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A KINETIC MODEL FOR THE DIRECT CONVERSION OF ETHANOL TO 1,3-BUTADIENE

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It is presented the development of a kinetic model for the direct transformation of ethanol into butadiene, over a catalyst having the structure K_2O: ZrO_2: ZnO / MgO-SiO_2, based on experimental data published by Da Ros et al. [1]. The model is developed using a reaction scheme published by the same authors, which, in addition to the formation of butadiene, includes the formation of ethene, butene and diethyl ether, as side products. The used rate expressions are of the power law type, considering the reversibility of the reactions for which the chemical equilibrium constants have low and medium values. The adequacy of the proposed kinetic model is demonstrated by the good concordance between the calculated and experimental values of ethanol conversion, butadiene yield and selectivity in reaction products. It is also confirmed by the high value of the correlation coefficient and the relatively tight statistical intervals of its parameters respectively.

Keywords: ethanol, butadiene, catalyst, kinetics, Lebedev process

1. Introduction

1,3-Butadiene (BD) is an important monomer, used in the manufacture of synthetic rubber, elastomers, and resins. Currently BD is obtained from petroleum derivatives (by-product of C4+ hydrocarbons thermal cracking and by dehydrogenation of the C4 fraction respectively).

Published economic evaluations have highlighted the advantages of BD manufacturing from ethanol, in terms of economic, ecological and sustainability [2,3].

A process for direct transformation (in a single stage of chemical transformation/ single chemical reactor) of ethanol into butadiene was patented by the Soviet researcher Lebedev in 1928 and commercially implemented in the Soviet Union at the end of 1930s, being known as the 'one-stage process' or the 'Lebedev process'. During the same period, Ostromislensky developed, in USA, an industrial process for ethanol transformation into BD, in two stages: (i) dehydrogenation of ethanol to acetaldehyde (AcH); (ii) conversion of the AcH-ethanol mixture into BD (‘Ostromislensky process’ or ‘two-stage process’) [4,5].

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After 1960, these processes were practically abandoned, due to the lower costs of BD manufacturing from petroleum derivatives, which were very affordable at that time. In the last two decades, due to the diminution of oil resources and the increase of concerns related to environmental protection, the interest in the production of BD from ethanol has resurfaced, initiating new research to improve existing technologies, especially by synthesizing new catalysts, more efficient from activity, selectivity, and stability points of view.
The processes of catalytic ethanol transformation into BD, mentioned above, are barely studied from the engineering point of view (heterogeneous process kinetics, catalytic reactor design, plant synthesis and optimization).

The main catalysts studied for the Lebedev process are MgO/SiO_2 or $M/Mox/SiO_2$ systems, where M is a metal (Ag, Cu etc.) having catalytic activity in the dehydrogenation step, and Mox a metal oxide that catalyzes the formation of BD from the AcH -ethanol mixture [5,6].

There are several theories regarding the mechanism of ethanol transformation into BD. In accord with the most widely accepted one, known as the Toussaint-Kagan mechanism [4], the transformation proceeds by the following successive-parallel reactions: (i) dehydrogenation of ethanol to acetaldehyde; (ii) condensation of acetaldehyde to 3-hydroxy-butanal; (iii) dehydration of 3-hydroxybutanal to crotonic- aldehyde (2-butenal); (iv) reduction of crotonaldehyde with ethanol to crotyl alcohol (2-butenol), accompanied by conversion of ethanol to acetaldehyde (Meerwein-Ponndorf-Verley-Oppenauer / MPVO /mechanism); (v) dehydration of crotyl alcohol to butadiene (Fig. 1).

The kinetics of the process transforming the ethanol into BD through the one stage (Lebedev) process is scarcely studied, only three kinetic models of this process having been published so far.

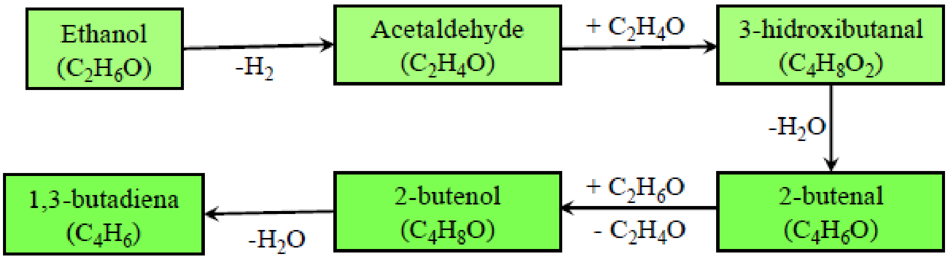

Fig. 1. Chemical steps of the Toussaint-Kagan mechanism [4]

The first one is published by Tretyakov and his research group, for the $ZnO-Al_2O_3$ catalyst (25 wt. % ZnO), doped with K (0.25 wt %), in the presence or absence of hydrogen peroxide as initiator (1 wt %). The authors published two versions of this model, close to each other, based on the same hypotheses regarding the mechanism of transformation and the same set of experimental studies [7, 8]. The authors adopted a modified Toussaint-Kagan mechanism, in which butadiene is formed by hydrogenation of crotonaldehyde with molecular hydrogen (less thermodynamically favored than the MPVO alternative), by the reaction of acetaldehyde with ethene, and dehydrogenation of butene respectively.

The second kinetic model for the one stage process was published by Cabello Gonzalez et al. [9], for an Hf-Zn-Si catalyst (hemimorphite-HfO_2/SiO_2). The model was developed based on the Toussaint-Kagan mechanism, reduced to two steps: dehydrogenation of ethanol to acetaldehyde and formation of butadiene from acetaldehyde and ethanol. In addition to BD, formation reactions for ethene, diethyl ether, butene, butanol, butanal and diphenyl ketone (which lumps the heavy products) were considered. The proposed reaction rate expressions are of the power law type, adjusted by a factor including the inhibitory effect of water.

An interesting study of the one stage ETB process was published by Da Ros et al. [1], over a catalyst having the composition $K_2O:ZrO_2:ZnO/MgO\text{-}SiO_2$. The aim of this work is to further exploit the data published in the paper of Da Ros et al. [1], by developing a power law kinetic model of the one stage ETB process, for the mentioned catalyst.

2. Development of a kinetic model for one stage ETB process, using the data published by Da Ros et al. [1]

2.1 The study of Da Ros et al. [1]

An extensive study of the one-step ETB process was published by Da Ros et al. [1], on a catalyst with the composition $K_2O:ZrO_2:ZnO/MgO\text{-}SiO_2$ (particle smaller than 200 μm), using a fixed bed reactor (quartz), at temperatures (T) between 300 and 400 ° C, weight space velocities (WHSV) 0.3-2.5 h^{-1} (reported to ethanol), and ethanol feed molar fractions between 0.41 and 0.85 (in presence of argon as a carrier gas). The main results obtained by the authors are presented in Table 1. These were calculated from experimental measurements, using the following relations:

$$X = \frac{N_{EtOH,0} - N_{EtOH}}{N_{EtOH,0}}; \qquad S_i = N_i / \sum_{j=1}^{n_p} N_j; \tag{1}$$

Table 1

Experimental data published by Da Ros et al. [1](*

Exp.	T(°C)	WHSV (h^{-1})	X (%)	S_i (mol %)					η_{BD} (%)	P_{BD} ($g_{BD}/g_{cat}h$)
				BD	Ac	Etena	DEE	Butene		
1.	325	0.62	17.0	65.9	15.0	5.6	3.3	7.3	14.8	0.06
2.	325	1.24	16.4	49.4	37.1	4.3	2.8	4.2	9.0	0.08
3.	375	0.62	25.8	54.5	21.0	8.8	2.8	8.4	28.5	0.13
4.	375	1.24	26.2	48.8	32.7	7.4	2.5	5.5	22.4	0.20
5.	350	0.93	23.6	51.3	31.2	6.1	2.9	5.6	18.1	0.12

6.	350	0.93	26.2	52.1	30.5	5.9	2.9	5.7	18.3	0.12
7.	350	0.93	32.9	49.6	33.6	5.8	2.9	5.2	19.5	0.13
8.	350	0.93	29.0	58.7	22.2	7.0	2.8	6.2	17.9	0.12
9.	300	0.93	13.4	55.2	31.5	3.9	3.0	4.2	4.9	0.03
10.	400	0.93	41.8	50.1	22.0	11.2	2.4	9.1	31.4	0.21
11.	350	0.31	43.6	63.4	14.6	7.2	2.6	8.0	26.1	0.05
12.	350	1.55	13.6	51.7	32.4	5.9	2.6	4.9	14.6	0.16
13.	325	0.93	21.7	48.2	38.6	3.7	3.5	4.0	8.2	0.05
14.	375	0.93	39.1	54.3	25.9	7.2	2.8	6.4	25.3	0.16
15.	325	2.49	6.5	33.3	57.3	3.5	2.3	2.3	5.5	0.10
16.	350	2.49	9.9	41.4	45.5	5.1	2.5	3.6	13.5	0.25
17	375	2.49	12.3	43.4	40.6	7.0	2.2	4.4	20.0	0.37
18	400	2.49	19.1	46.4	33.0	9.3	2.3	5.7	26.8	0.49

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$$\eta_{BD} = \frac{2\,N_{BD}}{N_{EtOH,0}} \; ; \qquad (2)$$

$$P_{BD} = \frac{m_{BD}}{m_{cat}\,t} \quad \left[g_{BD} \,/\, (\, g_{cat}\, h\,) \right]; \qquad (3)$$

N_j – molar flow rate of the product ‚i’ at the exit of the reactor; $N_{EtOH,0}$ – molar flow rate of ethanol in the reactor feed; m_{BD} – mass of BD collected during the time interval, t; m_{cat}- amount of the catalyst used in the reactor; X - ethanol conversion; S_i- selectivity of ethanol transformation into the product ‚i’; η_{BD} – yield of ethanol transformation into BD; P_{BD} – reactor productivity in BD.

Based on the experimental results presented in Table 1, the authors developed polynomial correlations that define the dependencies for the ethanol conversion and for the selectivity of the main reaction products, in relation to the weight hourly space velocity (WHSV) and temperature. Such correlations, although very useful in some applications, such as global plant analyses, are less suitable in the calculation of chemical reactors. In particular, the evolutions of composition and temperature along a catalyst bed, important in the reactor design, are hardly calculable using this kind of model. However, it is worth to emphasize that in the paper of Da Ros there are published valuable experimental data that characterize rather completely the dependencies of ethanol conversion, BD yield and products selectivity in respect with the working conditions. Therefore, these data can be further exploited to develop a classical kinetic model of the ETB process.

2.2 Development of the kinetic model

In this work, we used the experimental data published by Da Ros et al. [1], to develop an empirical power law type kinetic model, for ethanol transformation into BD, over K_2O:ZrO_2: ZnO/MgO-SiO_2 catalyst. The considered reaction scheme is that proposed by the same authors and corresponds to the Toussaint-Kagan mechanism (Fig. 1). To these, the authors added secondary reactions accounting for the formation of ethylene, diethyl ether and butene (Table 2). To appreciate the degree of reversibility of the considered reactions, we calculated the associated chemical equilibrium constants, $K_{p,i}$, in the hypothesis of ideal behavior of reaction mixture. In this aim there were used the classical thermodynamic relations (Banu et al. [10]):

$$\Delta G^0_{R,0,i}(T)=\sum_{j=1}^{n_c}\nu_{i,j}G^0_{f,j}(T)=-RT\ln K_{p,i} \tag{4}$$

$$\frac{d\ln K_{p,i}}{dT}=\frac{\Delta H_{R,i}(T)}{RT^2} \tag{5}$$

$$\Delta H_{R,i}(T)=\sum_{j=1}^{n_c}\nu_{i,j}H^0_{f,j}=\Delta H^0_{R,0,i}+\int_{T_0}^{T}\Delta C_{p,i}(T)dT;\quad \Delta C_{p,i}(T)=\sum_{j=1}^{n_c}\nu_{i,j}C_{p,j}(T) \tag{6}$$

In these relations: $\Delta H^0_{R,0,i}$ – enthalpie variation in reaction ‚i' at 298 K; $\Delta G^0_{R,0,i}$ - standard free energy variation in the reaction ‚i'; $\Delta H_{R,i}$ - enthalpie variation in reaction ‚i' in the current conditions; $H^0_{f,j}, G^0_{f,j}$-standard enhalpies and standard Gibbs free energy of formation for species ‚j'; C_{p_j} – molar heat capacity of ‚j'; $K_{p,i}$– Equilibrium constant of reaction ‚i', defined in respect with partial pressures.

In the equilibrium constants calculations, we used thermodynamic data extracted from the database of Aspen Plus v11 process simulator. The calculated temperature dependencies of the chemical equilibrium constants for the seven reactions, describing the ETB process chemistry, are plotted in Figure 2. As can be observed from this diagram, the equilibrium constants for the reactions R3, R4, R6 and R7 have values superior to 100, over the working temperature interval, therefore these reactions were considered as ireversible. The other ones (R1, R2 and R5) were considered reversible, including reverse reaction terms, in their rate expressions (Table 2).

Table 2

The equations of chemical reactions and the corresponding rate expressions

i	**Reaction**	**Rate expression**	$k_i=\mathbf{k_{m,i}}\exp\left[\frac{E_i}{R}(\frac{1}{T_m}-\frac{1}{T})\right]$; $T_m=626\ K$	
			$k_{m,i}$ $^{(*}$**,** **kmol/(kg·h·bar^{m_i})**	**E_i/R, K**
R1	$C_2H_5OH \Leftrightarrow C_2H_4O+H_2$	$r_1=k_1(p_{EtOH}-\frac{p_{AcH}p_{H2}}{K_{p1}})$	$4.025\cdot10^{-3}\cdot$ (1 ± 0.0006)	$7439.8\cdot$ (1 ± 0.0012)

R2	$2C_2H_5OH \Leftrightarrow C_4H_{10}O + H_2O$	$r_2 = k_2(p^2_{EtOH} - \frac{p_{DEE}\, p_{H2O}}{K_{p1}})$	$3.826 \cdot 10^{-4} \cdot$ (1 ± 0.012)	$6638.2 \cdot$ (1 ± 0.0095)
R3	$C_2H_5OH \Rightarrow C_2H_4 + H_2O$	$r_3 = k_3 p_{EtOH}$	$5.921 \cdot 10^{-4} \cdot$ (1 ± 0.0098)	$1324.5 \cdot$ (1 ± 0.051)
R4	$2C_2H_4 \Rightarrow C_4H_8$	$r_4 = k_4 p^2_{C2H4}$	$17.253 \cdot$ (1 ± 0.005)	$3008.3 \cdot$ (1 ± 0.019)
R5	$2C_2H_4O \Leftrightarrow C_4H_6O + H_2O$	$r_5 = k_5(p^2_{AcH} - \frac{p_{C4H6O}\, p_{H2O}}{K_{p5}})$	$11.312 \cdot$ (1 ± 0.0016)	$4005.8 \cdot$ (1 ± 0.0055)
R6	$C_4H_6O + C_2H_5OH \Rightarrow C_4H_6 +$ $+ C_2H_4O + H_2O$	$r_6 = k_6 p_{EtOH}\, p_{C4H6O}$	$503.75 \cdot$ (1 ± 0.013)	$1018.2 \cdot$ (1 ± 0.034)
R7	$C_4H_{10}O \Rightarrow 2C_2H_4 + H_2O$	$r_7 = k_7 p_{DEE}$	$5.839 \cdot 10^{-2} \cdot$ (1 ± 0.023)	$13655 \cdot$ (1 ± 0.018)

Subscripts in the rate expressions: EtOH- ethanol; AcH - acetaldehyde; DEE -diethyl ether; C_4H_6O -crotonaldehyde;

*) m_i=1 for i=1,3 and 7 ; m_i=2, for i=2,4,5 and 6.

The seven power law rate expressions presented in Table 2 include 14 unknown Arrhenius parameters, k_{m1}, k_{m2},..k_{m7}, E_1, E_2,...E_7. To estimate the values of these parameters we applied the least squares method, using the experimental data presented in Table 1. These data include a set of measured values for ethanol conversion, BD yield, the product selectivities (for BD, acetaldehyde, ethene, diethylether and butene) respectively BD productivity, for 18 experiments, that differ by temperature and/or WHSV values. Da Ros et al. [1] modified the WHSV value by the intermediate of the ethanol feed, this leading to simultaneous variations in both the reaction time and composition of the mixture (the reactor feed consisting of ethanol and an inert gas, used as entrainer).

The error function, to be minimized, has the expression:

$$\varepsilon = \sum_{j=1}^{Ne} [(\sigma_{AcH,j} - \sigma^{(e)}_{AcH,j})^2 + (\sigma_{C2H4,j} - \sigma^{(e)}_{C2H4,j})^2 + (\sigma_{DEE,j} - \sigma^{(e)}_{DEE,j})^2 + (\sigma_{C4H8,j} - \sigma^{(e)}_{C4H8,j})^2 + (\eta_{BD,j} - \eta^{(e)}_{BD,j})^2 + (X_j - X^{(e)}_j)^2] \quad (7)$$

In the expression (7), σ_j, η_j and X_j are the calculated values for absolute selectivity, BD yield and ethanol conversion. The significances of the subscripts appearing in the notations are the same as in the rate expressions (Table 2).

The BD yield is defined by the classical expression:

$$\eta_{BD} = \frac{2\,N_{BD}}{N_{EtOH,0}}; \quad (8)$$

As seen from the relations (1), to characterize the ethanol transformation in different products Da Ros et al. used the relative selectivity (S_i). However, a more meaningful characterization of the transformation is achievable by using the absolute selectivity (σ_i), calculated on the carbon atoms basis:

$$\sigma_i = \frac{n_i\, N_i}{2\, N_{EtOH,0} X}\ ; \tag{9}$$

n_i – number of carbon atoms in the molecule of product 'i'; X – ethanol conversion.

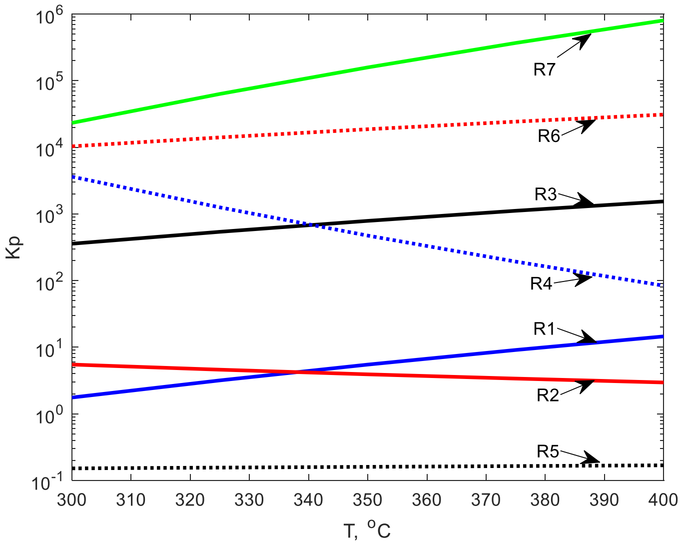

Fig. 2. Temperature dependencies of the chemical eqilibrium constants for the considered reactions. K_p units are $bar^{\Delta \nu i}$ ($\Delta\nu_i$- moles number variation in the associated reaction, R_i).

The relation interlinking the absolute selectivity and the relative selectivity is:

$$\sigma_i = n_i S_i \Big/ \sum_{j=1}^{n_p} (n_j S_j); \tag{10}$$

Before demonstrating the expression (10), lets notice that the defining relation (9), represents the ratio between the flow rate of carbon atoms contained in the product ,i' (n_i N_i) and the overall flow rate of carbon atoms contained in all the products at the reactor outlet, equal to the overall carbon atoms flow rate in the transformed ethanol. So, the relation (9) can be expressed alternatively:

$$\sigma_i = \frac{n_i\, N_i}{\sum_{j=1}^{n_p} n_j\, N_j}\ ; \tag{11}$$

N_i is deduced from (1) as:

$$N_i = S_i \sum_{j=1}^{n_p} N_j \tag{12}$$

From the last two relations, it is readily obtainable the relation (10). In the study of Da Ros et al. [1], there are also published the values of the BD productivity achieved in each experiment, defined by the relation (3) equivalent with (13):

$$P_{BD} = \frac{M_{BD}\,N_{BD}}{m_{cat}} \quad \left[g_{BD}\,/\,(\,g_{cat}\,h\,)\right]; \tag{13}$$

M_{BD}- molar weight of BD.

As the values for the molar flow rate, N_{BD}, is not directly available from the above mentioned paper, it can be replaced with its expression derived from the relation (2), obtaining:

$$P_{BD} = \frac{M_{BD}\,N_{EtOH,0}\eta_{BD}}{2\,m_{cat}} = \frac{M_{BD}\,F_{m,EtOH,0}\eta_{BD}}{2\,m_{cat}\,M_{EtOH}} \tag{14}$$

$F_{m,EtOH,0}$ – mass flow rate of ethanol in the reactor feed.

By introducing the space velocity,WHSV=$F_{m,EtOH,0}/m_{cat}$:

$$P_{BD} = \frac{M_{BD}\,WHS\,\eta_{BD}}{2\,M_{EtOH}} \tag{15}$$

Thus, the BD productivity is directly calculable using the BD yield and WHSV.

The minimization of the error function (7) in respect with the parameter values was performed by using the function ‚lsqnonlin' of Matlab scientific software. To calculate the theoretical values of conversion, yield, and selectivity, we used the mass balance equations in the experimental reactor. Ross et al. [1] demonstrated that the influence of the mass transport steps on the overall kinetics, in their working conditions, was negligible. The catalytic transformation in the experimental reactor is described by the ideal plug flow model, the mass balance equation for a species 'j' being defined by the equation:

$$\frac{d(u\,C_j)}{d\,z} = r_j^{'}, \quad j=1,2...Ns \tag{16}$$

Considering the nature of experimental data available from the paper of Da Ros et al. [1], the equation (16) is more advantageously to be expressed in respect with WHSV and the rates of reactions. In this aim, there are used the following additional relations:

$$u\,C_j = \frac{N_j}{S_T} = \frac{F_m\,g_j}{S_T} = \frac{F_{m,EtOH,0}\,g_j}{w_{EtOH,0}\,S_T}; \;\; WHSV = \frac{F_{m,EtOH,0}}{m_{cat}} = \frac{F_{m,EtOH,0}}{S_T\,L\,\rho_{bed}}; \tag{17}$$

$$g_j = g_{j,0} + \sum_{i=1}^{Nr} \nu_{ij}\,\xi_{m,i}\,; \quad r_j^{'} = \sum_{i=1}^{Nr} \nu_{ij}\,r_i; \quad x=z/L \tag{18}$$

Using these relations, the equation (16) can be written in the equivalent form:

$$\frac{d\xi_{m,i}}{dx} = \frac{w_{EtOH,0}}{WHSV} r_i, \quad i=1,2..N_r \tag{19}$$

The significances of notations used in the equations (16)-(19) are the following:

C_j, g_j, -concentrations of species j in the reaction mixture (kmol/m^3 and kmol/kg respectively); u- the flow velocity of gas (m/s); r_j' - rate of formation for species j, reported to the volume of the bed (kmol/(m^3 h)); N_j- flowrate of ‘j’ (kmol/h); S_T – cross surface area of the catalyst bed; F_m- mass flow rate of the reaction mixture (kg/h); $w_{EtOH,0}$- feed mass fraction of ethanol (kg/kg); m_{cat}- weight of catalyst in the bed (kg); ρ_{bed}- density of catalyst in the bed (kg/m^3); L- height of the bed (m); r_i- rate of the reaction ‘i’ (kmol/(kg$_{cat}$ h)); ν_{ij}-stoichiometric coefficient of species ‘j’ in the reaction ‘i’, ξ_{mi} – reaction extent reported to the mass of the reaction mixture (kmol/kg); Nr, Ns – number of reactions and number of chemical species respectively.

The numerical values of the parameters obtained by the estimation procedure are given in Table 2, along with their 95 % confidence intervals.

The activation energy estimated in this work for ethanol dehydrogenation (E_1=7.4398·8.314 kJ/mol= 61.854 kJ/mol) is in good agreement with the value determined experimentally by Da Ros et al. [11, Support Info.] for ethanol consumption, in the interval 60.2 to 61.6 kJ/mol (depending on the catalyst composition). This result could be explained by the low rate of the ethanol dehydrogenation step, one of the slowest steps of the ETB process. This characteristic of the ethanol dehydrogenation step could also explain the apparent activation energy of 62 kJ/mol determined for BD synthesis by Da Ros et al. [1, Support Info.].

A comparison of the calculated and experimental values for ethanol conversion, BD yield and by-products selectivity are presented graphically in the figures 3-a to 3-d.

The parity diagrams, shown in these figures, reveal a relatively good agreement between the calculated and experimental values, confirming the suitability of the kinetic model. A relatively modest quality of the fit is obtained for the side products (ethylene, diethyl ether and butene). Nevertheless, these are generated in relatively small concentrations, and, in addition, they are lumping other secondary products not included in the kinetic model.

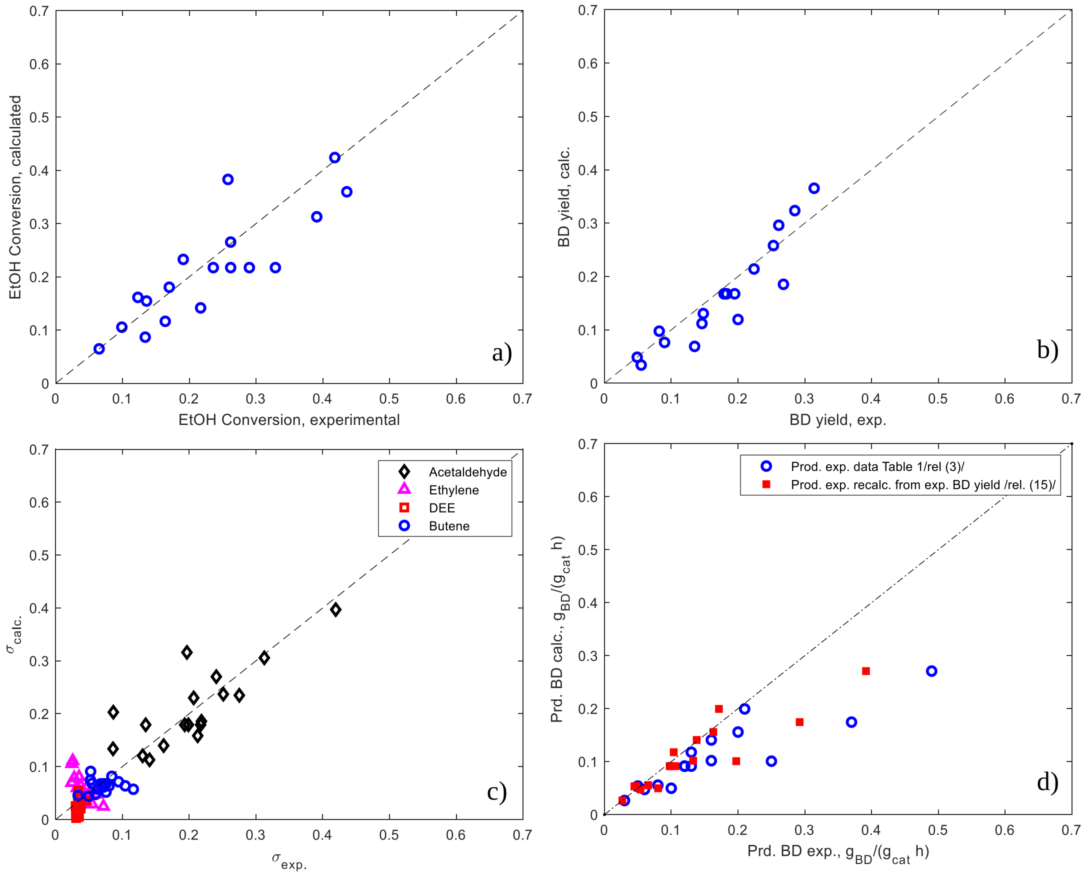

Fig. 3. Calculated versus measured values for: a) ethanol conversion; b) butadiene yield; c) secondary products selectivities; d) butadiene productivity (blue circles- abscissa representing the values from Table 1; solid red squares- abscissa calculated using relation (15), from experimental BD yield and WHSV).

We notice that, in the parity diagram for the productivity, given in Fig. 3-d, there are compared the calculated values, with both experimentally derived productivity (given in Table 1), and with the productivity deduced from the experimental values of BD yield and WHSV, using rel. (15). As observed, the quality of the fit of productivity is poorer in first case, probably due to higher experimental errors involved in the application of the relation (3). The adequate quality of the model is also supported by the relatively tight 95% confidence intervals of parameter values, and a very good correlation coefficient (ro2 = 0.99).

3. Conclusion

In this work was developed a kinetic model for the one stage synthesis of BD from ethanol (Lebedev process), using the experimental data and a reaction scheme published by Da Ros et al. [1]. The reaction scheme describing the stoichiometry of ethanol transformation is based on Toussaint-Kagan mechanism, to which were added few reactions describing the formation of side products. Empirical power law rate expressions, having the partial reaction orders equal to corresponding molecularities, were used to develop the kinetic model. There were calculated the chemical equilibrium constants of the reactions describing the transformation and their values were used to appreciate the reactions degree of reversibility. For the reactions having equilibrium constants over 100 bar$^{\Delta \nu i}$, there were used rate expressions specific for irreversible reactions. The results of the experimental reactor simulations, using the developed kinetic model, are in good agreement with the experimental data published in the reference paper of Da Ros et al. [1].

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