volume at the vapour pressure, *Pv*. T_r is the reduced temperature (T/T_C) and ω_{SRK} is the acentric factor that causes the Soave equation of state to give the best fit to pure component vapour pressures. It can be found as a tabulated value for several compounds [26].

Vs values can be obtained using the following relations [28]:

$$V_S = V^{*}V^{(0)}\left[1 - \omega_{SRK}\,V^{(\delta)}\right] \qquad (E3)$$

$$V^{(0)} = 1 + \; a\,(1-T_r)^{1/3} + b\,(1-T_r)^{2/3} + \; c\,(1-T_r) + d\,(1-T_r)^{4/3} \,\text{(E4)}$$

$$V^{(\delta)} = \frac{e + f\,T_r + g\,T_r^2 + h\,T_r^3}{T_r - 1.00001} \qquad \text{(E5)}$$

where:

a = -1.52816
b = 1.43907
c = -0.81446
d = 0.190454
e = -0.296123
f = 0.386914
g = -0.296123
h = -0.0480645

Equation E3 can be used in the range between $0.25 < T_r < 0.95$, and Equation E4 in the range between $0.25 < T_r < 1.0$. Values of V^* are tabulated parameters, which are close to the critical volume. If values of V^* are not available, V_C values can be used instead. Values of P_v, are estimated through Antoine equation [29].

- Antoine equation:

The following equation was used to estimate the vapour pressure, P_v, [29]:

$$log_{10}P_v = A - \frac{B}{T+C} \quad \text{(E6)}$$

where values of the parameters of the Antoine equation are:

Table E1. Coefficients for the estimation of vapor pressure using Antoine equation [29].

Compound	A	B	C
1-butanol	7.3013	1285.0227	173.247
Isobutene	6.99678	984.2258	246.124
Butyl *tert*-butyl ether	7.15548	1540.4709	219.410
Isobutane	6.93551	954.1820	247.077
Trans-2-butene	7.05731	1036.5415	247.135

Units used for the equation E6 are: Pv [mmHg] and T [ºC].

To estimate the acentric factor, if needed, (as the butyl *tert*-butyl ether case) the following equations are used:

$$\omega = -lnP_{vr} - 1 \quad \text{(E7)}$$

where P_{vr} is the reduced vapor pressure, that can be estimated by the method of Gómez-Thodos, as [26]:

- Method of Gómez-Thodos for the estimation of the reduced vapor pressure:

The following relations were used to estimate the reduced vapor pressure, P_{vr} [25, 26]:

$$lnP_{vr} = \beta \left(\frac{1}{T_r^m - 1}\right) + \gamma \left(T_r^7 - 1\right) \quad \text{(E8)}$$

$$\gamma = ah + b\beta \quad \text{(E9)}$$

$$a = \frac{1 - 1/T_{br}}{T_{br}^7 - 1} \quad \text{(E10)}$$

$$b = \frac{1 - 1/T_{br}^7}{T_{br}^7 - 1} \quad \text{(E11)}$$

$$h = T_{br} \frac{ln(P_C/1.01325)}{1 - T_{br}} \quad \text{(E12)}$$

where P_{vr}, T_r, T_{br} are reduced vapor pressure, reduced temperature and reduced boiling temperature, respectively. Depending of the type of compound considered, the procedure to obtain β, γ, and *m* are different.

Compounds are divided into three categories: non polar, polar and hydrogen-bonded compounds.

- For nonpolar compounds (e.g., olefins and ethers), the following equations are used:

$$\beta = -4.26700 - \frac{221.79}{h^{2.5} exp(0.0384 h^{2.5})} + \frac{3.81262}{exp\left(\frac{227244}{h^3}\right)} + \Delta^* \quad \text{(E13)}$$

$$m = 0.78425 \exp(0.089315h) - \frac{8.5217}{\exp(0.74826h)} \quad \text{(E14)}$$

where Δ^* value is zero, except for hydrogen and helium, and γ is calculate by equation E9.

- For polar compounds other than alcohol and water, the following equations are used:

$$m = 0.466 T_C^{0.166} \qquad \text{(E15)}$$

$$\gamma = 0.08594 \exp(7.462x10^{-4} T_C) \quad \text{(E16)}$$

and for water and alcohols:

$$m = 0.0052 M^{0.29} T_C^{0.72} \qquad \text{(E17)}$$

$$\gamma = \frac{2.464}{M} \exp\,(9.8x10^{-6} M T_C) \qquad \text{(E18)}$$

where M is the molar weight. For these two categories, β is calculated as:

$$\beta = \frac{\gamma}{b} - \frac{ah}{b} \qquad \text{(E19)}$$

Finally, the molar volume of liquid mixtures is estimated [25, 26]:

- Estimation of liquid mixtures molar volume

The following equation is a recommended mixing rule for the HBT method [26]:

$$V_m^* = \frac{1}{4}\left[\sum_i x_i V_i^* + 3\left(\sum_i x_i V_i^{*2/3}\right)\left(\sum_i x_i V_i^{*1/3}\right)\right] \qquad \text{[E20]}$$

where x_i are molar fractions of the compounds. The sub index *m* in Equation E20 indicates that the corresponding property is referred to that of the mixture.

3.7. Kinetic Model

At this point of the work, HSPs of mixtures for every point of the synthesis of BTBE have been estimated. Therefore, the proposed kinetic model [1] can now be fitted to the experimental data, so, the parameters of equation (2) will be obtained.

$$r = k' \frac{\left(a_{IB}\, a_{BuOH} - \frac{a_{BTBE}}{K_{eq}}\right)}{a_{BuOH} + K_{BTBE} a_{BTBE}}\, exp\left(\frac{\bar{V}_M \phi_P^2}{RT}\,(\delta_M - \delta_P)\right) \qquad (2)$$

Fitted parameters

Estimated parameters

To fit the kinetic model, the Levenberg-Marquardt algorithm was used to minimize the residual sum of squares (RSS) defined as:

$$RSS = \sum_i^N \left(r_{exp} - r_{calc}\right)_i^2 \qquad \text{(F1)}$$

where r_{exp} is the experimental reaction rate, r_{calc} is the calculated value, and N is the number of experimental data (N = 136). In the original work [1], alternative objective functions were also tested to fit experimental data, which consisted of weighted residual sum of squares with different weighting factors being considered. Since results were statistically the same in terms of model ranking, distribution of residual and parameters values, further analysis refers to RSS (Equation F1).

In the present work, the fit of the kinetic equations to experimental data has been applied using Python Programming Language.

Python is an interpreted language with expressive syntax that some have compared to executable pseudocode. Python unique features offer an environment that makes it a better choice for scientist and engineers seeking a high-level language for writing scientific applications [30].

Thus, the procedure used to fit the fitted parameters of (equation 2) is as follows:

First of all, introduce a list of values of all the parameters previously estimated needed to fit k’, KBTBE and δ_P. These parameters are:

- Temperature.
- Activities of the three main components of BTBE synthesis.
- Molar volume obtained from HBT method
- Hansen solubility parameters of mixtures.

Then, calculate parameter K_{eq}. The parameter K_{eq} stands for the chemical equilibrium constant for the synthesis of BTBE, whose value was determined experimentally in a previous work [32]:

$$lnK_{eq,BTBE} = 870.35 + \frac{105348}{RT} - \frac{1425.42}{R} lnT + \frac{11.0849}{2R} T - \frac{28.316x10^{-3}}{6R} T^2 + \frac{2.1305x10^{-5}}{12R} T^3 \quad (F2)$$

Once all these data are obtained, the following parameters are fitted:

- Kinetic term k':

It is a kinetic constant of the rate determining step (assumed to follow the Arrhenius law) and, depending on the considered mechanism, adsorption equilibrium constants and the chemical equilibrium constant (assumed to follow the van't Hoff equation).

$$k' = exp\left(k'_1 + k'_T\left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \quad (F3)$$

Parameters k'_1 and k'_T are the parameters to be fitted and the mean experimental temperature, Tm, is used to reduce the correlation between both parameters.

- Adsorption equilibrium constant K_{BTBE}:

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

$$K_{BTBE} = exp\left[K_{BTBE,1} + K_{BTBE,T}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \quad (F4)$$

In case that the temperature dependence of K_{BTBE} is no significant, the parameter $K_{BTBE,T}$ should be taken as equal to zero and, thus, K_{BTBE1} is the only parameter to be fitted as the K_{BTBE} estimate.

- Solubility parameter of the resin δ_P:

Solubility parameter of the resin, δ_P, that could be considered constant within the temperature or temperature dependent. In the case of temperature dependence, the equation to be considered is the following [34, 35]:

$$\delta_P = k_{P1} + k_{P2}(T - T_m) \qquad \text{(F5)}$$

where K_{P1} and K_{PT} are the fitting parameters, the mean temperature T_m being included to reduce the correlation between both parameters.

3.8. Search of the best kinetic model

Due the BTBE synthesis is a heterogeneously catalysed system, the proposed models have been developed from the Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) formalisms. The form of a given kinetic equation is characterized by: a set of compounds that absorb on the catalyst, a set of elementary reactions, and the reaction step considered the rate-determining step.

Following the approach of previous works [1, 33], the search of the best kinetic model starts with the proposal of all kinetic equations to be tested. The kinetic equations proposed are extracted from a previous study [1] where they take into account the following characteristics:

- All possible rate-determining steps
- Absorbed and non-absorbed species on the catalyst
- Significant or non-significant temperature dependence of every parameter
- Possible inclusion of a term accounting for the effect on rates of the interaction between the resin (catalyst) and the liquid mixture.

The aim of this procedure is to obtain the model that fits the best with the experimental data.

All proposed equations match the same general expression (Equation 1.2). Models differ in the developed form of each equation term (Table F1):

Table F1. Considered alternative forms of the kinetic model terms.

Term	Form	Observation	Equation number
{kinetic term}	$k' = exp\left(k_1' + k_T'(1/T - 1/T_m)\right)$		F3
{driving force}	$a_{BuOH} - \left(a_{BTBE}/K_{eq}a_{IB}\right)$	Surface reaction is the rate-determining step	F6
	$a_{IB} - \left(a_{BTBE}/k_{eq}\, a_{BuOH}\right)$	BuOH adsorption is the rate-determining step	F7
	$a_{IB}a_{BuOH} - \left(a_{BTBE}/k_{eq}\right)$	IB adsorption is the rate-determining step	F8
	$a_{IB}a_{BuOH} - \left(a_{BTBE}/K_{eq}\right)$	BTBE desorption is the rate-determining step	F9
{adsorption term	$b_i + \sum_j b_j K_j a_j$	b_1=1, and b_j=1 or 0	F10
	$a_l + \sum_{j \neq l} b_j K_j a_j$	Derived from Eq.F10 when b_1=0; then b_l=1 or 0	F11
{resin-medium interaction}	$exp\left[b_p \frac{V_M \phi_P^2}{RT}(\delta_M - \delta_P)^2\right]$	Where b_p can equal 1 or 0	F12

where: *b* are binary-type variables (allowed values: 1 or 0), used to present generalized equations; Subscripts indices *j* and *l* refer to the involved compounds (IB, BuOH and BTBE)

As seen in Table 1, there is only one kinetic term considered that is an apparent kinetic coefficient, k', with the temperature dependence shown in Equation F3.

About driving force terms, three different possibilities appears in Table F1 depending on the considered rate-determining step for the global reaction process. The parameter K_{eq} in Equations F6 to F9 stands for the chemical equilibrium constant for the synthesis of BTBE, whose value is determined by Equation F2.

As seen in Table F1, two adsorption terms have been considered: the fraction of unoccupied active sites in the catalyst surface affecting the reaction rate (Equation F10 with b_1=1), and the number of vacant active sites being non-significant (Equation F11, a particular case of Equation F10 with b_1=0). Parameters K_j, as K_{BTBE} mentioned before, are adoption equilibrium constant whose temperature dependence is expressed according to the Van’t Hoff equation as follows:

$$K_j = exp\left(K_{j,1} + K_{j,\ T}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \qquad \text{(F13)}$$

Table F2. 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	$1 + K_{BuOH}a_{BuOH} + K_{BTBE}a_{BTBE} + K_{IB}a_{IB}$

4. RESULTS AND DISCUSSION

4.1. Method for the HSPs estimation

From the four methods of Hansen solubility parameters estimation proposed before, the results obtained for isobutylene and 1-butanol are shown in the table G1.

Table G1. Isobutylene solubility parameters obtained with group contribution methods.

Isobutylene				
	Solubility parameters [$MPa^{1/2}$]			
Estimation Methods	δ_D	δ_P	δ_H	δ_T
Hansen solubility parameters	14.5	2	1.5	14.71
Stefanis-Panaytou method	14.90	1.32	1.02	14.99
Hoftyzer-Van Krevelen	14.64	0	0	14.64
Hoy’s method	4.98	10.40	15.04	18.95
Hiroshi Yamamoto method	12.29	1.33	1.36	12.43

Table G2. 1-Butanol solubility parameters obtained with group contribution methods.

1-Butanol				
	Solubility parameters [$MPa^{1/2}$]			
Estimation Methods	δ_D	δ_P	δ_H	δ_T
Hansen solubility parameters	16	5.7	15.8	23.20
Stefanis-Panaytou method	15.92	5.94	13.15	21.49
Hoftyzer-Van Krevelen	15.61	5.43	14.74	22.16
Hoy’s method	9.73	19.10	13.94	25.57
Hiroshi Yamamoto method	17.20	4.28	7.39	19.21

In tables G1 and G2, Hansen solubility parameters extracted from references 16 and 23 are compared with Hansen Solubility parameters estimated using the four different group-contribution methods.

The method that offers the best results (more similar to real HSP of isobutylene and 1-butanol) is the Hoftyzer-Van Krevelen method. Hence, HSP of BTBE and isobutane will be obtained using Hoftyzer-Van Krevelen method. Values of Hansen solubility parameters of each component detected in the BTBE synthesis are shown in Table G3 (isobutane and trans-2butene are byproducts).

Table G3. Hansen solubility parameters estimated by the Hoftyzer-Van Krevelen method

Hansen solubility parameters				
Compound	δ_D	δ_P	δ_H	δ_T
1-Butanol	16[a]	5.7[a]	15.8[a]	23.20[a]
Isobutylene	14.5[a]	2[a]	1.5[a]	14.71[a]
BTBE	14.47[b]	2.30[b]	4.15[b]	15.23[b]
Isobutane	13.67[b]	0[b]	0[b]	13.67[b]
trans-2-Butene	14.6[a]	0[a]	2.9[a]	14.89[a]

[a] values obtained from [16, 23].[b] values estimated using Hoftyzer-Van Krevelen method.

4.2. Temperature dependence of Hansen solubility parameters

Values of the components of the Hansen solubility parameters for individual compounds and different temperatures are shown in Tables H1 to H4.

Table H1. Dispersion solubility parameter for individual compounds, δ_D, at different temperatures.

Compound	δ_D [MPa$^{1/2}$]						
	Temperature [K]						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
1-Butanol	15.90	15.70	15.50	15.30	15.11	14.92	14.73
Isobutene	14.30	13.92	13.55	13.18	12.82	12.47	12.14
BTBE	14.36	14.15	13.94	13.73	13.53	13.32	13.13
Isobutane	13.57	13.37	13.17	12.97	12.78	12.59	12.40
Trans-2-butene	14.50	14.30	14.11	13.91	13.72	13.54	13.35

Table H2. Polar solubility parameter for individual compounds, $\delta_{P.}$ at different temperatures.

Compound	δ_P [MPa$^{1/2}$]						
	Temperature [K]						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
1-Butanol	5.69	5.66	5.63	5.60	5.57	5.54	5.51
Isobutene	1.99	1.97	1.95	1.93	1.90	1.88	1.86
BTBE	2.29	2.28	2.27	2.25	2.24	2.23	2.21
Isobutane	0	0	0	0	0	0	0
Trans-2-butene	0	0	0	0	0	0	0

Table H3. Hydrogen bonding solubility parameter for individual compounds, δ_H, at different temperatures.

Compound	δ_H [MPa$^{1/2}$]						
	Temperature [K]						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
1-Butanol	15.66	15.40	15.13	14.87	14.62	14.37	14.12
Isobutene	1.48	1.45	1.42	1.38	1.35	1.32	1.29
BTBE	4.46	4.38	4.30	4.22	4.15	4.07	4.00
Isobutane	0	0	0	0	0	0	0
Trans-2-butene	2.87	2.82	2.77	2.73	2.68	2.63	2.58

Table H4. Hansen solubility parameter for individual compounds, δt, at different temperatures.

Compound	δ_t [MPa$^{1/2}$]						
	Temperature [K]						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
1-Butanol	23.03	22.70	22.38	22.06	21.75	21.44	21.13
Isobutene	14.52	14.13	13.76	13.39	13.03	12.68	12.35
BTBE	15.21	14.98	14.76	14.54	14.32	14.11	13.90
Isobutane	13.57	13.37	13.17	12.97	12.78	12.59	12.40
Trans-2-butene	14.78	14.58	14.38	14.18	13.98	13.79	13.60

As temperature increases, partial solubility parameters decrease as mentioned in Chapter 3. This solubility parameter variation is more noticeable for the hydrogen bond parameter because hydrogen bond parameter, δ_H. It is the most sensitive to temperature. As the temperature increases, hydrogen bonds are progressively broken or weakened, and this parameter will decrease more rapidly than the others.

4.3. Hansen solubility parameters of the mixture

The estimation of Hansen solubility parameters of the mixture requires, molar volumes to be estimated. The Hankinson-Brobst-Thomson method (HBT) has been applied:

Table I1. Critical temperature, critical pressure, V*, and ω_{SRK}

Compound	T_b^a [K]	T_C^a [K]	P_C^a [MPa]	V^{*a} [L mol^{-1}]	ω_{SRK}^a
1-butanol	390.60	563.05	4.423	0.275	0.594
Isobutene	266.15	417.9	3.999	0.23888	0.189
Butyl *tert*-butyl ether	397^b	576.09^c	25.4^c	0.4905^c	0.380^d
Isobutane	261.43	408.14	36.5^b	0.2568^e	0.183^e
Trans-2-butene	274.03	428.63	39.9^b	0.2367^e	0.215^e

^{a}Unless specified, values from [36]. ^{b}[37]. ^{c} Estimated by Joback method. ^{d} ω from Equation E7, through estimation of P_{vr} by Gómez-Thodos method. ^{e}[26].

Table I1, provides all the data needed to estimate molar volumes at each temperature and pressure. Obtained molar volumes at different temperatures are shown in Tables I2 and I3:

Table I2. Compounds molar volumes, V, by HBT method at 1.5 MPa

Compound	**V [L mol^{-1}]**						
	Temperature [K]						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
1-butanol	0.088	0.089	0.090	0.091	0.093	0.094	0.095
Isobutylene	0.098	0.100	0.102	0.105	0.107	0.112	0.116
Butyl *tert*-butyl ether	0.160	0.162	0.164	0.166	0.168	0.171	0.173
Isobutane	0.107	0.110	0.113	0.121	0.119	0.124	0.129
Trans-2-butene	0.095	0.097	0.099	0.101	0.104	0.106	0.110

Table I3. Compounds molar volumes, V, by HBT method at 2 MPa

Compound	**V [L mol^{-1}]**						
	Temperature [K]						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
1-butanol	0.088	0.089	0.090	0.091	0.093	0.094	0.095
Isobutylene	0.098	0.100	0.102	0.105	0.107	0.111	0.116
Butyl *tert*-butyl ether	0.160	0.162	0.164	0.166	0.168	0.171	0.173
Isobutane	0.107	0.110	0.113	0.129	0.119	0.124	0.129
Trans-2-butene	0.095	0.097	0.099	0.101	0.104	0.106	0.110

On the one hand, it can be seen that molar volume values increases as the temperature increases.

On the other, molar volumes re slightly affected by pressure in the range from 1.5 MPa to 2MPa.

Then, Hansen solubility parameters of mixtures can be estimated. The results of obtained HSP for the reaction mixtures of the previous work [1] without taking into account temperature dependence are shown in Appendix 2, and HSPs of mixture taking into account temperature dependence are shown in Appendix 3. It can be seen that HSP depending on temperature decrease with temperature.

4.4. Fitting of the kinetic model proposed and differences between constant and temperature dependent HSP

At this point, all necessary parameters to fit the kinetic model proposed in a previous study [1] are obtained. Using the Python code that appears in Appendix 5, introducing in the program as data all estimated parameters (obtained in this work), compound activities and experimental reaction rates [1], the adjustment of the fitted parameters of the equation 2 can be obtain as well as the fitting of the kinetic equation to experimental data.

Values of compound activities and experimental reaction rates are shown in Appendix 4.

Equation 2:

$$r = k' \frac{\left(a_{IB}\, a_{BuOH} - \frac{a_{BTBE}}{K_{eq}}\right)}{a_{BuOH} + K_{BTBE} a_{BTBE}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\, (\delta_M - \delta_P)^2\right) \qquad (2)$$

Fitted parameters

Estimated parameters

Fitted parameters values obtained are the following:

$$k'\left[\frac{mol}{g\,h}\right] = exp\left[2.115 - 8.574 \cdot 10^{4}\left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$K_{BTBE} = exp\left[-0.0301 + 2.042 \cdot 10^{5}\left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$\delta_P\left[MPa^{1/2}\right] = 11.270$$

$$RSS = 7.80$$

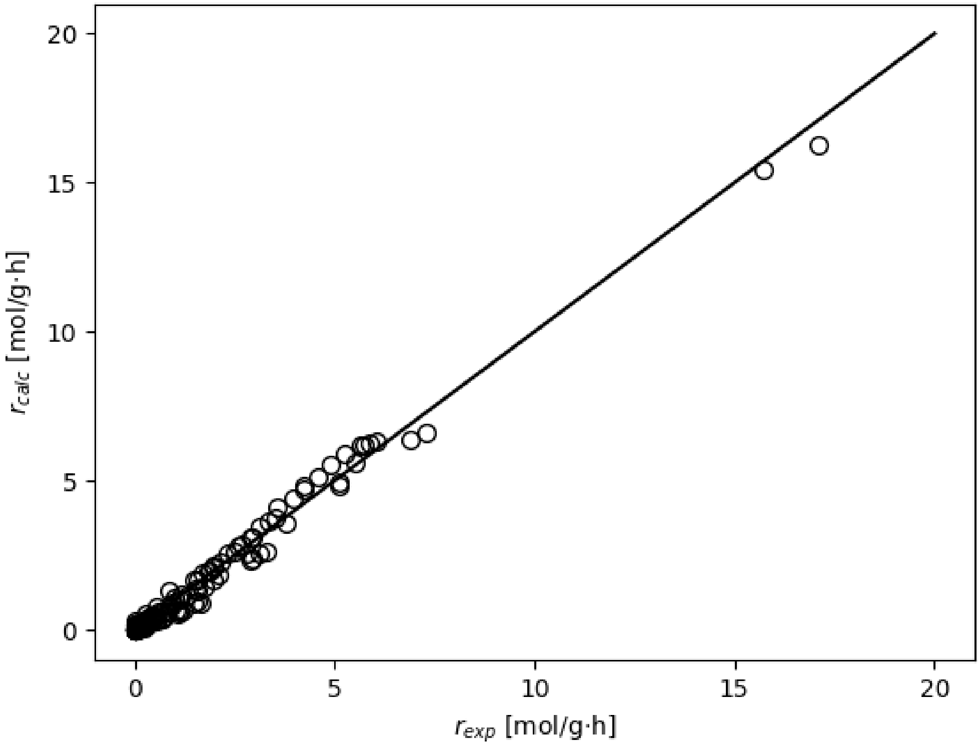

Figure 9. Fitting of the kinetic model proposed to experimental data with non-temperature dependent Hansen solubility parameters

The fit of Equation 2 to the experimental reaction rate data, is shown in Figure 9. As seen, the kinetic equation predicts the experimental data obtained in both batch and fixed-bed reactor systems. Also, there is a deviation on the points (below the line) that can be explained as the temperature dependence factor. So, a better prediction could be obtained taking into account the temperature dependence of Hansen solubility parameter.

Fitted parameters values obtained are the following:

$$k'\left[\frac{mol}{g\ h}\right] = exp\left[0.462 - 8.386 \cdot 10^4 \left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$K_{BTBE} = exp\left[0.259 - 4.0365 \cdot 10^4 \left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$\delta_P\left[MPa^{1/2}\right] = 19.82$$

$$RSS = 6.71$$

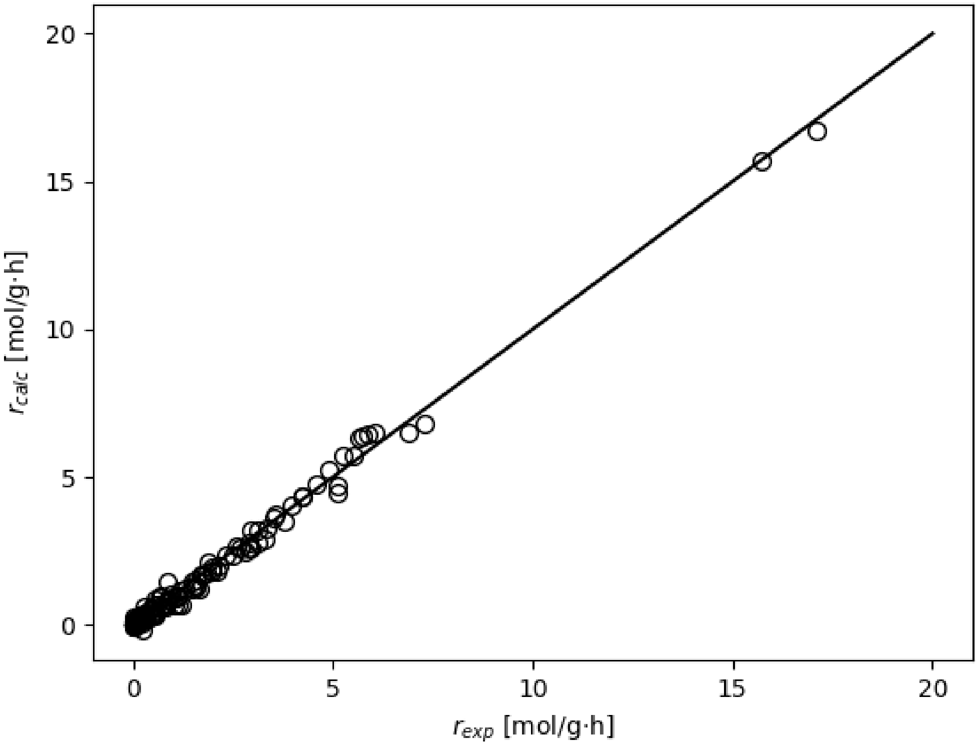

Figure 10. Fitting of the kinetic model proposed to experimental data with temperature dependence.

The fit of Equation 2 to the experimental reaction rate data taking into account the temperature dependence, is shown in Figure 10. In this case, the kinetic model proposed fits better with the experimental data. So, the temperature dependence factor, provides an enhancement in the fitting.

Comparing the mathematical fitting results using Hildebrand solubility parameters and Hansen solubility parameters with temperature dependence, (Fig. 9 and 10) it can be appreciated almost an identical fitting or very similar.

4.5. Test of an alternative best kinetic model

At this point, using the best kinetic fit obtained, in this case using Hansen solubility parameters with temperature dependence, some alternative kinetic models have been checked. They are based mainly on the kinetic equation proposed in the reference work [1], but introducing some slight variations with the aim of testing if such variation could facilitate to find a better kinetic model due to the introduction of the Hansen solubility parameters instead of the Hildebrand solubility parameters. As examples, the variations in considering a different rate-determining step (isobutylene or 1-butanol adsorption) are shown below. This particular cases affect the driving force term of the kinetic equation.

If isobutylene adsorption were the rate-determining step, the driving force terms becomes $a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}$. Although isobutylene adsorbs, it has not been included in the adsorption term of the kinetic equation, because in the reference work [1] its adsorption was found to be negligible in front of the 1-butanol and BTBE adsorption. As the result, the fitted kinetic equation is:

$$r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{a_{BuOH} + K_{BTBE} a_{BTBE}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right) \text{(G1)}$$

The fitted parameters are the following:

$$k' \left[\frac{mol}{g\ h}\right] = exp\left[0.344 - 8.287 \cdot 10^4 \left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$K_{BTBE} = exp\left[0.435 - 4.0198 \cdot 10^4 \left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$\delta_P\left[MPa^{1/2}\right] = 37.99$$

$$RSS = 7.31$$

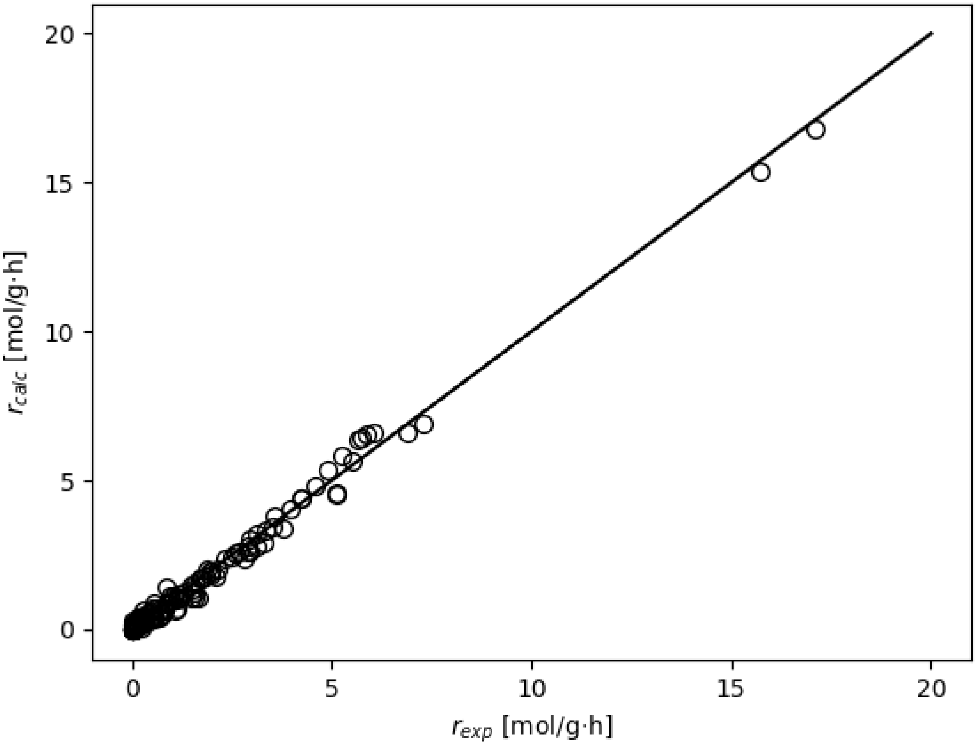

Figure 11. Fitting of the kinetic model taking into account that the IB adsorption is the rate-determining step.

Considering that isobutylene adsorption is the rate-determining step of the BTBE synthesis, the obtained results are similar but, worse, than considering surface reaction as the rate-determining step of BTBE synthesis.

Similarly, the results of the fit of the kinetic model where 1-butanol adsorption is the rate-determining step is presented below. In this case, the force driving term of the kinetic equation is $a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}$, thus the model to be fitted is:

$$r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{a_{BuOH} + K_{BTBE} a_{BTBE}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right) \text{(G2)}$$

The fitted parameters are the following:

$$k' \left[\frac{mol}{g\ h}\right] = exp\left[1.526 - 8.917 \cdot 10^4 \left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$K_{BTBE} = exp\left[1.57 - 2.206 \cdot 10^4 \left(\frac{1}{T} - \frac{1}{329.4}\right)\right]$$

$$\delta_P \left[MPa^{1/2}\right] = 4.25$$

$$RSS = 16.74$$

The plot of calculated vs experimental reaction rates is shown in Figure 12.

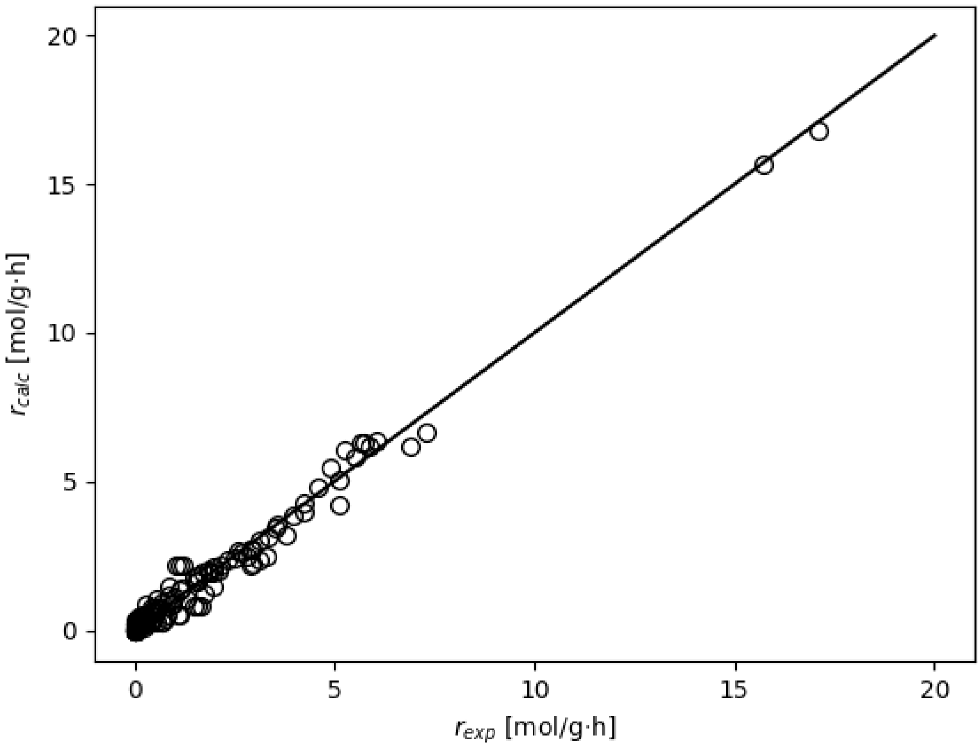

Figure 12. Fitting of the kinetic model taking into account that the BuOH adsorption is the rate-determining step.

In Figure 12, a worse kinetic fit is observed, so the consideration of BuOH adsorption of the rate-determining step of BTBE synthesis is discarded.

The result of the rest of tested options in this case changing the rate-determining step and also changing the adsorption term are shown in *Appendix* 6.

In conclusion, the best kinetic model is the proposed in Figure 10. Therefore, using HSPs there is not a significant enhancement of the fitting of the kinetic model.

5. CONCLUSIONS

Hansen solubility parameters presents an advantage over Hildebrand solubility parameters in the description of interactions between components. In kinetic modelling of the studied reaction, the results are similar, therefore, due to the ease of using Hildebrand solubility parameters and the possible sum of errors due to the multiple estimates using Hansen solubility parameters, Hildebrand is a suitable estimation method for solubility parameters.

- The Hoftyzer-Van Krevelen method has been found to be the most appropriate to estimate the Hansen solubility parameters (HSP) of the reaction medium for each experimental point.
- Fitting kinetic equation to experimental data has been done neglecting and taking into account temperature dependence of HSP. The best results have been obtained using temperature dependence.
- The results of the fitting of the same kinetic model used in the reference work to experimental data are similar to those obtained in the previous work, so, at first impression, HSP does not provide an improvement in the fitting.
- Using an alternative kinetic equation, a significant improvement of the fit has not been obtained. Therefore, the best kinetic equation is the same as the obtained in the reference work.

6. NOTATION

ϕ	Catalyst porosity
δ_M	Mixture solubility parameter [$MPa^{1/2}$]
δ_p	Catalyst solubility parameter [$MPa^{1/2}$]
δ_D	Dispersion solubility parameter [$MPa^{1/2}$]
δ_P	Polar solubility parameter [$MPa^{1/2}$]
δ_H	Hydrogen bounding solubility parameter [$MPa^{1/2}$]
δ_T	Total solubility parameter [$MPa^{1/2}$]
δ_{Hil}	Hildebrand solubility parameter [$MPa^{1/2}$]
Φ_i	Volume fraction
ρ_k	Density of a compound [$kg/(m^3)$]
$\Delta H_{vap,i}$	Enthalpy of vaporization of the compound *i* [kJ/mol]
δ_{Dvdw}	Universal interaction force (Yamamoto method) [$MPa^{1/2}$]
δ_{Dfg}	Interaction based on the polarizability of the functional group (Yamamoto method) [$MPa^{1/2}$]
α	Thermal expansion coefficient [K^{-1}]
α	Molecular aggregation number for Hoy method
ω_{SRK}	Acentric factor
a_{IB}	Isobutylene activity
a_{BuoH}	1-butanol activity
a_{BTBE}	Butyl tert-butyl ether activity
C_i	Contribution of the first-order group of Stefanis-Panayotou method [$MPa^{1/2}$]
D_j	contribution of the second-order group of Stefanis Panayotou method [$MPa^{1/2}$]
E_a	Activation energy, [$kJ \cdot mol^{-1}$]
E_{coh}	Cohesive energy [MPa]
E_{hi}	Hydrogen energy for Hoftyzer-Van Krevelen method [$MPa^{1/2}$]
F_{di}	Group contributions to the dispersion component of Hoftyzer-Van Krevelen method [$MPa^{1/2}$]
F_{pi}	Group contributions to the polar component of Hoftyzer-Van Krevelen method [$MPa^{1/2}$]

F_t	Molar attraction used in Hoy's method.
F_p	Polar component for Hoy's method
k'	Kinetic term [mol/(g·h)]
K_{BTBE}	Adsorption equilibrium constant of BTBE
K_{IB}	Adsorption equilibrium constant of isobutylene
K_{BuoH}	Adsorption equilibrium constant of 1-butanol
K_{eq}	Chemical equilibrium constant
M_j	Molar mass of compound j [kg/mol]
M_j	Times that appears a second-order group in a compound (Stefanis-Panayotou method)
N_i	Times that appears first-order groups in a compound (Stefanis-Panayotou method)
P	Pressure [MPa]
P_C	Critical pressure [MPa]
r_{exp}	Experimental reaction rate [mol/(g·h)]
r_{calc}	Calculated reaction rate [mol/(g·h)]
r_{BTBE}	Butyl tert-butyl reaction rate [mol/(g·h)]
R	Gas constant, [J/(mol·K)]
T	Temperature [K]
T_b	Boiling temperature [K]
T_C	Critical temperature [K]
T_m	Mean Temperature [K]
T_0	Initial temperature [K]
T_f	Final temperature [K]
V^*	Molar volume at 25ºC, [L/mol]
$\bar{V}_M$	Molar volume of the mixture [L/mol]
V_i	Molar volume of a pure solvent [L/mol]
W	Parameter that indicates whether or not there are second-order groups in a compound
x_k	Molar fraction

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8. APPENDICES

APENDIX 1. Typical properties of Amberlyst™ 35

Physical Properties	
Copolymer	Styrene-divinylbenzene
Matrix	Macroporous
Type	Strong acid cation
Functional Group	Sulfonic acid
Physical Form	Gray to Black, opaques, spherical beads
Nitrogen BET	
Surface Area	$50m^2/g$
Tota Pore volume	0.35cc/g
Avrage Pore Diameter	300 A
Chemical Properties	
Ioinic Form as Shipped	H^+
Concentration of Acid Sites*	≥ 5.00eq/kg
Catalyst Volatiles	≤ 3..0%
Article Size	
<300 µm	≤ 0.3%
> 850 µm	≤ 10.0%
Swelling (in solvent)	
Phenol	27%
Density	
Shipping Weight	560 g/L

*Dry Weight Capacity ≥ 5.00 eq/kg

APENDIX 2. HSPs of mixture without temperature dependence results.

			Molar fraction [%]									
#	**T [K]**	**P [MPa]**	**BuOH**	**IB**	**BTBE**	**Isobutan**	**Trans-2**	**Vm**	**δ_{MD}**	**δ_{MP}**	**δ_{MH}**	**δ_{MT}**
1	333,15	1,5	0,13612	0,20323	-	0,34654	0,31412	0,10731	14,37924	1,05744	2,98235	14,72329
2	333,15	1,5	0,18048	0,19259	-	0,32885	0,29808	0,10647	14,45043	1,26120	3,54595	14,93249
3	333,15	1,5	0,19729	0,18888	-	0,32197	0,29185	0,10615	14,47785	1,33993	3,76202	15,01853
4	313,15	1,5	0,49121	0,50866	-	-	-	0,09445	15,19328	3,71008	8,10923	17,61703
5	313,15	1,5	0,45455	0,54532	-	-	-	0,09485	15,13881	3,57573	7,58998	17,30830
6	303,15	1,5	0,51717	0,48269	-	-	-	0,09248	15,23591	3,81524	8,51565	17,86632
7	323,15	1,5	0,51526	0,48461	-	-	-	0,09599	15,22497	3,78825	8,41136	17,80173
8	323,35	2	0,50220	0,49780	-	-	-	0,09625	15,20502	3,73906	8,22124	17,68508
9	323,35	2	0,49114	0,48845	0,01948	-	-	0,09731	15,17976	3,68900	8,07653	17,58591
10	323,35	2	0,38686	0,35491	0,25823	-	-	0,11240	14,94928	3,24760	6,87729	16,77275
11	323,35	2	0,22630	0,28502	0,48868	-	-	0,12825	14,71732	2,76700	5,38477	15,91388
12	323,35	2	0,19889	0,13817	0,64710	-	-	0,13517	14,67158	2,71035	5,38975	15,86350
13	323,35	2	0,16242	0,09159	0,73217	-	-	0,14138	14,62744	2,62596	5,16116	15,73198
14	323,35	2	0,15547	0,07263	0,75566	-	-	0,14246	14,61906	2,61246	5,13751	15,71419
15	323,35	2	0,14159	0,05946	0,78231	-	-	0,14425	14,60398	2,58254	5,05088	15,66707
16	323,35	2	0,13681	0,05221	0,79416	-	-	0,14503	14,59868	2,57267	5,02558	15,65236
17	323,35	2	0,13383	0,04807	0,80130	-	-	0,14552	14,59541	2,56651	5,00929	15,64308
18	323,35	2	0,13081	0,04741	0,80429	-	-	0,14561	14,59246	2,56013	4,98822	15,63254
19	323,35	2	0,13089	0,05199	0,80005	-	-	0,14543	14,59281	2,55973	4,98163	15,63070
20	323,35	2	0,13108	0,05179	0,79977	-	-	0,14535	14,59302	2,56024	4,98362	15,63162
21	323,35	2	0,13024	0,05237	0,80026	-	-	0,14544	14,59220	2,55828	4,97626	15,62819
22	318,45	2	0,50756	0,49244	0,00000	-	-	0,09526	15,21527	3,76434	8,31893	17,74484
23	318,45	2	0,50290	0,48887	0,00768	-	-	0,09565	15,20483	3,74347	8,25774	17,70285
24	318,45	2	0,43594	0,40252	0,14950	-	-	0,10241	15,05525	3,45706	7,47981	17,16273
25	318,45	2	0,39225	0,31629	0,26843	-	-	0,10776	14,96339	3,29050	7,07537	16,87576
26	318,45	2	0,34347	0,24609	0,37891	-	-	0,11320	14,87724	3,12715	6,63987	16,58913
27	318,45	2	0,31110	0,20817	0,44489	-	-	0,11667	14,82632	3,02815	6,36332	16,41588
28	318,45	2	0,27210	0,17950	0,50880	-	-	0,12023	14,77162	2,91712	6,02944	16,21926
29	318,45	2	0,25172	0,14282	0,56366	-	-	0,12335	14,74113	2,86134	5,89130	16,13058
30	318,45	2	0,22939	0,11982	0,60817	-	-	0,12615	14,71135	2,80257	5,72262	16,03205
31	318,45	2	0,21852	0,10687	0,63139	-	-	0,12758	14,69717	2,77503	5,64591	15,98699
32	318,45	2	0,19269	0,08671	0,68447	-	-	0,13255	14,66390	2,70748	5,44263	15,87396
33	318,45	2	0,19578	0,06754	0,69215	-	-	0,13132	14,66715	2,71982	5,50757	15,90145
34	318,45	2	0,19007	0,05820	0,70714	-	-	0,13230	14,65987	2,70628	5,47289	15,88044
35	318,45	2	0,18413	0,04323	0,72688	-	-	0,13336	14,65211	2,69317	5,44619	15,86186
36	318,45	2	0,17945	0,04149	0,73350	-	-	0,13386	14,64685	2,68197	5,41005	15,84272
37	318,45	2	0,17850	0,03869	0,73617	-	-	0,13382	14,64578	2,68035	5,40780	15,84069
38	318,45	2	0,17748	0,03732	0,74004	-	-	0,13437	14,64425	2,67734	5,39921	15,83583
39	318,45	2	0,17734	0,03524	0,74161	-	-	0,13434	14,64402	2,67739	5,40183	15,83653
40	344,95	2	0,50810	0,49190	0,00000	-	-	0,10019	15,20586	3,74111	8,22917	17,68992
41	344,95	2	0,50068	0,48020	0,01735	-	-	0,10094	15,18796	3,70778	8,14349	17,62777
42	344,95	2	0,46320	0,39615	0,12353	-	-	0,10455	15,09925	3,55131	7,78724	17,35627
43	344,95	2	0,41956	0,32863	0,22479	-	-	0,10903	15,00987	3,38401	7,35246	17,05305
44	344,95	2	0,38125	0,26143	0,32478	-	-	0,11424	14,93439	3,24466	7,00056	16,80987
45	344,95	2	0,35594	0,21220	0,39523	-	-	0,11788	14,88776	3,15992	6,79376	16,66690
46	344,95	2	0,34144	0,16800	0,45213	-	-	0,12105	14,85874	3,11119	6,69646	16,59229
47	344,95	2	0,31301	0,14885	0,49797	-	-	0,12383	14,81788	3,02748	6,44107	16,43845
48	344,95	2	0,29808	0,11838	0,54262	-	-	0,12654	14,79352	2,98346	6,33499	16,36708
49	344,95	2	0,28596	0,09354	0,57727	-	-	0,12831	14,77515	2,95052	6,25692	16,31440
50	344,95	2	0,28129	0,08420	0,59130	-	-	0,12923	14,76792	2,93738	6,22485	16,29321
51	344,95	2	0,28790	0,07076	0,59946	-	-	0,12987	14,77333	2,95343	6,29760	16,32893
52	344,95	2	0,27444	0,07413	0,60832	-	-	0,13037	14,75802	2,91851	6,17404	16,26147
53	344,95	2	0,27259	0,07339	0,61059	-	-	0,13047	14,75579	2,91380	6,15893	16,25288
54	344,95	2	0,26764	0,06539	0,62182	-	-	0,13086	14,74927	2,90170	6,12810	16,23313
55	344,35	2	0,52177	0,47823	0,00000	-	-	0,09978	15,22728	3,79395	8,43337	17,81532
56	344,35	2	0,52138	0,47588	0,00052	-	-	0,09940	15,22818	3,79651	8,44455	17,82194
57	344,35	2	0,51718	0,45139	0,00937	-	-	0,09637	15,23312	3,81440	8,53643	17,87368
58	344,35	2	0,50425	0,43146	0,03309	-	-	0,09621	15,20879	3,76949	8,42310	17,78946
59	344,35	2	0,48758	0,40915	0,06421	-	-	0,09674	15,17480	3,70500	8,25096	17,66579
60	344,35	2	0,47181	0,38793	0,09679	-	-	0,09795	15,14002	3,63870	8,07239	17,53921
61	344,35	2	0,45897	0,37107	0,12511	-	-	0,09943	15,11043	3,58193	7,91767	17,43115
62	344,35	2	0,44195	0,35650	0,15507	-	-	0,10103	15,07550	3,51231	7,71452	17,29511
63	344,35	2	0,43109	0,32566	0,19332	-	-	0,10267	15,04827	3,46573	7,61654	17,21840
64	344,35	2	0,42168	0,32034	0,20822	-	-	0,10366	15,03014	3,42856	7,50290	17,14508
65	344,35	2	0,41398	0,29101	0,23993	-	-	0,10455	15,01184	3,39994	7,45820	17,10379
66	344,35	2	0,40328	0,27841	0,26221	-	-	0,10576	14,99101	3,35942	7,34485	17,02830

			Molar fraction [%]									
#	**T [K]**	**P [MPa]**	**BuOH**	**IB**	**BTBE**	**Isobutan**	**Trans-2**	**Vm**	**δ_{MD}**	**δ_{MP}**	**δ_{MH}**	**δ_{MT}**
67	344,35	2	0,39317	0,26454	0,28496	-	-	0,10695	14,97142	3,32196	7,24333	16,96009
68	344,35	2	0,38894	0,26133	0,29332	-	-	0,10765	14,96307	3,30507	7,19281	16,92789
69	344,35	2	0,38406	0,23597	0,31806	-	-	0,10808	14,95204	3,29006	7,18343	16,91123
70	344,35	2	0,37533	0,23208	0,33173	-	-	0,10917	14,93675	3,25815	7,08331	16,84919
71	344,35	2	0,37233	0,21781	0,34602	-	-	0,10947	14,93029	3,24904	7,07530	16,83834
72	344,35	2	0,36926	0,21315	0,35363	-	-	0,10992	14,92447	3,23801	7,04582	16,81869
73	344,35	2	0,36796	0,19479	0,37443	-	-	0,11132	14,91698	3,22833	7,04355	16,80922
74	344,35	2	0,36144	0,19298	0,37924	-	-	0,11103	14,90906	3,21134	6,98805	16,77574
75	355,55	2	0,49698	0,50302	0,00000	-	-	0,10325	15,18013	3,67766	7,98391	17,54150
76	355,55	2	0,49053	0,49501	0,01357	-	-	0,10392	15,16536	3,64957	7,90866	17,48869
77	355,55	2	0,30921	0,25948	0,42185	-	-	0,12824	14,81819	2,99196	6,15914	16,32377
78	355,55	2	0,24882	0,18145	0,55824	-	-	0,13689	14,73160	2,82779	5,72162	16,05470
79	355,55	2	0,22426	0,15403	0,60945	-	-	0,14022	14,69997	2,76668	5,55278	15,95547
80	355,55	2	0,21255	0,13418	0,64053	-	-	0,14218	14,68469	2,73896	5,48546	15,91327
81	355,55	2	0,20874	0,13321	0,64503	-	-	0,14246	14,68043	2,72986	5,45583	15,89759
82	355,55	2	0,20712	0,12675	0,65247	-	-	0,14279	14,67810	2,72661	5,45323	15,89399
83	355,55	2	0,20702	0,12243	0,65682	-	-	0,14304	14,67755	2,72666	5,45906	15,89548
84	355,55	2	0,20840	0,12783	0,65026	-	-	0,14267	14,67959	2,72959	5,46194	15,89887
85	355,55	2	0,21198	0,12978	0,64469	-	-	0,14226	14,68377	2,73822	5,48864	15,91340
86	355,55	2	0,21038	0,12582	0,64924	-	-	0,14234	14,68182	2,73505	5,48295	15,90909
87	355,55	2	0,21309	0,12378	0,64779	-	-	0,14203	14,68479	2,74217	5,50965	15,92227
88	334,25	2	0,50019	0,49981	0,00000	-	-	0,09855	15,19598	3,71675	8,13499	17,63264
89	334,25	2	0,49557	0,49214	0,01229	-	-	0,09929	15,18331	3,69318	8,07458	17,58895
90	334,25	2	0,37156	0,35326	0,26556	-	-	0,11351	14,92984	3,20328	6,72052	16,68312
91	334,25	2	0,29764	0,24943	0,43928	-	-	0,12392	14,80507	2,96826	6,10201	16,28605
92	334,25	2	0,23532	0,18101	0,56794	-	-	0,13211	14,71793	2,79903	5,63015	16,00471
93	334,25	2	0,19382	0,13548	0,65381	-	-	0,13772	14,66568	2,69754	5,34712	15,84142
94	334,25	2	0,14334	0,13944	0,70986	-	-	0,14396	14,61048	2,57513	4,92883	15,63300
95	334,25	2	0,13298	0,11409	0,74494	-	-	0,14617	14,59806	2,55473	4,89072	15,60606
96	334,25	2	0,14784	0,08468	0,74916	-	-	0,14401	14,61248	2,59430	5,05967	15,67977
97	334,25	2	0,14322	0,07819	0,76038	-	-	0,14480	14,60723	2,58445	5,03396	15,66497
98	334,25	2	0,13886	0,07903	0,76314	-	-	0,14488	14,60300	2,57484	5,00014	15,64860
99	334,25	2	0,14036	0,07490	0,76567	-	-	0,14499	14,60421	2,57864	5,01803	15,65609
100	334,25	2	0,13952	0,07731	0,76388	-	-	0,14484	14,60358	2,57659	5,00811	15,65198
101	334,25	2	0,13968	0,07863	0,76225	-	-	0,14471	14,60386	2,57686	5,00744	15,65207
102	333,15	2	0,49945	0,50055	0,00000	-	-	0,09831	15,19562	3,71586	8,13156	17,63056
103	333,15	2	0,49905	0,50038	0,00057	-	-	0,09834	15,19475	3,71407	8,12607	17,62690
104	333,15	2	0,43079	0,40403	0,14611	-	-	0,10390	15,04890	3,43944	7,40388	17,12065
105	333,15	2	0,37189	0,30315	0,29028	-	-	0,10994	14,93374	3,22789	6,87536	16,75429
106	333,15	2	0,32521	0,24394	0,38575	-	-	0,11408	14,85680	3,08066	6,47590	16,49703
107	333,15	2	0,28877	0,19783	0,46383	-	-	0,11824	14,79976	2,97128	6,17798	16,31039
108	333,15	2	0,26080	0,16360	0,52260	-	-	0,12140	14,75906	2,89291	5,96289	16,17884
109	333,15	2	0,23622	0,14205	0,56512	-	-	0,12354	14,72656	2,82803	5,77310	16,06854
110	333,15	2	0,22154	0,11962	0,60082	-	-	0,12557	14,70625	2,79014	5,67530	16,00836
111	333,15	2	0,20754	0,10515	0,62676	-	-	0,12681	14,68868	2,75567	5,57733	15,95173
112	333,15	2	0,19876	0,09073	0,65099	-	-	0,12858	14,67656	2,73322	5,52027	15,91683
113	344,45	2	0,51030	0,48970	0,00000	-	-	0,09998	15,20992	3,75113	8,26788	17,71357
114	344,45	2	0,50650	0,48785	0,00565	-	-	0,10035	15,20152	3,73397	8,21571	17,67842
115	344,45	2	0,44414	0,34146	0,18298	-	-	0,10534	15,05950	3,48620	7,66682	17,25462
116	344,45	2	0,39056	0,28515	0,28221	-	-	0,10972	14,96210	3,29533	7,12593	16,89682
117	344,45	2	0,32425	0,18525	0,44095	-	-	0,11837	14,84476	3,07406	6,54241	16,51120
118	344,45	2	0,28187	0,17690	0,48482	-	-	0,12022	14,78958	2,95522	6,15195	16,28839
119	344,45	2	0,26029	0,15079	0,52965	-	-	0,12260	14,75854	2,89536	5,98712	16,18775
120	344,45	2	0,25228	0,12891	0,55914	-	-	0,12437	14,74525	2,87302	5,94248	16,15517
121	344,45	2	0,24207	0,11545	0,57872	-	-	0,12487	14,73210	2,84807	5,87591	16,11436
122	344,45	2	0,23237	0,12102	0,58969	-	-	0,12704	14,71894	2,81758	5,76593	16,05714
123	343,45	2	0,54464	0,45536	0,00000	-	-	0,09905	15,26380	3,88404	8,78156	18,03289
124	343,45	2	0,52839	0,39899	0,03007	-	-	0,09334	15,25830	3,89007	8,88303	18,07917
125	343,45	2	0,43565	0,31646	0,24342	-	-	0,11363	15,01497	3,40345	7,45491	17,10580
126	343,45	2	0,38553	0,23449	0,37419	-	-	0,12179	14,91746	3,22019	6,97489	16,77943
127	343,45	2	0,33667	0,18632	0,47003	-	-	0,12803	14,84088	3,06817	6,53436	16,50343
128	343,45	2	0,31097	0,14081	0,54107	-	-	0,13270	14,79983	2,99210	6,34078	16,37660
129	343,45	2	0,29123	0,12234	0,57882	-	-	0,13523	14,77292	2,93833	6,18316	16,28203
130	343,45	2	0,28108	0,09239	0,61873	-	-	0,13781	14,75639	2,91061	6,12802	16,24116
131	343,45	2	0,27386	0,09201	0,62577	-	-	0,13824	14,74813	2,89245	6,06664	16,20734
132	343,45	2	0,27046	0,08404	0,63723	-	-	0,13902	14,74304	2,88349	6,04633	16,19351
133	343,45	2	0,26743	0,07862	0,64571	-	-	0,13960	14,73879	2,87563	6,02644	16,18083

			Molar fraction [%]									
#	**T [K]**	**P [MPa]**	**BuOH**	**IB**	**BTBE**	**Isobutan**	**Trans-2**	**Vm**	**δ_{MD}**	**δ_{MP}**	**δ_{MH}**	**δ_{MT}**
134	343,45	2	0,26571	0,07494	0,65073	-	-	0,13986	14,73644	2,87147	6,01685	16,17438
135	343,45	2	0,26529	0,07264	0,65360	-	-	0,14008	14,73561	2,87027	6,01566	16,17296
136	343,45	2	0,26452	0,07261	0,65395	-	-	0,14002	14,73487	2,86863	6,01008	16,16992

APENDIX 3. HSP of mixture with temperature dependence results.

			Molar fraction [%]									
#	**T [K]**	**P [MPa]**	**BuOH**	**IB**	**BTBE**	**Isobutan**	**Trans-2**	**Vm**	**δ_{MD}**	**δ_{MP}**	**δ_{MH}**	**δ_{MT}**
1	333,15	1,5	0,13612	0,20323	-	0,34654	0,31412	0,10731	13,56070	1,03088	2,81156	13,88741
2	333,15	1,5	0,18048	0,19259	-	0,32885	0,29808	0,10647	13,63730	1,23139	3,34186	14,09469
3	333,15	1,5	0,19729	0,18888	-	0,32197	0,29185	0,10615	13,66659	1,30885	3,54514	14,17945
4	313,15	1,5	0,49121	0,50866	-	-	-	0,09445	14,74086	3,67256	7,89469	17,12036
5	313,15	1,5	0,45455	0,54532	-	-	-	0,09485	14,67631	3,53861	7,38828	16,80781
6	303,15	1,5	0,51717	0,48269	-	-	-	0,09248	15,08607	3,80258	8,44011	17,69985
7	323,15	1,5	0,51526	0,48461	-	-	-	0,09599	14,48897	3,72557	8,04464	16,98607
8	323,35	2	0,50220	0,49780	-	-	-	0,09625	14,45724	3,67613	7,85948	16,86111
9	323,35	2	0,49114	0,48845	0,01948	-	-	0,09731	14,43852	3,62701	7,72100	16,77021
10	323,35	2	0,38686	0,35491	0,25823	-	-	0,11240	14,28567	3,19504	6,57388	16,04694
11	323,35	2	0,22630	0,28502	0,48868	-	-	0,12825	14,08955	2,72204	5,14481	15,24448
12	323,35	2	0,19889	0,13817	0,64710	-	-	0,13517	14,09519	2,66886	5,15078	15,24230
13	323,35	2	0,16242	0,09159	0,73217	-	-	0,14138	14,06608	2,58628	4,93213	15,12843
14	323,35	2	0,15547	0,07263	0,75566	-	-	0,14246	14,06347	2,57324	4,90961	15,11645
15	323,35	2	0,14159	0,05946	0,78231	-	-	0,14425	14,05226	2,54389	4,82670	15,07430
16	323,35	2	0,13681	0,05221	0,79416	-	-	0,14503	14,04909	2,53425	4,80252	15,06199
17	323,35	2	0,13383	0,04807	0,80130	-	-	0,14552	14,04702	2,52823	4,78693	15,05409
18	323,35	2	0,13081	0,04741	0,80429	-	-	0,14561	14,04422	2,52193	4,76675	15,04401
19	323,35	2	0,13089	0,05199	0,80005	-	-	0,14543	14,04321	2,52146	4,76041	15,04097
20	323,35	2	0,13108	0,05179	0,79977	-	-	0,14535	14,04348	2,52198	4,76231	15,04192
21	323,35	2	0,13024	0,05237	0,80026	-	-	0,14544	14,04248	2,52002	4,75526	15,03842
22	318,45	2	0,50756	0,49244	0,00000	-	-	0,09526	14,61211	3,71345	8,02298	17,07839
23	318,45	2	0,50290	0,48887	0,00768	-	-	0,09565	14,60370	3,69289	7,96391	17,03905
24	318,45	2	0,43594	0,40252	0,14950	-	-	0,10241	14,49516	3,41141	7,21334	16,54629
25	318,45	2	0,39225	0,31629	0,26843	-	-	0,10776	14,43734	3,24828	6,82343	16,29562
26	318,45	2	0,34347	0,24609	0,37891	-	-	0,11320	14,37634	3,08784	6,40329	16,03796
27	318,45	2	0,31110	0,20817	0,44489	-	-	0,11667	14,33798	2,99046	6,13641	15,88005
28	318,45	2	0,27210	0,17950	0,50880	-	-	0,12023	14,29234	2,88097	5,81407	15,69632
29	318,45	2	0,25172	0,14282	0,56366	-	-	0,12335	14,27267	2,82631	5,68088	15,61953
30	318,45	2	0,22939	0,11982	0,60817	-	-	0,12615	14,24940	2,76844	5,51808	15,52929
31	318,45	2	0,21852	0,10687	0,63139	-	-	0,12758	14,23876	2,74136	5,44405	15,48854
32	318,45	2	0,19269	0,08671	0,68447	-	-	0,13255	14,21097	2,67474	5,24780	15,38328
33	318,45	2	0,19578	0,06754	0,69215	-	-	0,13132	14,21912	2,68723	5,31065	15,41452
34	318,45	2	0,19007	0,05820	0,70714	-	-	0,13230	14,21422	2,67396	5,27720	15,39620
35	318,45	2	0,18413	0,04323	0,72688	-	-	0,13336	14,21023	2,66117	5,25149	15,38151
36	318,45	2	0,17945	0,04149	0,73350	-	-	0,13386	14,20536	2,65010	5,21659	15,36321
37	318,45	2	0,17850	0,03869	0,73617	-	-	0,13382	14,20498	2,64853	5,21443	15,36185
38	318,45	2	0,17748	0,03732	0,74004	-	-	0,13437	14,20379	2,64556	5,20614	15,35743
39	318,45	2	0,17734	0,03524	0,74161	-	-	0,13434	14,20409	2,64564	5,20869	15,35858
40	344,95	2	0,50810	0,49190	0,00000	-	-	0,10019	13,85058	3,62519	7,56955	16,19502
41	344,95	2	0,50068	0,48020	0,01735	-	-	0,10094	13,84534	3,59329	7,49072	16,14671
42	344,95	2	0,46320	0,39615	0,12353	-	-	0,10455	13,83736	3,44474	7,16360	15,95794
43	344,95	2	0,41956	0,32863	0,22479	-	-	0,10903	13,80939	3,28450	6,76351	15,72362
44	344,95	2	0,38125	0,26143	0,32478	-	-	0,11424	13,78978	3,15131	6,43984	15,54221
45	344,95	2	0,35594	0,21220	0,39523	-	-	0,11788	13,78045	3,07050	6,24972	15,43981
46	344,95	2	0,34144	0,16800	0,45213	-	-	0,12105	13,78289	3,02458	6,16060	15,39705
47	344,95	2	0,31301	0,14885	0,49797	-	-	0,12383	13,75523	2,94344	5,92506	15,26357
48	344,95	2	0,29808	0,11838	0,54262	-	-	0,12654	13,75087	2,90149	5,82755	15,21399
49	344,95	2	0,28596	0,09354	0,57727	-	-	0,12831	13,74808	2,87013	5,75582	15,17817
50	344,95	2	0,28129	0,08420	0,59130	-	-	0,12923	13,74664	2,85761	5,72634	15,16334
51	344,95	2	0,28790	0,07076	0,59946	-	-	0,12987	13,76053	2,87378	5,79372	15,20454
52	344,95	2	0,27444	0,07413	0,60832	-	-	0,13037	13,74284	2,83948	5,67955	15,13888
53	344,95	2	0,27259	0,07339	0,61059	-	-	0,13047	13,74102	2,83490	5,66562	15,13115
54	344,95	2	0,26764	0,06539	0,62182	-	-	0,13086	13,73922	2,82333	5,63726	15,11675

			Molar fraction [%]									
#	**T [K]**	**P [MPa]**	**BuOH**	**IB**	**BTBE**	**Isobutan**	**Trans-2**	**Vm**	**δ_{MD}**	**δ_{MP}**	**δ_{MH}**	**δ_{MT}**
55	344,35	2	0,52177	0,47823	0,00000	-	-	0,09978	13,89991	3,67899	7,76669	16,34209
56	344,35	2	0,52138	0,47588	0,00052	-	-	0,09940	13,90196	3,68156	7,77706	16,34934
57	344,35	2	0,51718	0,45139	0,00937	-	-	0,09637	13,92116	3,69987	7,86233	16,41048
58	344,35	2	0,50425	0,43146	0,03309	-	-	0,09621	13,91466	3,65692	7,75798	16,34555
59	344,35	2	0,48758	0,40915	0,06421	-	-	0,09674	13,90199	3,59501	7,59934	16,24621
60	344,35	2	0,47181	0,38793	0,09679	-	-	0,09795	13,88839	3,53131	7,43476	16,14414
61	344,35	2	0,45897	0,37107	0,12511	-	-	0,09943	13,87610	3,47673	7,29213	16,05643
62	344,35	2	0,44195	0,35650	0,15507	-	-	0,10103	13,85626	3,40944	7,10468	15,94041
63	344,35	2	0,43109	0,32566	0,19332	-	-	0,10267	13,85647	3,36539	7,01474	15,89133
64	344,35	2	0,42168	0,32034	0,20822	-	-	0,10366	13,84404	3,32934	6,90982	15,82680
65	344,35	2	0,41398	0,29101	0,23993	-	-	0,10455	13,84968	3,30268	6,86906	15,80839
66	344,35	2	0,40328	0,27841	0,26221	-	-	0,10576	13,83988	3,26364	6,76453	15,74650
67	344,35	2	0,39317	0,26454	0,28496	-	-	0,10695	13,83197	3,22763	6,67095	15,69212
68	344,35	2	0,38894	0,26133	0,29332	-	-	0,10765	13,82672	3,21128	6,62432	15,66435
69	344,35	2	0,38406	0,23597	0,31806	-	-	0,10808	13,83468	3,19765	6,61609	15,66512
70	344,35	2	0,37533	0,23208	0,33173	-	-	0,10917	13,82309	3,16664	6,52362	15,60971
71	344,35	2	0,37233	0,21781	0,34602	-	-	0,10947	13,82710	3,15831	6,51646	15,60858
72	344,35	2	0,36926	0,21315	0,35363	-	-	0,10992	13,82492	3,14771	6,48929	15,59319
73	344,35	2	0,36796	0,19479	0,37443	-	-	0,11132	13,83140	3,13902	6,48752	15,59644
74	344,35	2	0,36144	0,19298	0,37924	-	-	0,11103	13,82445	3,12245	6,43623	15,56567
75	355,55	2	0,49698	0,50302	0,00000	-	-	0,10325	13,52059	3,53679	7,20488	15,72341
76	355,55	2	0,49053	0,49501	0,01357	-	-	0,10392	13,51693	3,51009	7,13688	15,68321
77	355,55	2	0,30921	0,25948	0,42185	-	-	0,12824	13,43681	2,88508	5,55627	14,82375
78	355,55	2	0,24882	0,18145	0,55824	-	-	0,13689	13,41646	2,72903	5,16098	14,63163
79	355,55	2	0,22426	0,15403	0,60945	-	-	0,14022	13,40618	2,67075	5,00833	14,55822
80	355,55	2	0,21255	0,13418	0,64053	-	-	0,14218	13,40571	2,64461	4,94762	14,53224
81	355,55	2	0,20874	0,13321	0,64503	-	-	0,14246	13,40215	2,63579	4,92076	14,51823
82	355,55	2	0,20712	0,12675	0,65247	-	-	0,14279	13,40450	2,63289	4,91852	14,51911
83	355,55	2	0,20702	0,12243	0,65682	-	-	0,14304	13,40708	2,63311	4,92387	14,52335
84	355,55	2	0,20840	0,12783	0,65026	-	-	0,14267	13,40521	2,63575	4,92639	14,52296
85	355,55	2	0,21198	0,12978	0,64469	-	-	0,14226	13,40795	2,64407	4,95058	14,53522
86	355,55	2	0,21038	0,12582	0,64924	-	-	0,14234	13,40881	2,64115	4,94548	14,53374
87	355,55	2	0,21309	0,12378	0,64779	-	-	0,14203	13,41320	2,64815	4,96973	14,54733
88	334,25	2	0,50019	0,49981	0,00000	-	-	0,09855	14,13386	3,62714	7,62683	16,46483
89	334,25	2	0,49557	0,49214	0,01229	-	-	0,09929	14,12831	3,60436	7,57017	16,42888
90	334,25	2	0,37156	0,35326	0,26556	-	-	0,11351	13,98710	3,12889	6,29936	15,65602
91	334,25	2	0,29764	0,24943	0,43928	-	-	0,12392	13,92754	2,90141	5,71920	15,33310
92	334,25	2	0,23532	0,18101	0,56794	-	-	0,13211	13,87768	2,73708	5,27631	15,09705
93	334,25	2	0,19382	0,13548	0,65381	-	-	0,13772	13,84776	2,63853	5,01065	14,96091
94	334,25	2	0,14334	0,13944	0,70986	-	-	0,14396	13,79143	2,51812	4,61724	14,76019
95	334,25	2	0,13298	0,11409	0,74494	-	-	0,14617	13,79036	2,49868	4,58166	14,74480
96	334,25	2	0,14784	0,08468	0,74916	-	-	0,14401	13,81745	2,53829	4,74085	14,82702
97	334,25	2	0,14322	0,07819	0,76038	-	-	0,14480	13,81501	2,52877	4,71674	14,81542
98	334,25	2	0,13886	0,07903	0,76314	-	-	0,14488	13,81033	2,51929	4,68492	14,79934
99	334,25	2	0,14036	0,07490	0,76567	-	-	0,14499	13,81336	2,52313	4,70179	14,80817
100	334,25	2	0,13952	0,07731	0,76388	-	-	0,14484	13,81166	2,52105	4,69244	14,80326
101	334,25	2	0,13968	0,07863	0,76225	-	-	0,14471	13,81136	2,52128	4,69179	14,80282
102	333,15	2	0,49945	0,50055	0,00000	-	-	0,09831	14,16444	3,62895	7,63859	16,49693
103	333,15	2	0,49905	0,50038	0,00057	-	-	0,09834	14,16378	3,62720	7,63342	16,49359
104	333,15	2	0,43079	0,40403	0,14611	-	-	0,10390	14,09217	3,36113	6,95469	16,07029
105	333,15	2	0,37189	0,30315	0,29028	-	-	0,10994	14,04403	3,15673	6,45827	15,77685
106	333,15	2	0,32521	0,24394	0,38575	-	-	0,11408	14,00254	3,01385	6,08273	15,56130
107	333,15	2	0,28877	0,19783	0,46383	-	-	0,11824	13,97141	2,90768	5,80263	15,40537
108	333,15	2	0,26080	0,16360	0,52260	-	-	0,12140	13,94870	2,83159	5,60039	15,29537
109	333,15	2	0,23622	0,14205	0,56512	-	-	0,12354	13,92693	2,76836	5,42181	15,19932
110	333,15	2	0,22154	0,11962	0,60082	-	-	0,12557	13,91752	2,73168	5,32992	15,15148
111	333,15	2	0,20754	0,10515	0,62676	-	-	0,12681	13,90668	2,69814	5,23777	15,10331
112	333,15	2	0,19876	0,09073	0,65099	-	-	0,12858	13,90132	2,67643	5,18416	15,07599

			Molar fraction [%]									
#	**T [K]**	**P [MPa]**	**BuOH**	**IB**	**BTBE**	**Isobutan**	**Trans-2**	**Vm**	**δ_{MD}**	**δ_{MP}**	**δ_{MH}**	**δ_{MT}**
113	344,45	2	0,51030	0,48970	0,00000	-	-	0,09998	13,87055	3,63633	7,61214	16,23452
114	344,45	2	0,50650	0,48785	0,00565	-	-	0,10035	13,86492	3,61969	7,56398	16,20345
115	344,45	2	0,44414	0,34146	0,18298	-	-	0,10534	13,85647	3,38472	7,05976	15,91535
116	344,45	2	0,39056	0,28515	0,28221	-	-	0,10972	13,80789	3,20068	6,56097	15,61885
117	344,45	2	0,32425	0,18525	0,44095	-	-	0,11837	13,76708	2,98844	6,02341	15,32138
118	344,45	2	0,28187	0,17690	0,48482	-	-	0,12022	13,71769	2,87248	5,66265	15,11594
119	344,45	2	0,26029	0,15079	0,52965	-	-	0,12260	13,70416	2,81488	5,51070	15,03647
120	344,45	2	0,25228	0,12891	0,55914	-	-	0,12437	13,70513	2,79382	5,46978	15,01847
121	344,45	2	0,24207	0,11545	0,57872	-	-	0,12487	13,70025	2,76988	5,40844	14,98734
122	344,45	2	0,23237	0,12102	0,58969	-	-	0,12704	13,68409	2,73987	5,30671	14,93058
123	343,45	2	0,54464	0,45536	0,00000	-	-	0,09905	13,98014	3,77046	8,10198	16,59225
124	343,45	2	0,52839	0,39899	0,03007	-	-	0,09334	14,01102	3,77840	8,19677	16,66650
125	343,45	2	0,43565	0,31646	0,24342	-	-	0,11363	13,86765	3,30759	6,87686	15,82856
126	343,45	2	0,38553	0,23449	0,37419	-	-	0,12179	13,83374	3,13174	6,43392	15,57483
127	343,45	2	0,33667	0,18632	0,47003	-	-	0,12803	13,79090	2,98480	6,02684	15,34343
128	343,45	2	0,31097	0,14081	0,54107	-	-	0,13270	13,77880	2,91195	5,84829	15,24917
129	343,45	2	0,29123	0,12234	0,57882	-	-	0,13523	13,76302	2,85993	5,70261	15,16970
130	343,45	2	0,28108	0,09239	0,61873	-	-	0,13781	13,76397	2,83376	5,65197	15,14668
131	343,45	2	0,27386	0,09201	0,62577	-	-	0,13824	13,75581	2,81599	5,59514	15,11482
132	343,45	2	0,27046	0,08404	0,63723	-	-	0,13902	13,75525	2,80747	5,57644	15,10581
133	343,45	2	0,26743	0,07862	0,64571	-	-	0,13960	13,75403	2,79995	5,55809	15,09654
134	343,45	2	0,26571	0,07494	0,65073	-	-	0,13986	13,75372	2,79599	5,54926	15,09227
135	343,45	2	0,26529	0,07264	0,65360	-	-	0,14008	13,75418	2,79489	5,54819	15,09209
136	343,45	2	0,26452	0,07261	0,65395	-	-	0,14002	13,75342	2,79328	5,54302	15,08921

APPENDIX 4. Compound activities and reaction rates.

Activities			r_{BTBE}
a_{BuOH}	a_{IB}	a_{BTBE}	[mol/(gh)]
0,48437	0,21523	-	1,12930
0,45775	0,21609	-	1,03112
0,47158	0,21491	-	1,21205
0,63669	0,79940	-	0,66593
0,62223	0,80859	-	0,68006
0,60311	0,83176	-	0,25527
0,63460	0,78242	-	1,63991
0,62740	0,79152	-	1,56006
0,62402	0,76370	0,02443	1,50348
0,59073	0,46951	0,30107	0,83256
0,48029	0,31342	0,51024	0,44431
0,43954	0,14385	0,67959	0,25063
0,38898	0,09144	0,75860	0,13375
0,37740	0,07182	0,78161	0,07685
0,35546	0,05796	0,80507	0,02537
0,34736	0,05061	0,81602	0,01431
0,34212	0,04645	0,82261	0,00709
0,33726	0,04570	0,82468	0,00195
0,33771	0,05017	0,82016	0,00110
0,33802	0,04998	0,81994	0,00059
0,33663	0,05051	0,82017	0,00029
0,63060	0,79265	0,00000	1,13294
0,62904	0,78148	0,00988	1,09538
0,61206	0,57591	0,18219	0,78187
0,59708	0,41997	0,31851	0,55809
0,57160	0,30412	0,43478	0,39836
0,55043	0,24643	0,49955	0,27802
0,52085	0,20304	0,55660	0,19623
0,50196	0,15708	0,61064	0,13850
0,47961	0,12843	0,65107	0,09886
0,46783	0,11309	0,67228	0,06978
0,43664	0,08924	0,72006	0,04502
0,43975	0,06943	0,72999	0,03361
0,43215	0,05941	0,74406	0,02346
0,42374	0,04376	0,76322	0,00721
0,41765	0,04182	0,76841	0,00514
0,41633	0,03894	0,77092	0,00242
0,41472	0,03752	0,77473	0,00167
0,41439	0,03540	0,77641	0,00105
0,62882	0,76399	0,00000	7,27667
0,62732	0,73640	0,02093	6,87970
0,62165	0,56526	0,14689	5,10074
0,60479	0,43669	0,26070	3,78179
0,58439	0,32675	0,36996	2,80389
0,56769	0,25479	0,44531	2,11810
0,55593	0,19642	0,50778	1,57040
0,53397	0,16830	0,54921	1,12158

Activities			r_{BTBE}
a_{BuOH}	a_{IB}	a_{BTBE}	[mol/(gh)]
0,51991	0,13088	0,59502	0,83156
0,50775	0,10161	0,62998	0,55110
0,50309	0,09082	0,64400	0,31449
0,50808	0,07649	0,65665	0,22045
0,49610	0,07925	0,66046	0,11894
0,49425	0,07832	0,66225	0,08655
0,48926	0,06932	0,67280	0,06298
0,63655	0,75491	0,00000	5,74310
0,63537	0,75211	0,00064	5,64533
0,62537	0,71962	0,01190	5,27061
0,61704	0,67830	0,04201	4,89968
0,60773	0,62947	0,08103	4,57446
0,59983	0,58317	0,12118	4,25252
0,59429	0,54628	0,15530	3,97025
0,58530	0,51222	0,19004	3,58158
0,57906	0,45907	0,23696	3,32953
0,57444	0,44531	0,25289	3,10852
0,56749	0,39968	0,29270	2,90219
0,56079	0,37644	0,31761	2,69794
0,55419	0,35232	0,34306	2,49733
0,55191	0,34578	0,35179	2,32157
0,54583	0,30975	0,38323	2,14895
0,54104	0,30079	0,39616	1,95529
0,53771	0,28078	0,41385	1,81768
0,53506	0,27364	0,42243	1,68976
0,53500	0,24799	0,44767	1,56411
0,52867	0,24446	0,45178	1,46658
0,61376	0,76820	0,00000	17,09982
0,62725	0,73053	0,01552	15,70921
0,54475	0,29308	0,44612	4,21869
0,48797	0,19047	0,57993	1,96627
0,45909	0,15745	0,62941	0,99758
0,44573	0,13510	0,65948	0,50611
0,44001	0,13378	0,66381	0,23589
0,43874	0,12690	0,67126	0,11471
0,43940	0,12237	0,67553	0,05820
0,44053	0,12812	0,66910	0,02492
0,44562	0,13048	0,66384	0,01023
0,44386	0,12627	0,66861	0,00457
0,44833	0,12442	0,66761	0,00091
0,62549	0,78143	0,00000	3,28664
0,62494	0,76300	0,01507	3,10549
0,57923	0,45358	0,29974	1,72860
0,53033	0,28869	0,47855	0,96219
0,47244	0,19419	0,60106	0,51572
0,42310	0,13864	0,68083	0,29254
0,35496	0,13673	0,72327	0,14538
0,33571	0,11033	0,75817	0,07941

Activities			**r_{BTBE}**
a_{BuOH}	**a_{IB}**	**a_{BTBE}**	**[mol/(gh)]**
0,35593	0,08246	0,76845	0,04337
0,34814	0,07575	0,77903	0,01477
0,34146	0,07632	0,78050	0,00332
0,34345	0,07235	0,78375	0,00134
0,34232	0,07467	0,78154	0,00080
0,34270	0,07598	0,77984	0,00046
0,62518	0,78313	0,00000	2,93880
0,62506	0,78240	0,00070	2,90387
0,60837	0,56390	0,17157	1,98067
0,58393	0,38506	0,33017	1,31905
0,55555	0,29058	0,42683	0,89970
0,52761	0,22470	0,50368	0,61367
0,50252	0,17948	0,55993	0,41857
0,47826	0,15163	0,59819	0,27217
0,46137	0,12539	0,63258	0,18564
0,44513	0,10853	0,65596	0,10970
0,43317	0,09263	0,67960	0,07305
0,63011	0,76314	0,00000	6,04522
0,62891	0,75587	0,00686	5,86543
0,61724	0,46939	0,21651	3,51073
0,59107	0,36288	0,32168	2,59584
0,54615	0,21418	0,48663	1,53045
0,51294	0,19595	0,52006	1,16630
0,49211	0,16267	0,56302	0,84945
0,48247	0,13733	0,59371	0,66718
0,47205	0,12149	0,61173	0,51617
0,46125	0,12640	0,62035	0,39934
0,64970	0,73860	0,00000	5,50541
0,62684	0,65117	0,04030	5,11152
0,61180	0,42797	0,29058	2,95105
0,58383	0,29268	0,43435	1,86247
0,54953	0,21800	0,52877	0,87346
0,52741	0,15862	0,60143	0,54314
0,50983	0,13457	0,63620	0,29549
0,49869	0,09986	0,67794	0,17574
0,49216	0,09879	0,68246	0,09561
0,48838	0,08975	0,69407	0,06034
0,48507	0,08361	0,70238	0,03484
0,48317	0,07950	0,70733	0,02199
0,48259	0,07698	0,71043	0,01327
0.48178	0.07691	0.71050	0.00863

APPENDIX 5. Python programming code.

An example of a Python programming code to fit one of the considered kinetic equations is shown below. In this case, the rate-determining step is the surface reaction and the adsorption term is the contribution of 1-butanol and BTBE. Thus the kinetic equation is the following:

$$r = k' \frac{\left(a_{IB}\, a_{BuOH} - \frac{a_{BTBE}}{K_{eq}}\right)}{a_{BuOH} + K_{BTBE} a_{BTBE}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT}\, (\delta_M - \delta_P)^2\right) \quad (2)$$

```
# Càrrega de mòduls
import argparse
import os
import traceback

import numpy as np
import scipy.optimize as opt
from scipy.special import expit
import matplotlib.pyplot as plt

parser = argparse.ArgumentParser()
parser.add_argument('-f', '--filename', default='dadesVelocitat.txt')
args = parser.parse_args()

# Definició de funcions
def Kequil(T): # Càlcul de la constant d'equilibri
    expon = 870.35 +(-105348 / T - 1425.42 * np.log(T) +
           11.0849 / 2 * T - 28.316e-3 / 6 * T**2 +
           2.1305e-5 / 12 * T**3) / 8.314
    return(np.exp(expon))
def veloc(data, Preexp, Ea, Prem, Ib ,pp): #Càlcul de la velocitat de reacció
    # Preexp = factor preexponencial
    # Ea = energia d'activació
    # KBTBE = constant al terme d'adsorció
    Temp, aBuOH, aIB, aBTBE, Kequilib, Vm, HSP = data # assignació de dades
    k = Preexp * np.exp(-Ea/8.314*(1/Temp-1/Tmitj)) # constant cinètica
    KBTBE= Prem * np.exp(-Ib/8.314*(1/Temp-1/Tmitj)) # constant cinètica
    numer = aIB * aBuOH - (aBTBE / Kequilib) # terme potencial
    denom =  aBuOH+KBTBE*aBTBE# terme d'adsorció
    resina = np.exp(((Vm*(0.513**2))/(8.314*Temp))*(HSP-pp)**2)
    return k * (numer / denom) * resina
# Lectura de dades del fitxer
dadesfitxer = np.loadtxt(fname=args.filename, delimiter='\t', skiprows=1, dtype='longdouble')
Keq = Kequil(dadesfitxer[:,0]) # Constant equilibri reacció BTBE Kequil(T)
# Preparació de dades per a passar a la funció veloc
dadesfunc = (dadesfitxer[:,0], dadesfitxer[:,1], dadesfitxer[:,2],
          dadesfitxer[:,3], Keq, dadesfitxer[:,5], dadesfitxer[:,6]) # T, aBuOH, aIB, aBTBE, Keq, Vm, HSP
rBTBE = dadesfitxer[:,4] # Velocitat de reacció experimental
Tmitj = 329.4 # Temperatura mitjana experimental per al càlcul de k a veloc
# Ajust de la funció
```

```
popt, pcov = opt.curve_fit(veloc, dadesfunc, rBTBE)
print('Paràmetres:',popt) # Paràmetres ajustats
print('Covariància:',pcov) # Matriu de covariància dels paràmetres ajustats
# Gràfic r_calculada vs r_experimental
plt.plot([min(rBTBE), 20], [min(rBTBE), 20], 'k-')
plt.plot(rBTBE, veloc(dadesfunc, *popt), 'bo', markersize=7, markerfacecolor="none",
markeredgecolor='black')
plt.xlabel('$r_{exp}$ [mol/g·h]')
plt.ylabel('$r_{calc}$ [mol/g·h]')
plt.yticks(range(0, 25, 5))
plt.xticks(range(0, 25, 5))
nombre = input('Nombre gráfica') + '.png'
plt.savefig(os.path.join('Graficas',nombre))
plt.show()
```

APPENDIX 6. Tested kinetic models:

There are many variants of the kinetic equation contemplate in the present work changing:

- The rate-determining step
- The adsorption term

All possibilities are shown in Tables F1 and F2:

Table F1. Considered alternative forms of the kinetic model terms.

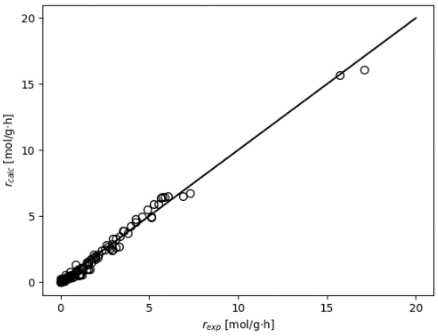
Term	Form	Observation	Equation number
{kinetic term}	$k' = exp\left(k_1' + k_T'(1/T - 1/T_m)\right)$		F3
{driving force}	$a_{BuOH} - \left(a_{BTBE}/K_{eq} a_{IB}\right)$	Surface reaction is the rate-determining step	F6
	$a_{IB} - \left(a_{BTBE}/k_{eq}\, a_{BuOH}\right)$	BuOH adsorption is the rate-determining step	F7
	$a_{IB} a_{BuOH} - \left(a_{BTBE}/k_{eq}\right)$	IB adsorption is the rate-determining step	F8
	$a_{IB} a_{BuOH} - \left(a_{BTBE}/K_{eq}\right)$	BTBE desorption is the rate-determining step	F9

Table F2. Alternative forms of the adsorption term in a LHHW or ER kinetic model for the BTBE synthesis.

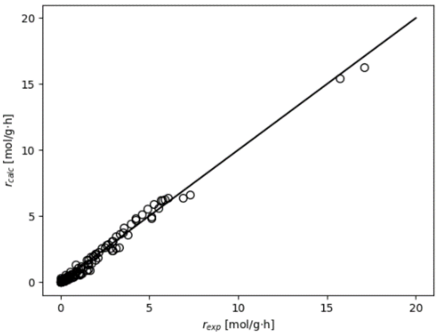
No.	Adsorption term	No.	Adsorption term
1	1	8	$1 + K_{BuOH} a_{BuOH}$
2	a_{BuOH}	9	$1 + K_{BTBE} a_{BTBE}$
3	a_{IB}	10	$1 + K_{IB} a_{IB}$
4	$a_{BuOH} + K_{BTBE} a_{BTBE}$	11	$1 + K_{BuOH} a_{BuOH} + K_{BTBE} a_{BTBE}$
5	$a_{BuOH} + K_{IB} a_{IB}$	12	$1 + K_{BuOH} a_{BuOH} + K_{IB} a_{IB}$
6	$a_{BTBE}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

Thus, the kinetic equations and plots of calculated vs experimental reaction rates of the rest of the tested options are shown below:

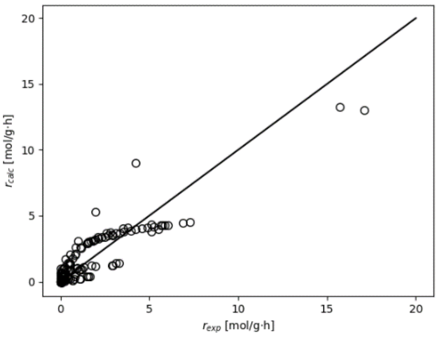
- $r = k' \frac{\left(a_{BuOH} a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{1} exp\left(\frac{\bar{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h1)



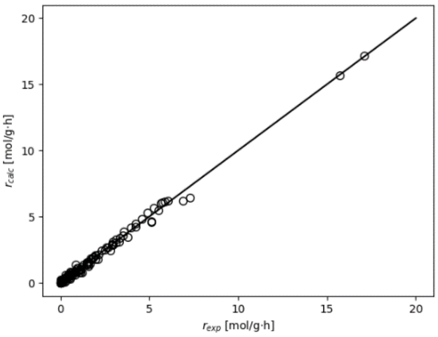
- $r = k' \frac{\left(a_{BuOH} a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{a_{BuOH}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h2)



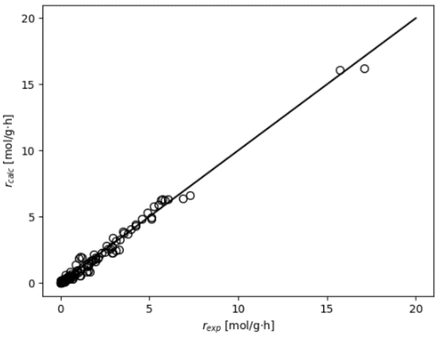
- $r = k' \frac{\left(a_{BuOH}\ a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{a_{IB}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h3)



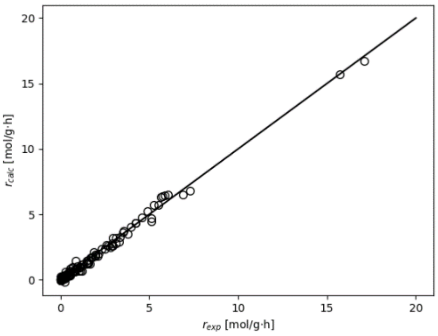
○ $r = k' \frac{\left(a_{BuOH}\, a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{a_{BuOH} + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h4)



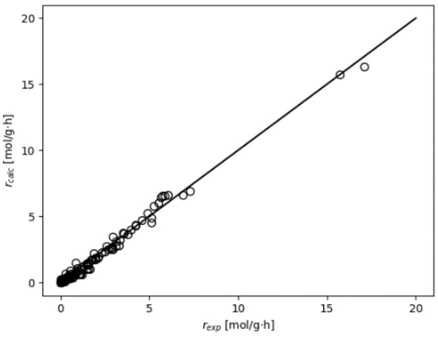
○ $r = k' \frac{\left(a_{BuOH}\, a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{a_{BTBE} + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h5)



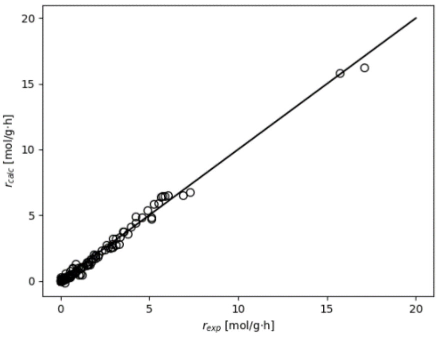
○ $r = k' \frac{\left(a_{BuOH} a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{a_{BuOH} + K_{IB} a_{IB} + K_{BTBE} a_{BTBE}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h6)



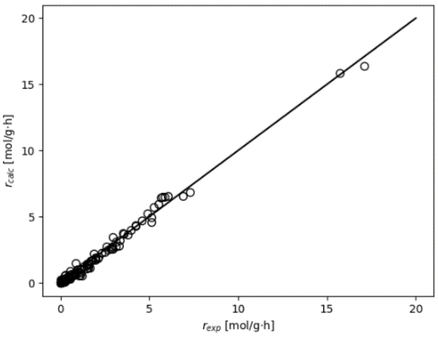
○ $r = k' \frac{\left(a_{BuOH}a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{1+ K_{BTBE}a_{BTBE}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h7)



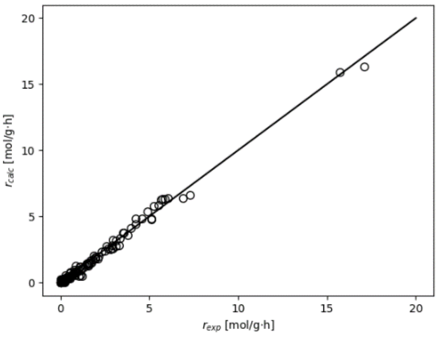
○ $r = k' \frac{\left(a_{BuOH}\ a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{1+ K_{IB}a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h8)



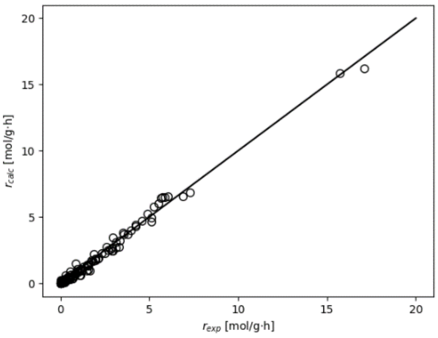
$$r = k' \frac{\left(a_{BuOH}a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{1+ K_{BuOH}a_{BuOH}+ K_{BTBE}a_{BTBE}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right) \quad (h9)$$



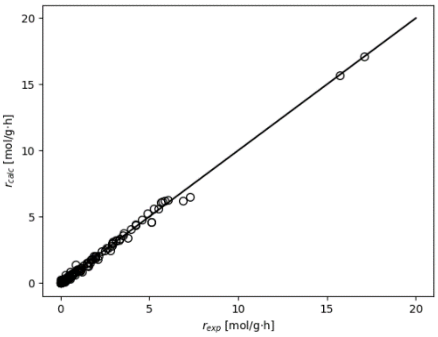
- $r = k' \frac{\left(a_{BuOH}\, a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{1+ K_{BuOH}a_{BuOH} + K_{IB}a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h10)



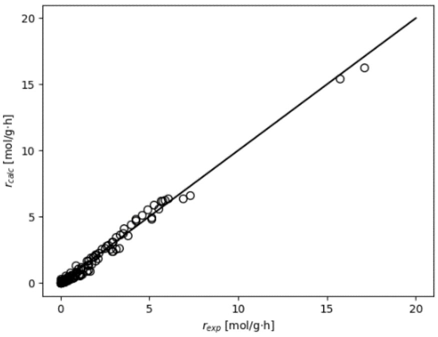
- $r = k' \frac{\left(a_{BuOH}a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{1+ K_{BTBE}a_{BTBE} + K_{IB}a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h11)



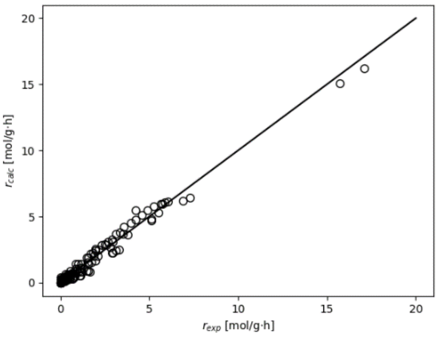
- $r = k' \frac{\left(a_{BuOH}a_{IB} - \frac{a_{BTBE}}{K_{eq}}\right)}{1+ K_{BTBE}a_{BTBE} + K_{IB}a_{IB} + K_{BuOH}a_{BuOH}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h12)



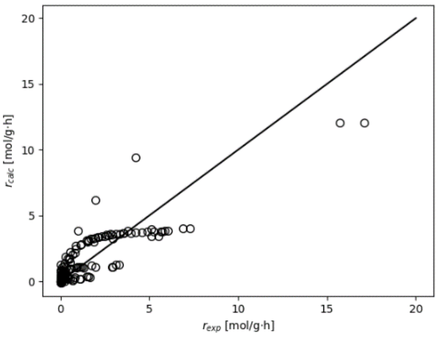
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq}*a_{BuOH}}\right)}{1} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h13)



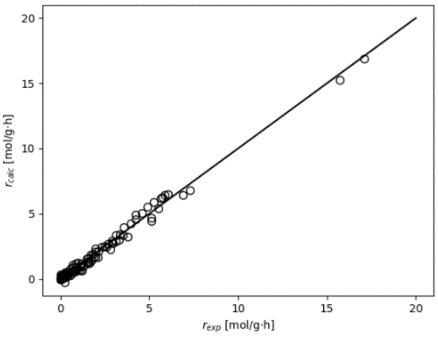
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq}*a_{BuOH}}\right)}{a_{BuOH}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h14)



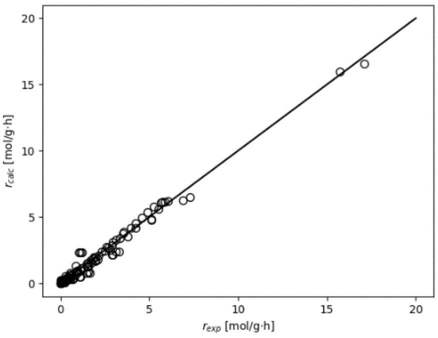
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq}*a_{BuOH}}\right)}{a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h15)



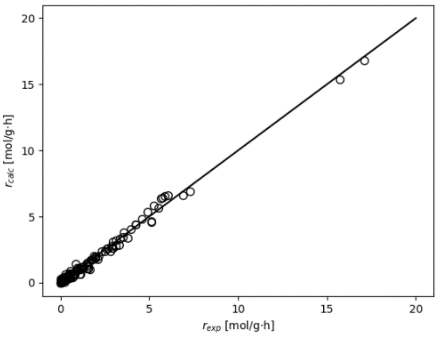
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{a_{BuOH} + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h16)



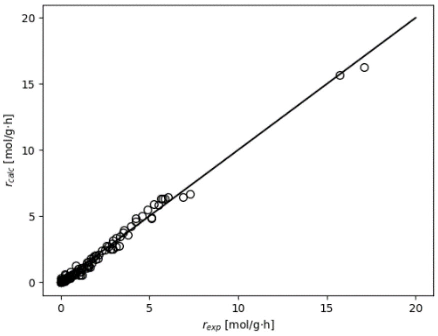
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{a_{BTBE} + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h17)



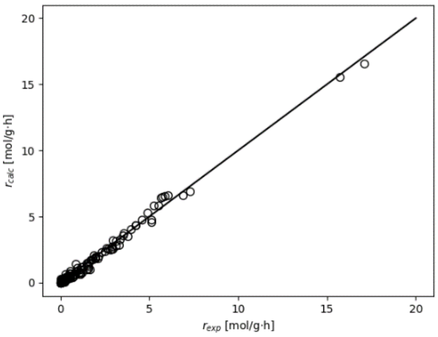
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{a_{BuOH} + K_{BTBE} a_{BTBE} + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT}\ (\delta_M - \delta_P)^2\right)$ (h18)



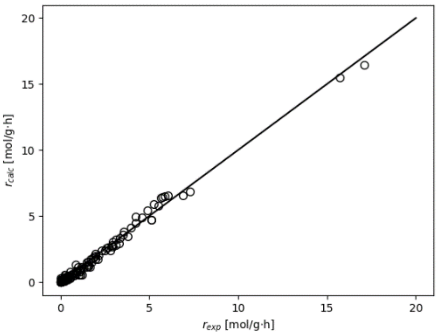
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{1 + K_{BuOH} a_{BuOH}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \ (\delta_M - \delta_P)^2\right)$ (h19)



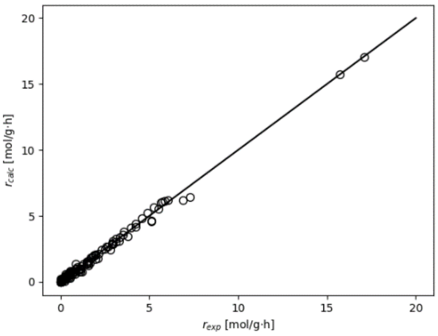
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{1 + K_{BTBE} a_{BTBE}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \ (\delta_M - \delta_P)^2\right)$ (h20)



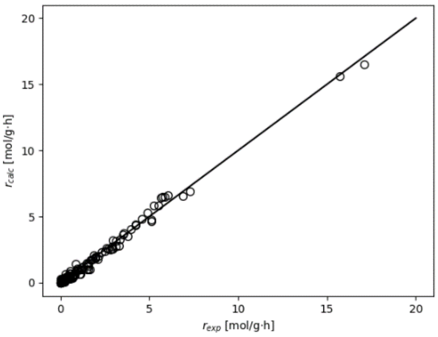
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{1 + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \ (\delta_M - \delta_P)^2\right)$ (h21)



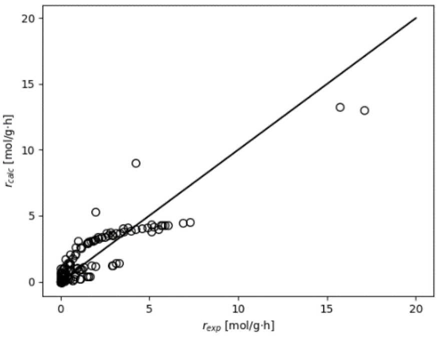
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{1 + K_{IB} a_{IB} + K_{BuOH} a_{BuOH}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right)$ (h22)



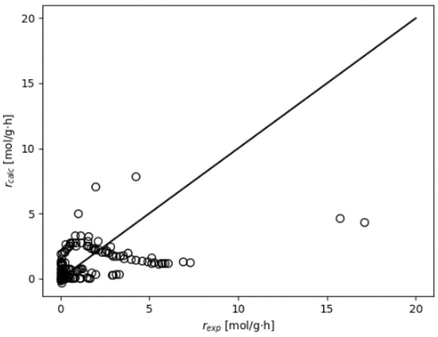
- $r = k' \frac{\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} * a_{BuOH}}\right)}{1 + K_{IB} a_{IB} + K_{BTBE} a_{BTBE}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right)$ (h23)



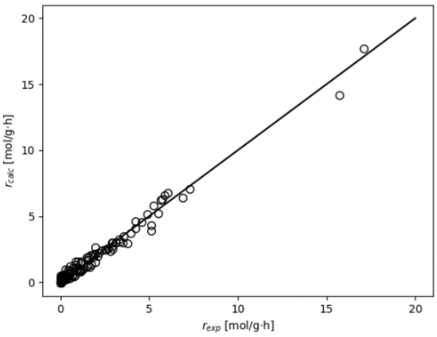
- $r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{1} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right)$ (h24)



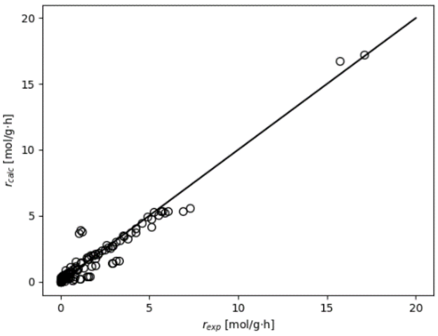
- $r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right)$ (h25)



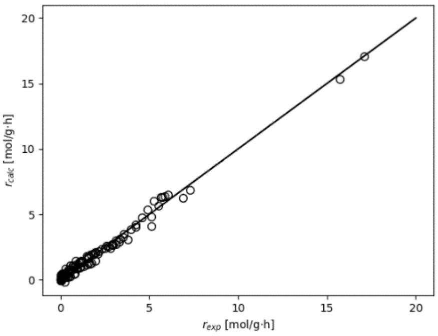
- $r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{a_{BuOH} + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right)$ (h26)



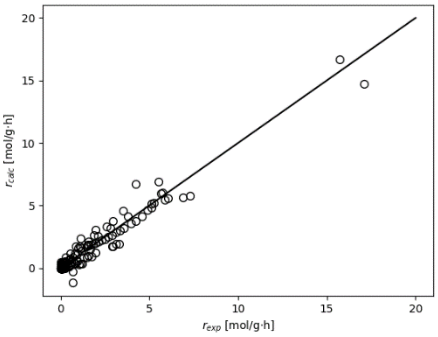
- $r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{a_{BTBE} + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right)$ (h27)



- $r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{a_{BuOH} + K_{IB} a_{IB} + K_{BTBE} a_{BTBE}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT} \ (\delta_M - \delta_P)^2\right)$ (h28)



- $r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{1 + K_{BuOH} a_{BuOH}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT} \ (\delta_M - \delta_P)^2\right)$ (h29)



- $r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{1 + K_{BTBE} a_{BTBE}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT} \ (\delta_M - \delta_P)^2\right)$ (h30)

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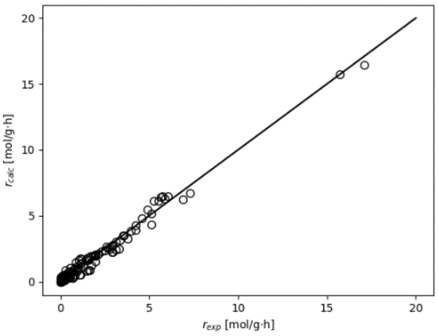
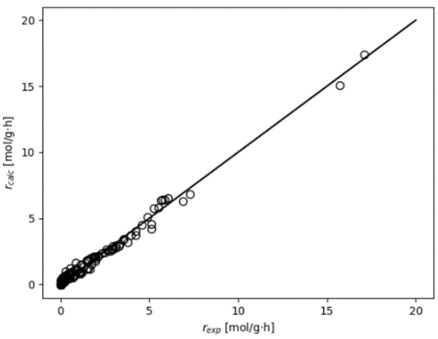
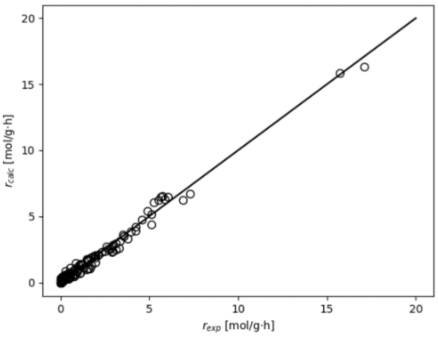


- $$r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{1 + K_{IB} a_{IB}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right) \text{(h31)}$$



- $$r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{1 + K_{BuOH} a_{BuOH} + K_{BTBE} a_{BTBE}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right) \text{(h32)}$$



- $$r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{1 + K_{BuOH} a_{BuOH} + K_{IB} a_{IB}} exp\left(\frac{\bar{V}_M \phi_P^2}{RT} \left(\delta_M - \delta_P\right)^2\right) \text{(h33)}$$

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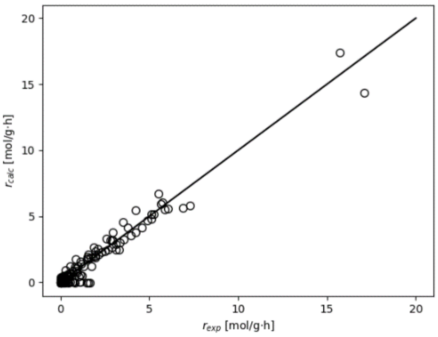

- $r = k' \frac{\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} * a_{IB}}\right)}{1 + K_{BTBE} a_{BTBE} + K_{IB} a_{IB}} exp\left(\frac{\overline{V}_M \phi_P^2}{RT} \ (\delta_M - \delta_P)^2\right)$ (h34)