## NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY POLITEHNICA BUCHAREST

## DOCTORAL SCHOOL CHEMICAL ENGINEERING AND BIOTECHNOLOGY

## Analysis, modelling and simulation of ethanol conversion to 1,3-butadiene process

Summary of the PhD thesis

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## **THESIS OVERVIEW**

Butadiene (1,3-BD) is an important monomer for the industrial sector, mainly used in the synthesis of elastomers. Currently, it is obtained from petroleum derivatives (through the thermal cracking of gasoline and the dehydrogenation of n-butane and n-butenes).

The production of 1,3-BD from ethanol has been known since the beginning of the last century, when two processes were developed and applied on an industrial scale: the one-step process patented by Lebedev and the two-step process developed by Ostromislensky. However, these processes were abandoned in the 1960s due to the competition of petroleum-based technologies.

In recent decades, research on the synthesis of 1,3-butadiene (1,3-BD) from ethanol has been revived due to the decline of petroleum resources and the focus of researchers on developing technologies based on renewable feedstocks. The synthesis of 1,3-BD from ethanol is important from an economic, environmental, and sustainable development perspective. Ethanol can be obtained relatively easily from renewable resources. The majority of studies published in recent years have focused on the development of new catalysts with improved performance, through laboratory-scale investigations. Aspects related to technological development, such as new catalysts the behavior under industrial working conditions, manufacturing costs, kinetics of chemical transformation, plant design, are things that are poorly studied and require further investigation.

The main objective of the research carried out within the PhD stage was to analyze the process of ethanol conversion to 1,3-BD, in order to develop useful procedures for the design of fixed-bed catalytic reactors that can be used for this process. After analyzing the results published in recent decades regarding this transformation, the research was focused on the one-step process (Lebedev). The thesis is organized into four chapters presenting the research carried out and its results, an introductory section and a section of general conclusions.

**Chapter 1** of the paper presents an analysis of the main published studies, related to the identification of new catalysts with activity and selectivity superior to those used in the industrial process practiced before 1960. For this purpose, the influences of the composition and synthesis method of different materials on catalytic performances and chemical species (promoters/dopants) that improve these performances are sought, both for the one-step process (Lebedev) and for the two-step process (Ostromislensky).

Considering the performances in terms of activity and selectivity, resistance to deactivation and cost of preparation, for the Lebedev process the most interesting appear to be catalysts based on MgO-SiO<sub>2</sub> mixtures, promoted with different chemical species. The theoretical developments in this work refer to this type of catalysts.

For the two-step process (Ostromislensky), in the second step, of the synthesis of 1,3-BD from the acetaldehyde-ethanol mixture, the most interesting catalysts are  $Ta_2O_5/SiO_2$  and respectively  $ZrO_2/SiO_2$ .

Several theories have been proposed to explain the chemical transformation of ethanol into 1,3-BD. Among these, the most accepted seems to be the Toussaint-Kagan mechanism, which includes several successive and parallel chemical steps common to both processes (Lebedev and Ostromislensky). According to this mechanism, the main intermediates that appear during the transformation of ethanol into 1,3-BD are acetaldehyde, acetaldol, crotonaldehyde and crotyl alcohol (2-butenol).

From the analysis of the published works, no clear conclusion can be drawn regarding the comparative performances of the two ethanol conversion processes into 1,3-BD. Both processes are interesting from a commercial point of view, but there are performance differences, largely dependent on the catalysts used and the working conditions. In several published studies, the superiority of the two-step process is highlighted in terms of chemical transformation performance (higher 1,3-BD yield). On the other hand, the comparative evaluation of the two ETB processes, using economic and environmental criteria, led to the conclusion that the one-step process is more advantageous.

Taking into account the state of research related to obtaining 1,3-BD from ethanol, the following specific research objectives were set during the PhD stage, all related to the one-step process (Lebedev):

- Study of the thermodynamics of the transformation of ethanol into 1,3-BD: the temperature ranges over which the transformation is thermodynamically possible and, respectively, the characteristics of the state of chemical equilibrium for this transformation.

- Formulation of a kinetic model for the conversion process of ethanol to 1,3-BD, in a single step, on MgO-SiO<sub>2</sub> catalysts, using published experimental data.

- Analysis, using the tools of mathematical modeling and simulation, of the particularities of the catalytic process at the level of the spherical catalyst granule. Influence of particle size on

conversion performance (selectivity and yield in 1,3-BD) and development of a catalyst grain size selection procedure for fixed bed catalytic reactor.

- Modeling and simulation of the process at the level of the catalytic reactor with a fixed bed of catalyst and the comparison of the performances of classic fixed bed reactors (multitubular type and respectively multibed adiabat with direct and indirect intermediate heating).

- The study of the sensitivity of the reactor in relation to the main operating parameters.

- Studies to optimize the operation of fixed bed reactors.

In **Chapter 2** of the paper, a thermodynamic analysis of the ETB process was carried out, taking into account specific calculation expressions and physical-chemical data existing in literature for chemical species involved in this transformation, identified in published experimental studies. In order to ensure the unitary nature of the presentation, it was preferred that the literature study related to the thermodynamics of ETB process to be included in this chapter, together with the original contributions.

In first part of the chapter, the temperature range calculation for ethanol conversion into 1,3-BD, on which it is possible from a thermodynamic point of view (spontaneous) is presented. For this purpose, the transformation was stoichiometrically characterized by a global chemical equation. The analysis revealed that the conventional rules for assessing spontaneity, according to which the range of spontaneity corresponds to the negative values of the standard free enthalpy change (values of the equilibrium constant of the reaction,  $K_a$  above 1), lead to an underestimation of the temperature range over which the transformation is spontaneous. Significant values of ethanol conversion at equilibrium (even above 70 %) were obtained at temperatures at which the equilibrium constant of the global reaction,  $K_a=K_p$ , is under 1.

In the second part of the chapter, rigorous calculations of the composition at equilibrium are presented, using method of equilibrium constants (based on some reaction schemes proposed in published studies) and the Gibbs method. The results of these calculations show practically total ethanol conversions at equilibrium state and very low yields in 1,3-BD (well below those currently obtained experimentally). This demonstrates that transformations of practically importance are kinetically controlled (they occur at states far from chemical equilibrium), the main factor influencing practical yields being the activity and selectivity of the catalyst.

**Chapter 3** of the thesis focuses on the kinetic aspects of the transformation. Similar to the thermodynamic analysis, the literature review is included in this chapter to ensure a cohesive presentation, alongside the original contributions. The literature study revealed a limited number of published kinetic models for ETB processes. This chapter presents the kinetic models reported in the literature for both the single-step and two-step processes. For the one-step process, only two kinetic models were identified. The first published model is the one proposed by Tretyakov et al. (2014) and Ezinkwo et al. (2013) for (K<sub>2</sub>O)ZnO/<sub>γ</sub>Al<sub>2</sub>O<sub>3</sub> catalyst and hydrogen peroxide. Recently, a second kinetic model for this process was published for the hemimorphite catalyst [(Zn<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>]- HfO<sub>2</sub> /SiO<sub>2</sub>, published by Cabello Gonzalez et al.(2021).

The chapter also presents kinetic models for the two-step ETB process. The most important and more specific, is the second step, the transformation of the ethanol-acetaldehyde mixture into 1,3-BD. Among the kinetic models published for this transformation, the most complete is the one published by Dussol et al., applicable with small adaptations to the one-step process as well. The test of this model, by simulating the experimental reactor, confirmed the correctness of the published kinetic equations and parameters. Stoichiometric information published in this kinetic model is used in the chemical equilibrium calculation in Chapter 2 of the thesis.

The large number of species involved in the transformation of ETB and its complex mechanism make the investigation of the physico-chemical phenomena occurring on the catalyst surface difficult, so that most of the published kinetic models propose expressions of the reaction rates of the power product type, formulated empirically.

In the theoretical studies carried out within the thesis, which refer to the one-step process on a modified MgO-SiO<sub>2</sub> catalyst, an own kinetic model was used, developed using experimental data published by Da Ros et al. (2017-b). The reaction scheme on which the kinetic model is based (proposed by the authors of the experimental study) conforms to the Toussaint-Kagan mechanism, to which reactions have been added that explain the formation of experimentally observed secondary products (diethyl ether, ethene and butene). In total, 7 consecutive-parallel chemical reactions are considered, of which 4 are main reactions, which explain the transformation of ethanol into 1,3-BD, and 3 are secondary reactions. Expressions of reaction velocities of the product-of-power type, including terms expressing reversibility, have been proposed for reactions having the values of the equilibrium constants on the working range, sufficiently small ( $K_p < 20$  bar<sup> $\Delta vi$ </sup>). The quality of the proposed kinetic model is demonstrated by the good agreement of the calculated values with the experimental ones (for the conversion of ethanol, the yield in 1,3-BD, respectively the selectivities of acetaldehyde and secondary products), the small intervals in which the calculated parameters fall with the probability of 95%, and the estimated values of some activation energies, close to values determined in other published studies.

In **Chapter 4** of the paper, a theoretical study is presented, using the tools of mathematical modeling and numerical simulation, of the performances of multitubular fixed bed reactors, respectively adiabatic multibed, in the realization of the direct transformation process (Lebedev) of ethanol into 1,3- BD on a modified MgO-SiO<sub>2</sub> catalyst.

The description of the process that takes place in the catalytic reactor is carried out with a heterogeneous mathematical model, which takes into account the stages of gas-particle mass and heat transfer and, respectively, the diffusive mass transport inside the porous particle (Fick type model). Given the moderately endothermic character of the chemical transformation and the significant conductivity of the catalyst particle, the temperature variation within the particle is neglected. This hypothesis is confirmed by the small value of the internal temperature gradient, evaluated from the Weisz-Prater criterion.

In the first part of the chapter, the simulation study of the process was carried out at the level of the spherical catalyst granule, from which the radial evolutions of the concentrations of chemical species, of the reaction velocities and respectively the selectivities of the transformation into 1.3-BD were obtained. The results show that the shape of the radial profiles of the reaction rate inside the particle depends on the position of the particles in the catalytic bed. The radial profiles for the rate of ethanol consumption and respectively the rate of formation of 1,3-BD, inside the particles located in the first zone of the catalytic bed, show maximum points, which disappear in the second half of the bed. The influence of side reactions is greater at higher ethanol concentrations, so that the selectivity value in 1,3-BD, averaged over the particle volume, is greater for particles placed in the second zone of the catalytic bed.

An interesting result refers to the dependence of the rates of ethanol consumption and 1,3-BD formation respectively, averaged over the volume of the particle, in relation to its size. Calculating the values of these velocities in the particle diameter range between 1 and 6 mm, a maximum evolution is obtained in the range of 2-3 mm. The selectivity of 1,3-BD increases continuously with particle size. These results are explained by the interaction of the ethanol diffusion stages and intermediate products with the chemical transformation steps inside the catalyst particle. Thus, a diameter of 3 mm of the catalyst particle appears as the most recommended, from the point of view of the transformation performances.

The simulation of the process at the level of the catalyst bed led to negligible values of the external gradients of temperature and concentration of ethanol along the catalytic bed, which highlights an insignificant influence of the resistances on the gas-particle heat transfer, respectively on the mass transfer of ethanol from the zone convective movement of the gas towards the external surface of the particle. Consequently, the only physical step that significantly influences the global kinetics of the process is the internal diffusion. For reactions in which ethanol is the only reactant, internal diffusion has a limiting effect (values less than 1 of the effectiveness factor), while for reactions in which intermediates act as reactants, internal diffusion has a positive effect of amplifying reaction rates (values over 1 of the effectiveness factors on the first zone of catalytic bed).

In order to simplify the mathematical model of the catalytic reactor, and reduce the calculation time, which is important in applications that require a large number of iterations, such as optimization calculations, temperature-dependent correlations of effectiveness factors were proposed for ethanol transformation reactions. These empirical correlations, which include three adjustable parameters, express the dependence of the subunitary effectiveness factors on the bed temperature. The results of the reactor simulation using the effectiveness factors calculated from these correlations are very close to those obtained using the heterogeneous model (balance equations at the level of the catalyst particle), which confirms the good quality of the correlation and makes it possible to use the reaction effectiveness factors in the calculation of reactions mean velocities in the granule.

A parametric sensitivity calculation for the multitubular reactor showed that, among the operating variables, the temperature of the heat agent and, respectively, the flow rate of the reactant mixture (gas-catalyst contact time) have the greatest influence on the yield in 1,3-BD.

In the presented simulation calculations, values of the operating variables were used within the limits that appear in the experiments used to derive the kinetic model (ethanol-inert gas mixture feed, feed temperature in the bed 400 °C). These working conditions correspond to limited ethanol conversions (generally below 50%), compensated by relatively high selectivities in 1,3-BD (over 80%). Consequently, there is a need to recirculate large amounts of ethanol.

Since the transformation of ETB results in significant amounts of water, the separation of pure ethanol is expensive, the more economically advantageous being the separation of the ethanol-water azeotrope. The calculations performed showed that, by replacing the pure ethanol in the feed with the cheaper ethanol-water azeotrope, at the same concentration of ethanol in the feed, the yield value in 1,3-BD decreases by ~4.8%, a relatively small decrease, compared to the economic advantage of using ethanol-water azeotrope instead of pure ethanol.

In order to compare the performance of reactors with multitubular fixed bed and respectively multibed adiabatic with heating between the beds, the sizing of the two types of reactors was done in such a way as to ensure operating conditions as close as possible (the same conditions at the entrance of the gas into the reactor, the same lengths of the catalytic beds, the same size of the catalytic particle).

The least performing in terms of yield in 1,3-BD was found to be the adiabatic multibed reactor with direct heating (by injection of hot reactant between the beds). The result is explained by the reduction of the reaction time, due to the bypassing of some catalytic beds by the hot reactant injected to heat the mixture.

The adiabatic multibed reactor with indirect heating (with heat exchangers between beds) ensures better performances as the number of beds increases, superior to that with direct heating, but inferior to the multi-tubular one heated with Dowtherm A saturated vapors. At a number of 6 beds, the adiabatic multibed reactor with indirect heating ensures the same yield in 1,3-BD as the multitubular reactor.

An optimization study of the operation of multibed adiabatic and respectively multitubular reactors, which aimed to determine the working parameters that maximize three objective functions: the yield of transformation into 1,3-BD, the flow rate of 1,3-BD and respectively a simplified expression of the economic efficiency of reactor operation. The results of the optimization calculations showed that obtaining a maximum yield of 1,3-BD requires working at low flow rates and relatively high conversions of ethanol (low production of 1,3-BD), while maximizing the flow rate of 1,3-BD it is carried out at relatively high flow rates and relatively low conversions of ethanol (high flows of recirculated ethanol). A compromise between these two extreme solutions can be represented by the maximization of an economic function, which represents the profit made by operating the reactor.

The last part of the paper presents the general conclusions of the studies carried out and the list of bibliographic references.

### **1. LITERATURE REVIEW**

Butadiene (1,3-BD) is an important monomer for the industrial sector, used in the synthesis of polymers such as polybutadiene, styrene-butadiene, acrylonitrile-butadiene styrene, etc. Currently, more than 95% of the world's total amount of 1,3-BD is produced, either by thermal cracking of gasolines or by dehydrogenation of n-butane and n-butenes (Gallo et al., 2014). Obtaining 1,3-BD from these processes, requires expensive extractive distillation separations with low 1,3-BD selectivity. On the other hand, the shale gas revolution led to an increase of C<sub>2</sub>-C<sub>3</sub> hydrocarbons in the feedstock used in thermal cracking and as consequent a decrease in 1,3-BD production from these processes, inducing difficulties in market demand coverage (Bruijnincx and Weckhuysen, 2013; DeRosa and Allen, 2015). In addition, the world production of 1,3-BD is facing problems due to the unstable price of petrochemical products, as consequences we have Japan case, where 3 of the 15 ethylene production plants were closed in 3 years, starting from June 2016 (Duan et al., 2016). Therefore, the chemical industry calls for the development of alternative processes for the production of 1,3-BD independent of petroleum, using renewable chemical raw materials (derived from biomass). These reasons have renewed interest in the catalytic conversion of ethanol into 1,3-BD, already known since the first decades of the 20th century (Pomalaza et al., 2020). Published studies demonstrate important advantages of 1,3-BD production from ethanol, from an economic, ecological and sustainability point of view (Patel et al., 2012; Cabrera Camacho et al., 2020). Industry interest in this process is also stimulated by the relatively high production of ethanol and its development prospect. In 2021, global ethanol production was 103.3 million m<sup>3</sup> (27,290 million gallons) and was projected to grow at an annual rate of 4.8% from 2021 to 2027. The world's largest producer of ethanol is the USA, accounting for 55% of global production in 2021 (~57 million m<sup>3</sup>/year) (https://ethanolrfa.org/markets-and-statistics/annual-ethanol-production). In the first decades of the 20th century, two catalytic processes were developed for the conversion of ethanol to 1,3-BD (the ETB process) the "one-step process" discovered by Lebedev (the conversion takes place in a single catalytic reactor) and respectively the "two-step process" developed by Ostromislensky

(ethanol is first converted to acetaldehyde in a dehydrogenation reactor and, further, 1,3-BD is synthesized from an ethanol-acetaldehyde mixture in a second reactor).

### 1.1. One step synthesis of 1,3-butadiene from ethanol

### 1.1.1. Catalysts

The first catalyst discovered for the one-step process, a mixture of zinc oxide and alumina, was developed and patented in the early 1930s by Sergei Lebedev, who developed the process that bears his name. A decade later, Natta and Rigamonti (1947a and 1947-b) identified that the best catalyst for a one-step process was a MgO-SiO<sub>2</sub> mixture. The authors claim that using this catalyst, prepared by special procedures, to prevent salinization of the two components, yields of 60% were obtained. Published studies show that, to date, the most active and selective catalysts for this reaction are still based on MgO/SiO<sub>2</sub>, even though almost a century has passed since it was discovered. MgO provides basic centers and has catalytic activity in aldol condensation and dehydrogenation steps, while SiO<sub>2</sub> provides acidic centers and catalyzes dehydration reactions. Also, published studies have shown that the performances of the MgO/SiO<sub>2</sub> catalyst are critically dependent on the composition and the preparation method. Several studies have concluded that a Mg/Si molar ratio greater than or equal to unity ensures high catalytic activity of the MgO/SiO<sub>2</sub> mixture, allowing yields in 1,3-BD of up to 42% (Makshina et al., 2014; Niiyama et al., 1972; Ohnishi et al., 1985; Kvisle et al., 1988; Makshina et al., 2012; Jones, 2014).

### 1.1.2. Theories regarding the process mechanism

The direct conversion of ethanol to 1,3-BD takes place in several steps, consisting of parallel and consecutive reactions, still incompletely known with certainty. This complex transformation involves the use of a bifunctional catalyst, capable of promoting dehydration and dehydrogenation reactions. In addition to the main product, 1,3-BD, an important number of secondary products result in the conversion process, with selectivity depending on the catalyst composition and working conditions: diethyl ether, ethylene, acetaldehyde, ethyl acetate, acetone, butanol, propane , pentene, hexene, etc. (Jones, 2014). In the following, the main chemical mechanisms proposed to explain the transformation of ethanol to 1,3-BD are presented.

It should be noted that these refer to the transformation into 1,3-BD and less to the formation of secondary products (see Bhattacharyya and Gangul, 1962-b).

The Toussaint-Kagan mechanism. It is the most widely accepted mechanism for the direct conversion of ethanol to the synthesis of 1,3-BD which was first formulated by Kagan et al. and then developed by other researchers (Niiyama et al., 1972; Bhattacharyya and Sanyal, 1967; Natta and Rigamonti, 1947-a). The main steps of this mechanism are shown in Figure 1.3-a. In this scheme, the greatest debate has been related to the conversion of 2-butenal (crotonaldehyde) to 2-butenol. The most widely accepted hypothesis is that of intermolecular hydrogen transfer between ethanol and 2-butenal molecules, following a so-called Meerwein-Ponndorf-Verley-Oppenauer (MPVO) mechanism, which involves the participation of the acidic and basic centers of the catalyst. The occurrence of crotonaldehyde reduction with ethanol (MPVO step), related to the presence of Lewis acid centers, was argued by thermodynamic calculations (Angelici et al., 2013, Angelici et al., 2014). The kinetic control step, in the general scheme shown in Figure 1.3a, appears to depend on the concentrations of acidic and basic centers in the MgO-SiO<sub>2</sub> catalyst. Bhattacharyya and Sanyal (1967) and Kvisle et al. (1988) hypothesized that the step that controls the kinetics of the process (the rate-determining step) is the aldol condensation. However, over basic catalysts with weak redox properties, the kinetically controlling step is assumed to be the dehydrogenation of ethanol to acetaldehyde (Niiyama et al., 1972; Pomalaza et al., 2016). Another theory states that, in the case of Lewis acidic catalysts, the slowest (kinetic controlling) step should be the MPVO reaction step (Pomalaza et al., 2016), and Jones et al. conclude, based on their own experimental data using a MgO-SiO<sub>2</sub> (1:1 mol) catalyst, that the kinetic control step is also temperature dependent. In the 300-400 ° C range, acetaldehyde condensation controls the overall kinetics, while at higher temperature the slowest step is expected to be ethanol dehydrogenation (Jones, 2014).

### 1.2. THERMODYNAMICS OF ETHANOL TRANSFORMATION TO BUTADIENE PROCESS

### 2.1. Published thermodynamic studies of the ETB process

As is known, thermodynamics provides data that allow the evaluation of the maximum transformation limits that can be reached under given working conditions. In addition, thermodynamic data are used to calculate the thermal effects of chemical reactions, which are

also important in the design and operation of chemical reactors. This chapter will review the published studies investigating the thermodynamics of the ethanol to 1,3-BD conversion process, re-examining and supplementing some of them, using the computational programs developed in the thesis, as well as the Aspen Plus process simulator facilities. Ethanol Conversion in a single step in 1,3-BD occurs according to the global reaction described by the equation:

$$2C_2H_5OH \leftrightarrow C_4H_6 + 2H_2O + H_2$$
(2.1)

Reaction (2.1) is endothermic, with the enthalpy variation ranging from 102 to 109 kJ/mol as the temperature increases from 200 to 500 °C (Banu et al., 2021)

### 2.3. Study of the spontaneity of ethanol conversion to 1,3-BD

Identifying the temperature range corresponding to the negative values of the standard free enthalpy ( $\Delta G_R^0 < 0$ ), above which the reaction is thermodynamically favored, does not provide the entire temperature range in which the reaction is thermodynamically (spontaneously) possible. A thermodynamically complete description requires the identification of the entire temperature range in which the reaction is thermodynamically possible (spontaneous), i.e. the temperature range that fulfills the condition dG<0, under given working conditions. In the following we will identify the intervals that ensure the spontaneity of the global reaction (2.1), assuming the ideal behavior of the reaction mixture and considering that the initial mixture contains ethanol and water. By integrating relation (2.17) we obtain:

$$G = \Delta G_{R}^{0}(T)\xi + 2RT[\xi \ln \frac{\xi P}{n_{0} + 2\xi} + \xi \ln \frac{(n_{30} + 2\xi)P}{n_{0} + 2\xi} - \xi \ln \frac{(n_{10} - 2\xi)P}{n_{0} + 2\xi} - \frac{n_{0}}{2}\ln(n_{0} + 2\xi) + \frac{n_{30}}{2}\ln(n_{30} + 2\xi) + \frac{n_{10}}{2}\ln(n_{10} - 2\xi)]d\xi + C;$$
(2.18)

C - the integration constant, which was determined using the initial condition.

The expression (2.18) was used to construct the diagrams shown in Figure 2.2, which describe the dependences of the free enthalpy, in relation to the molar degree of advancement, at P=1 bar and four temperatures. The curves  $G(\xi)$ , were calculated for an initial mixture containing pure ethanol ( $n_{10}=1$  mol şi  $n_{30}=0$ ). So, the range for possible values of global reaction

extent is  $\xi \in [0, 0.5]$ , the ethanol conversion being X=2 $\xi$ . The points representing the equilibrium state correspond to the minima of the curves shown in Figure 2.2.



Figure 2.2. Gibbs free energy of the mixture as function of the global reaction extent at four temperatures (pure ethanol; P=1 bar). The numbers on the diagrams represent the reaction extent value at minimum point.

On left domains to these minimum points, the transformation occurs spontaneously towards the equilibrium point. As expected, this range expands with increasing temperature, the transformation being endothermic. The four temperatures were selected to include the value corresponding to Kp=1 (~166 °C), considered in the publications mentioned above, as the lower limit, above which the reaction takes place with significant values of global reaction extent. However, as can be seen from these diagrams, equilibrium ethanol conversion values up to 0.8 (80 %) can be obtained at lower temperatures than those corresponding to Kp=1.

#### 2.4. Chemical equilibrium calculations of ETB processes

The chemical equilibrium composition of systems with multiple reactions can be evaluated, either using the equilibrium constants of the chemical reactions that define the transformation (the method of equilibrium constants), or by minimizing the free enthalpy of the system (Gmehling et al., 2019).

# 2.4.1. Evaluation of the composition at chemical equilibrium for the one-step ETB process

The characteristics of the reaction system at equilibrium will be evaluated using the reaction scheme proposed by Da Ros et al. (2017-b) (Table 2.1). In the calculations, transcrotonaldehyde and iso-butene were chosen as model compounds, considering their greater stability compared to the other isomers (Da Ros et al., 2016; Da Ros et al., 2017-a).

The results show that for the reactions R1, R4 and R6 to R8 there are no significant differences in the values of the equilibrium constants calculated using data from the two sources (the Yaws monograph, respectively the Aspen Plus database), over the working temperature range. The biggest differences are highlighted for reactions R2, R3 and R5. The Kp(T) dependencies for the reactions proposed by Da Ros demonstrate that four of them are endothermic (R1, R4, R5 and R7), the other three being exothermic (R2, R6 and R8). The major difference occurs in reaction R3, for which calculations by the two methods show opposite thermal effects. The data obtained from the Aspen Plus database show an endothermic character, while the data calculated on the basis of Yaws thermodynamic data (Yaws, 1999), show a slightly exothermic character. Comparing the values of the equilibrium constants for the ethanol consumption reactions (R1, R4, R6 and R7), it can be seen that, in the temperature range of practical interest, the highest value is the constant  $K_{p,7}$ , corresponding to the dehydration of ethanol to ethylene . Consequently, an important fraction of ethanol is expected to be converted to ethylene, limiting the yield of 1,3-BD obtained at chemical equilibrium.

The differences between the calculated values of the equilibrium constants are explained by the differences between the values of enthalpies of formation, free enthalpies of formation, and molar heats for the chemical compounds, respectively.

React	Reaction		
$C_2H_6O \Leftrightarrow C_2H_4O + H_2$	$Ethanol \Leftrightarrow AcH + H_2$	R1 <sup>(a)</sup>	
$2C_2H_4O \Leftrightarrow C_4H_8O_2$	$2AcH \Leftrightarrow Acetaldol$	R2 <sup>(a)</sup>	
$C_4H_8O_2 \Leftrightarrow C_4H_6O + H_2O$	$Acetaldol \Leftrightarrow Crotonaldehyde + H_2O$	R3 <sup>(a)</sup>	
$C_4H_6O + C_2H_6O \Leftrightarrow C_4H_8O + C_2H_4O$	$Crotonaldehyde + EtOH \Leftrightarrow$	$\mathbf{R4}^{(a,b)}$	
	2-buten-1-ol+AcH		
$C_4H_8O \Leftrightarrow C_4H_6 + H_2O$	$2-buten-1-ol \Leftrightarrow 1, 3-BD+H_2O$	$R5^{(a,b)}$	
$2C_2H_6O \Leftrightarrow C_4H_{10}O + H_2O$	$2EtOH \Leftrightarrow DEE + H_2O$	$R6^{(a,b)}$	
$C_2H_6O \Leftrightarrow C_2H_4 + H_2O$	$EtOH \Leftrightarrow Ethylene + H_2O$	$R7^{(a,b)}$	
$2C_2H_4 \Leftrightarrow C_4H_8$	$2Ethylene \Leftrightarrow Butene$	<b>R</b> 8 <sup>(a)</sup>	
$2C_2H_4O \Leftrightarrow C_4H_6O + H_2O$	$2AcH \Leftrightarrow Crotonaldehyde + H_2O$	R9 <sup>(b)</sup>	
$2C_2H_4O \Leftrightarrow C_4H_6O + H_2O$	$2AcH \Leftrightarrow MVK + H_2O$	R10 <sup>(b)</sup>	
$C_4H_6O + C_2H_6O \Leftrightarrow C_4H_8O + C_2H_4O$	$MVK + EtOH \Leftrightarrow$	R11 <sup>(b)</sup>	
	3-buten-2-ol+AcH		
$C_4 H_8 O \Leftrightarrow C_4 H_6 + H_2 O$	$3-buten - 2 - ol \Leftrightarrow 1, 3 - BD + H_2O$	R12 <sup>(b)</sup>	
$C_4H_8O \Leftrightarrow C_4H_8O$	$2-buten-1-ol \Leftrightarrow Butanal$	R13 <sup>(b)</sup>	
$C_4H_8O \Leftrightarrow C_4H_8O$	$3-buten-2-ol \Leftrightarrow MEK$	R14 <sup>(b)</sup>	
$C_4H_8O + C_2H_6O \Leftrightarrow C_4H_{10}O + C_2H_4O$	$Butanal + EtOH \Leftrightarrow 1 - Butanol + AcH$	R15 <sup>(b)</sup>	
$C_4H_8O + C_2H_6O \Leftrightarrow C_4H_{10}O + C_2H_4O$	$MEK + EtOH \Leftrightarrow 2 - Butanol + AcH$	R16 <sup>(b)</sup>	
$C_4H_{10}O \Leftrightarrow C_4H_8 + H_2O$	$1 - \text{Butanol} \Leftrightarrow 1 - \text{Butene} + H_2O$	R17 <sup>(b)</sup>	
$C_4 H_{10} O \Leftrightarrow C_4 H_8 + H_2 O$	$2 - \text{Butanol} \Leftrightarrow 2 - \text{Butane} + H_2O$	R18 <sup>(b)</sup>	
$2C_2H_4O \Leftrightarrow C_4H_8O_2$	$2AcH \Leftrightarrow Ethylacetate$	R19 <sup>(b)</sup>	
$2C_2H_4O \Leftrightarrow C_3H_6O + CH_2O$	$2AcH \Leftrightarrow Acetone + Formaldehyde$	R20 <sup>(b)</sup>	
$CH_2O + 2C_2H_6O \Leftrightarrow C_3H_6 + 2H_2O + C_2H_4O$	$Formaldehyde + 2EtOH \Leftrightarrow$	R21 <sup>(b)</sup>	
	Propene + $2H_2O + AcH$		
$C_{3}H_{6}O + C_{2}H_{6}O \Leftrightarrow C_{3}H_{6} + AcH + H_{2}O$	$Acetone + EtOH \Leftrightarrow C_{3}H_{6} + AcH + H_{2}O$	R22 <sup>(b)</sup>	
$C_3H_6O + C_2H_6O \Leftrightarrow C_5H_8 + 2H_2O$	Acetone + EtOH $\Leftrightarrow$ Pentadiene + 2H <sub>2</sub> O	R23 <sup>(b)</sup>	
$2C_2H_4O + C_2H_6O \Leftrightarrow C_6H_8 + 3H_2O$	$2AcH + EtOH \Leftrightarrow Hexatriene + 3H_2O$	R24 <sup>(b)</sup>	

Table 2.1. The chemical reactions taken into consideration by the schemes formulated Da Ros et al. (2017-b), respectiv Dussol et al.(2020)

(a) Da Ros reaction scheme; (b) Dussol reaction scheme

To evaluate the composition at chemical equilibrium based on the reaction scheme proposed by Da Ros et al. (2017-b), calculations were performed considering an initial state consisting of pure ethanol for a temperature range between 120 - 500 °C. The calculation consisted mainly in numerical solution of a nonlinear algebraic equations system that define the existing relationships between the equilibrium constants and global reaction extent of the eight reactions R1 to R8. Due to the large differences between the values of the equilibrium constants, some convergence difficulties appeared in the solution numerical calculation. These were circumvented by using a continuation method, making iterations on the values of the equilibrium constants, starting from values close to each other, which do not introduce convergence difficulties. The temperature dependences of steady-state ethanol conversion and selectivity to the most important reaction products are plotted in Figures 2.5 (A to F), for both sets of thermodynamic data considered in this study. The temperature dependence of the equilibrium conversion of ethanol shows that it is practically total (>0.9998) over the entire temperature range considered (Fig. 2.5-A). It is interesting to note the appearance of a minimum of the equilibrium conversion around the temperature of 325 °C. Practically, this variation in ethanol conversion is insignificant as it corresponds to a decrease of only 0.001%. The minimum occurs because at low temperatures the influence of ethanol esterification (exothermic) predominates, while at higher temperatures, the endothermic reactions of dehydration and dehydrogenation of ethanol predominate, respectively. This can also be evidenced by the evolution of the selectivity of diethyl ether (Figure. 2.5-D). Although the differences between the equilibrium constants highlighted in Figure 2.3 are significant, they do not induce an important change in the mixture composition at equilibrium over the studied parameter ranges. Since Da Ros's reaction scheme includes alternate transformations of ethanol to diethyl ether and ethylene, the maximum value achieved for 1,3-BD selectivity is 0.09, at the maximum temperature of 500 °C (Fig. 2.5-B). Also, the yield in 1,3-BD is practically equal to the selectivity of 1,3-BD, since the ethanol conversion is practically total. The conclusion is that the secondary reactions R6, R7 and R8, considered in the Da Ros reaction scheme, consume ethanol in parallel with the dehydrogenation to acetaldehyde, so that the products obtained with higher selectivities at equilibrium are ethylene and iso-butene (figures 2.5 E and F).



Figure 2.5. Temperature dependence of ethanol conversion (A) and selectivities in 1,3-butadiene (B), acetaldehyde (C), diethyl ether (D), ethylene (E), and i-butene (F) at chemical equilibrium (pressure 1 bar; initially pure ethanol).

At temperatures below 300 °C, a significant amount of iso-butene is formed, the calculated selectivity being close to 1.0. After this temperature, the selectivity in iso-butene drops slightly

to 0.55 at temperatures of 500 °C. At higher temperature, ethylene appears to be the most thermodynamically stable product (as the equilibrium constant of reaction R8 becomes very small), with the yield of 1,3-BD being considerably lower when dehydration of ethanol to ethylene is included in the analysis thermodynamics. When the temperature increases from 300 to 450°C, the ethylene selectivity value increases from 0.025 to 0.35 (Figure 2.5E). It is worth pointing out that neglecting the side reactions in the equilibrium calculation of the one-step ETB process (ie, considering only the main reactions R1 to R5), leads to a 1,3-BD yield of 96.5%. It is also important to point out that the yields in 1,3-BD obtained experimentally, which in some cases exceed 70%, are much higher than those calculated at equilibrium, this result proving that the experimental processes take place far from equilibrium, under a kinetic control, dependent on the performance of the catalyst.

### 2.4.2. Evaluation of the composition at chemical equilibrium for two-step ETB process

A rather complex reaction scheme for the synthesis of 1,3-BD from acetaldehyde-ethanol mixture has been recently proposed by Dussol et al. (2020) (hereafter referred to as the Dussol scheme). This scheme is defined by the reactions R4-R7 and R9-R24 in Table 2.1.

### 2.4.2.2. Evaluation of the equilibrium composition

The overall conversion and selectivities of the chemical compounds for the two-step process were calculated using relations (2.23):

$$X_{Global} = 1 - \frac{n_{EtOH} + n_{AcH}}{n_{EtOH,0} + n_{AcH,0}}; \sigma_{j/EtOH} = \frac{n_{C,j}}{n_{C,EtOH/AcH}} \cdot \frac{n_j - n_{j,0}}{n_{EtOH,0} + n_{AcH,0} - n_{EtOH} - n_{AcH}}$$
(2.23)

Where:  $n_{C,j}$  and  $n_{C,EtOH/AcH}$  represent the number of carbon atoms in product j and the main reactants (ethanol and acetaldehyde), respectively;  $n_j$ ,  $n_{EtOH}$ ,  $n_{AcH}$  – the number of moles of product j, ethanol and acetaldehyde at equilibrium;  $n_{j,0}$ ,  $n_{EtOH,0}$ ,  $n_{AcH,0}$  – the number of moles of product j, ethanol and acetaldehyde in the initial mixture.

The temperature dependences of ethanol conversion, acetaldehyde conversion and overall conversion, as well as selectivity values in different products, calculated over the temperature range 120 - 500 °C and an initial EtOH/AcH molar ratio of 3.6, are shown in Figures 2.10.



Figure 2.10. Characteristics of the equilibrium transformation calculated using the reaction scheme proposed by Dussol et al.;8 EtOH/AcH = 3.6; P = 1 bar.

A conclusion that can be drawn by analyzing the results in this figure is that the selectivity of 1,3-BD at equilibrium in is very low (below 5 % over the considered temperature range), compared to the experimental values reported in the study by Dussol et al. (2020). This proves again that the experimental process takes place in the kinetic regime without a significant

thermodynamic influence. The calculated EtOH conversion is practically total, while the acetaldehyde (AcH) conversion drops to about 80% (Figure 2.10-A), showing that at higher temperatures the influence of exothermic reactions of AcH consumption predominates. In addition, a minimum appears in the ethanol conversion around the temperature of 390 °C. The appearance of this minimum is explained by the predominance of exothermic reactions in the first temperature range (condensation of acetaldehyde into acetaldol, transformation of acetaldehyde into ethyl acetate, isomerizations of 2-buten-1-ol and respectively 3-buten-2-ol) and endothermic ones on the second zone of the temperature range. The selectivity profiles shown in Figure 2.10 highlight the fact that, among the exothermic reactions that control ethanol conversion at temperatures lower than 390 °C, the isomerization reaction of 3-buten-2-ol to MEK has the greatest influence. Of course, this variation in ethanol conversion is insignificant because it corresponds to a decrease of about 0.001%. At temperatures around 300 °C, large amounts of MEK, acetone and propene are formed, with selectivities between 15 - 20 % (Figure 2.10-C) and relatively important amounts of pentadiene (selectivity about 1.5 %) (Figure 2.10-F). The other intermediates are formed in fairly small amounts in the equilibrium mixture (ethylene, MVK, formaldehyde, butene, hexatriene, 1-butanal, ethyl acetate and DEE). When the temperature increases towards 500 °C, the main products are unsaturated hydrocarbons (butenes, pentadiene and propene), showing that the reactions in which these compounds are formed are rather irreversible.

### 2. KINETICS OF ETHANOL TRANSFORMATION TO BUTADIENE

As it is known, the kinetic data is one of the essential elements in the design of the chemical reactor. Despite its importance, a small number of published studies investigating the kinetics of the conversion process of ethanol to 1,3-BD.

Most of the published studies proposing kinetic models for the ETB process have appeared in the last decade. Unfortunately, there are no published kinetic models for all the best performing catalysts known in the literature.

Another problem related to the kinetics of ETB transformation is the lack of comprehensive studies on the catalyst deactivation phenomenon. The few published investigations do not provide sufficient information related to deactivation kinetics, referring to relatively short operating times and operating conditions specific to laboratory-scale installations. For this reason, the topic of deactivation of specific catalysts for the ETB transformation will not be addressed in this work.

In the following, the published kinetic studies will be presented, both for the one-step process and for the two-step process, which are useful especially for the analysis and design of reactors, but also for some thermodynamic calculations.

### **3.1.2.** Kinetic study published by Da Ros et al.

Da Ros et al. (2017-b) performed an in-depth kinetic study for the one-step ETB process in the presence of K<sub>2</sub>O:ZrO<sub>2</sub>:ZnO/MgO-SiO<sub>2</sub> catalyst (particles smaller than 200  $\mu$ m) in a fixedbed reactor (in quartz tube), the reactor being fed with a mixture of ethanol and inert gas. The reaction temperature (T) was varied between 300 and 400 °C and the WHSV (relative to ethanol), in the range of 0.3-2.5 h<sup>-1</sup>, by changing the ethanol flow rate (keeping fixed the mass of the catalyst and the flow rate of inert). This way of working led to simultaneous variations, both for the reaction time and for the composition of the feed mixture. The mole fractions of ethanol in the feed were worked out between 0.41 and 0.85 and the contact time (calculated as the ratio of the catalyst volume to the total gas flow at the reaction conditions) ranged from 1.3 to 5.3 s. The reactions considered by the authors are shown in Table 3.2-a and the experimental results are shown in Table 3.2-b.

# **3.3.** Development of a kinetic model for the one-step conversion of ethanol to butadiene based on data published by Da Ros et al

In the present work, a relatively simple kinetic model for the direct transformation of ethanol to 1,3-BD was developed, using the experimental data published by Da Ros et al. (2017b). Based on the reaction scheme proposed by the authors (in accordance with the Toussaint-Kagan mechanism), expressions of reaction rates of the product-of-power type were proposed. In order to appreciate the degree of reversibility of the considered reactions, the chemical equilibrium constants  $K_{p,i}$ , obtained in the study presented in chapter 2 of this paper, were used, assuming the ideal behavior of the reaction mixture.

The seven reaction rate expressions shown in Table 3.10 include 14 unknown Arrhenius parameters, km1, km2,...km7, E1, E2,...E7.

To estimate the values of these parameters, the least squares method was applied, using the experimental data presented in Table 3.2-b. These data include a set of measured values for ethanol conversion, 1,3-BD yield, selectivities of some products (1,3-BD, acetaldehyde, ethene, diethyl ether and butene) respectively 1,3-BD productivity, for 18 experiments, which differ by temperature, or WHSV values.

Table 3.10 presents the reaction equations that describe the process of direct transformation of ethanol into 1,3-BD, their proposed rate expressions, as well as the estimated values of the parameters together with their confidence intervals with 95% probability.

The estimation calculations were performed with a calculation program written in the Matlab language, using the lsqcurvefit function.

;	Ponotion	Propertion rate	$k_i = k_{m,i} \exp[\frac{E_i}{R}(\frac{1}{T_m} - \frac{1}{T})]; T_m = 626K$		
i	Reaction	Reaction Fate	$\mathbf{k_{m,i}}^{(*)}$	$E_i/R, K$	
			kmol/(kg h bar <sup>ni</sup> )		
R1	$C_2H_5OH$	$r_1 = k_1 (p_{E+OH} - \frac{p_{ACH} p_{H2}}{p_{H2}})$	$4.025 \cdot 10^{-3}(1 \pm 0.0006)$	7439.8(1	
	$\Leftrightarrow C_2 H_4 O + H_2$	$K_{p1}$	$+.025 \cdot 10  (1 \pm 0.0000)$	± 0.0012)	
P2	2 <i>C</i> <sub>2</sub> <i>H</i> <sub>5</sub> <i>OH</i>	$r_{0} = k_{0}(p_{1}^{2}, \dots, -\frac{p_{DEE}p_{H20}}{p_{DEE}})$	$2.026 \cdot 10^{-4} (1 \pm 0.012)$	6638.2(1	
K2	$\Leftrightarrow C_4 H_{10} 0 + H_2 0$	$K_{p1}$	$3.020 \cdot 10  (1 \pm 0.012)$	± 0.0095)	
R3	$C_2H_5OH$	r - k n	$5.021 \cdot 10^{-4} (1 \pm 0.0008)$	1324.5(1	
K5	$\Rightarrow C_2 H_4 + H_2 O$	$r_3 - \kappa_3 p_{EtOH}$	$3.921 \cdot 10  (1 \pm 0.0098)$	± 0.051)	
R4	$2C_2H_4 \Rightarrow C_4H_8$	$r_4 = k_4 p_{C2H4}^2$	17.253(1±0.005)	3008.3(1±0.019)	
25	$2C_{2}H_{4}O$	<i>r</i> <sub>5</sub>			
R5	$\Leftrightarrow C_4 H_6 0 + H_2 0$	$=k_5(p_{AcH}^2 - \frac{p_{C4H60}p_{H20}}{K_{p5}})$	$11.312(1 \pm 0.0016)$	4005.8(1±0.0055)	
	$C_4H_6O + C_2H_5OH$				
R6	$\Rightarrow C_4 H_6 +$	$r_6 = k_6 p_{EtOH} p_{C4H6O}$	503.75(1±0.013)	1018.2(1±0.034)	
	$+C_2H_4O+H_2O$				
R7	$C_4H_{10}O$	$r_{-} = k_{-}n_{-}n_{-}$	$5,839,10^{-2}(1+0.023)$	13655(1+0.018)	
К/	$\Rightarrow 2C_2H_4 + H_2O$	$r_7 - \kappa_7 p_{DEE}$	$5.657 \cdot 10 (1 \pm 0.025)$	15055(1±0.018)	

Table 3.10. Expressions of reaction rate and ranges of variation of parameters at one degree of confidence 95 %

Indices used in rate expressions: AcH- acetaldehyde; EtOH- ethanol; crotA- crotonic aldehyde; DEE- diethylether.

The activation energy estimated in this work for the dehydrogenation of ethanol  $(E_1=7.4398\cdot 8.314 \text{ kJ/mol} = 61.854 \text{ kJ/mol})$  is in good agreement with the values determined

experimentally by Da Ros et al. (2017-b, Support Info) for ethanol consumption, in the range of 60.2 and 61.6 kJ/mol (depending on the catalyst composition). This result could be explained by the low reaction rate of the ethanol dehydrogenation step, one of the slowest steps in the ETB process. This feature of the ethanol dehydrogenation step could also explain the apparent activation energy of 62 kJ/mol determined by Da Ros et al. (2017-a, Support Info) for the synthesis of 1,3-BD.

A comparison of calculated and experimental values for ethanol conversion, 1,3-BD yield and by-product selectivity are shown graphically in Figures 3.2-a - 3.2-d. The parity diagrams, presented 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 fit is obtained for the by-products ethylene, diethyl ether and butene, which are obtained in relatively low concentrations. The adequate quality of the model is also supported by the relatively narrow confidence intervals of the parameter values and a very good correlation coefficient (ro2 = 0.99).

## 4. ANALYSIS THROUGH MODELING AND SIMULATION OF THE PERFORMANCE OF FIXED-BED CATALYTIC REACTORS IN THE ONE-STEP SYNTHESIS PROCESS OF BUTADIENE FROM ETHANOL

In this chapter, a theoretical study is presented, which uses the tools of mathematical modeling and numerical simulation, of the performances of multitubular fixed bed reactors, respectively adiabatic multibed, in the realization of the direct transformation process (Lebedev) of ethanol into butadiene (1,3 - BD) on a modified MgO-SiO<sub>2</sub> catalyst. The multitube reactor is one of the most commonly used reactors, having two separate circulation spaces, one for the reactant mixture (usually inside the tubes, where the catalyst is also located) and the second for a heat agent, similar to a multitube heat exchanger. This reactor has the advantage of a relatively high intensity of heat transfer between the reaction mixture and the thermal fluid, an important advantage for the analyzed ETB process, whose performance strongly depends on the reaction temperature.



Figure 3.2. Calculated versus measured values for: A) ethanol conversion; B) butadiene yield; C) secondary products selectivities;

A novelty of this study consists in using the particularities of chemical transformation at the level of the catalyst particles, as criteria in the design of the catalytic reactor for complex chemical processes.

### 4.1 Analysis of the process at the catalyst granule level

The modeling and simulation of the process at the level of the catalyst granule was carried out using the Fick type diffusion model and aims to analyze the evolutions of the concentrations of reactants and reaction products inside the granule, as well as to evaluate the influence of the granule size on the performance of the process. In the mass balance equation at the catalyst grain level, both molecular diffusion and Knudsen type diffusion were taken into account. The mass balance equation (4.1) was written, assuming the spherical geometry of the catalyst particle:

$$\frac{D_{efj}}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_j}{dr}\right) + r_v^{(j)} = 0, \ j=1,2....N_c-1$$
(4.1)

Boundary conditions associated with equations (4.1) are:

$$r = 0 \qquad \qquad \frac{dC_j}{dr} = 0 \tag{4.2}$$

$$r = R \qquad \qquad k_{G_j} \cdot \left(C_{j_G} - C_{j_s}\right) = D_{ef_j}\left(\frac{dC_j}{dr}\right) \qquad (4.3)$$

The rate of formation of species j related to the unit volume of catalyst  $(r_v^{(j)})$ , is calculated according to the reaction rates  $(r_i)$ :

$$\mathbf{r}_{v}^{(j)} = \rho_{p} \sum_{i=1}^{Nr} (v_{ij} \mathbf{r}_{i})$$
(4.16)

The influence of the internal diffusion step, on the kinetics of reaction i, is characterized by the isothermal internal efficiency factor, calculated using the relation (4.17):

$$\eta_i = \frac{\overline{r_i}}{r_{i,s}}, i=1,2...N_r$$
 (4.17)

where: i = 1,..7, the number of chemical reactions involved in the process.

The average reaction rate inside the granule,  $\overline{r_i}$ , which appears in relation (4.17) is calculated by averaging the reaction rates over the volume of the catalyst particle (spherical geometry):

$$\overline{\mathbf{r}}_{i} = \frac{1}{V_{p}} \int_{0}^{V_{p}} \mathbf{r}_{i} \, d\mathbf{V} = 3 \int_{0}^{1} x^{2} \mathbf{r}_{i} \, d\mathbf{x}; \qquad \mathbf{x} = \frac{\mathbf{r}}{\mathbf{R}_{p}}$$
(4.18-a)

 $V=4\pi r^3/3$  – the volume of a spherical element of grain, radius r.

The rate of formation of species j, averaged per unit volume of particle, can be calculated using one of the two alternative expressions in relation (4.18-b).

$$\overline{\mathbf{r}}_{v}^{(j)} = \rho_{p} \sum_{i=1}^{Nr} (\mathbf{v}_{ij} \overline{\mathbf{r}}_{i}) = \frac{\mathbf{S}_{ext}}{\mathbf{V}_{p}} \mathbf{D}_{ef,j} \left(\frac{d\mathbf{C}_{j}}{dr}\right)_{r=\mathbf{R}_{p}}$$
(4.18-b)

For spherical particles,  $S_{ext}/V_p = 3/R_p$ .

An important parameter, which characterizes the transformation of ethanol in a point, is the local selectivity, defined as the ratio between the rate of transformation of ethanol into 1,3-BD and the total rate of ethanol consumption.

$$\sigma_{p} = \frac{2r_{v}^{(BD)}}{-r_{v}^{(EtOH)}}$$
(4.19)

The global selectivity at the catalyst particle level can be calculated with the same relation (4.19), by replacing the reaction rates, , with their values averaged over the particle volume . The values of the external concentration and temperature gradients, were determined starting from the mass balance equations of species j in the solid phase, respectively the heat balance equation in the solid phase (4.20) and (4.21). The influence of the gas-particle mass transfer step (external diffusion) is estimated from the value of the external concentration gradient, relative to the reactant concentration in the gas phase:

$$DC = \frac{C_{jS} - C_{jG}}{C_{jG}} = \frac{R_{p}}{3k_{Gj}C_{jG}} \overline{r}_{v}^{(j)}$$
(4.20)

Where:  $C_{AG}$  – concentration of ethanol in the external gas phase of the particle;  $C_{AS}$  – the concentration of ethanol at the surface of the catalyst grain.

The external temperature gradient, is a measure of the resistance to gas-particle heat transfer and can be calculated using the expression:

$$DT=T-T_{S} = \frac{R_{p} \rho_{p} \sum_{i=1}^{Nr} (\Delta H_{Ri} \overline{r}_{i})}{3\alpha_{GS}}$$
(4.21)

The assumption of isothermality of the catalyst particle is evaluated approximately by using the criterion Weisz-Prater.

The rate of ethanol consumption shows different forms of radial evolution in the particle, depending on its position in the catalytic bed (figure 4.5-A). In the catalyst particles next to feed section, the ethanol consumption rate shows a maximum, as a result of the evolutions of the reaction rates involving ethanol consumption (R1, R2, R3 and R6). In the particles located in the exit zone of the catalytic bed, the rate of ethanol consumption is continuously decreasing towards the center of the particle and is significantly lower, a consequence of the lower concentration of ethanol in the external gas phase. The rate of 1,3-BD formation shows similar evolutions (figure 4.5-B).



Figure 4.5. 1 Radial evolutions of ethanol (A) transformation rate in the catalyst particle at z=0and z=z (A);Radial evolution of 1,3-butadiene (1,3-BD) formation rate inside the catalyst particle at z=0and z=z (B)

As is known, the limiting effect of species diffusion inside the catalyst particles on the reaction rate is increasing with particle size. Therefore, it is expected that selectivity in 1,3-BD is also dependent on particle size. The dependence of the average rate of ethanol consumption and 1,3-BD formation, on particle size are shown in Figure 4.6-A for two concentrations of ethanol in the feed.

All these dependencies show a maximum at relatively small particle diameters: the ethanol consumption rate shows a maximum around  $d_p=2$  mm, respectively the 1,3-BD formation rate around  $d_p=3$  mm diameter. The occurrence of the maximum in the rate dependence on the particle size is explained using the second expression of averaged formation rate, given in the relation (4.18-b). Thus, the Sext/Vp ratio decreases with increasing particle size, while the molar flux (concentration gradient) increases with particle size (Figure 4.6-B). Their product goes through a maximum. From a physico-chemical point of view, the occurrence of maxima can be explained by the influence of the diffusion phenomenon on the concentrations of the intermediate products, inside the catalyst particle.

In small-sized particles, due to the small resistance of the porous particle to diffusive transport (small diffusion transport distance), intermediate products diffuse more easily, establishing small concentrations of them inside the particle and, consequently, lower rates of formation of butadiene. This phenomenon, doubled by the decrease in ethanol concentration in

the particle, also explains the increase in the selectivity of ethanol to butadiene conversion with increasing particle size (Figure 4.6-B). This result demonstrates that the influence of the rates of secondary reactions (which occur in parallel with the main ones) diminishes with increasing particle size. The results shown in figure 4.6 justify the choice of a catalyst particle with a diameter of 3 mm, which ensures relatively high reaction rates and a good selectivity of 1,3-BD. At the same time, it also corresponds to a relatively low pressure drop in the catalytic bed (see next paragraph).



0.8 в 0.7 3.5 9.0 Selectivity 9.0 1,3-BD Sel., y<sub>40</sub>=0.8 1,3-BD Sel., y<sub>A0</sub>=0.4 Flux, kmol/(m<sup>2</sup> Flux A, y<sub>A0</sub>=0.8 B lux 1,3-BD, y<sub>40</sub>=0.8 μ 0.4 5 0. 0.5 0.2 1.5 2.5 4.5 5.5 2 3 3.5 4 5 d<sub>p</sub>, mm

Figure 4.6-A. Mean rates of ethanol consumption and 1,3-BD formation, as functions of particle diameter (z=0) (yA0 –feed molar fraction of ethanol).

Figure 4.6-B. Global 1,3-BD selectivity and molar fluxes of ethanol (A) and BD at external particle surface, versus the particle diameter (z=0).).

## 4.2 Analysis of transformation at the bed level in the multitubular fixed bed reactor

In the development of the mathematical model for the multitubular fixed bed reactor, the following assumptions regarding the development of the ETB catalytic process were adopted:

- Considering the low working pressure and relatively high temperatures, the behavior of the reaction mixture is considered ideal.

- Axial mixing of the gas phase in the catalytic bed was neglected, given the relatively high gas velocity and high ratio of bed length to particle diameter,  $L/d_p > 50$  (Froment et al., 2011).

- Fick's theory of diffusion was used in modeling the process at the catalyst particle level.

- The catalyst particle is considered to be isothermal, a hypothesis supported by the moderate thermal effect of the 1,3-BD synthesis process, the relatively small size of the catalyst particles,

and a moderate ethanol conversion rate respectively. This hypothesis was also confirmed by applying the Weisz-Prater criterion (see previous paragraph).

- The radial heat and mass gradients accros the catalytic bed are neglected, this hypothesis being also supported by the moderate endothermic character of the chemical transformation.

- The thermal fluid used in the reactor is either liquid Dowtherm A (more resistant to pipe fouling) or saturated vapor Dowtherm A at 400 °C, at which the only vapor enthalpy given up in the reactor is the latent enthalpy of condensation (without subcooling the condensate ).

- Catalyst activity is considered constant (steady state).

- Operating parameters (independent variables of the process) were maintained within the limits presented in the experimental study of Da Ros et al. (2017-b), used in the development of the kinetic model.

### 4.2.1 The ideal one-dimensional heterogeneous mathematical model

Within this model, the following are taken into account: (i) property transport in axial direction by convective mechanism; (ii) the interphase concentration and temperature gradients and the intraparticle concentration gradient. The model consists of mass and heat balance equations written for the gas phase, as well as mass and heat balance equations for the solid phase. To these is added an equation for calculating the pressure variation, in the gas phase, along catalytic bed.

### Balance equations for the gas phase

According to the hypothesis presented above, the mass balance equations for the chemical species in the gas phase can be written in the form that describes the evolution of global reaction extent along catalytic bed:

$$\frac{\mathrm{d}\xi_{\mathrm{m,i}}}{\mathrm{d}z} = \frac{\rho_{\mathrm{str}}}{\dot{\mathrm{D}}_{\mathrm{m}}} \cdot \overline{\mathrm{r}}; \quad \mathrm{i} = 1,..,7$$
(4.23)

Similarly, the temperature evolution along the catalytic bed is described by the heat balance equation in the gas phase:

$$\frac{dT}{dz} = \frac{\frac{4}{d_t} K_T(T_a - T) - \rho_{str} \sum_{i=1}^{Nr} (\overline{r}_i \Delta H_{Ri})}{\dot{D}_m c_p}$$
(4.24)

For the case where the thermal agent is liquid, the mathematical model also includes a heat balance equation for the intertubular space (of circulation of the thermal agent):

$$\frac{dT_{a}}{dz} = -\frac{N_{t} \pi d_{t} K_{T} (T_{a} - T)}{D_{ma} c_{pa}}, \quad z = 0, \ T_{a} = T_{a,0}$$
(4.28)

To express the pressure drop, the Ergun equation was used:

$$\frac{dp}{dz} = -f \cdot \frac{u_0^2 \cdot \rho_{vap}}{d_p}$$
(4.29)

The mass balance of species j on a catalyst particle (4.20) can be transposed in the form:  $S_{ext}k_{Gj}(C_{jS}-C_{jG}) = V_p \overline{r}_v^{(j)}$ ; j=1,2...N<sub>c</sub>-1 (4.35)

Similarly, the heat balance equation for the particle (4.21) can be written in the form:

$$S_{ext} \alpha_{GS} (T-T_S) = V_p \rho_p \sum_{i=1}^{Nr} (\Delta H_{Ri} \overline{r}_i)$$
(4.36)

### 4.2.3. Simulation of the multitubular fixed bed reactor

The mathematical model of the reactor is described by the system of equations (ODE) (4.1), (4.23), (4.24), (4.28) and the algebraic (transcendental) equations (4.35) and (4.36). The first-order differential equations system described by (4.23), (4.24) and (4.28) expression, was integrated using ode15s Matlab function. At each point, z, where the derivatives were evaluated, the second-order ODE equations of the particle balance (4.1) with the boundary conditions (4.2) and (4.3) were also integrated (using the Matlab function bvp5c), and the algebraic equations (4.35) and (4.36) are solved (using the Newton Raphson method). In the integration of the ODE system of equations (4.1), each second-order differential equation was replaced by an equivalent set of two first-order differential equations.

Considering the current availability of ethanol, we chose a catalytic reactor of medium capacity (nominal processing capacity being 3800 kg/h, ethanol-inert gas mixture with ethanol molar fraction 0.8). For a space velocity, WHSV=1.3 h<sup>-1</sup>, this corresponds to an amount of 2537 kg of catalyst, distributed in pipes with an inner diameter of 0.04 m and a length of 3 m.

As the heating fluid, we selected the saturated vapor Dowtherm A, under the pressure of 10.7 bar. Dowtherm A properties are published on the manufacturer's website (Dowtherm A

Data Sheet). The heat transfer coefficient between Dowtherm vapors in condensation and pipes was considered constant, being estimated, using classical relations,  $\alpha_e=1650 \text{ W/(m}^2 \text{ K})$  (4.27). The values of the constructive and operational parameters of the reactor are given in Table 4.1. The catalyst particle diameter was selected considering the influence of particle size on reaction kinetics and selectivity in 1,3-BD (see previous paragraph).

Parameter	Value	Parameter	Value
Catalyst particle	3 mm	Weight hourly space velocity in	1.3 h <sup>-1</sup>
diameter (spherical), d <sub>p</sub>		respect with ethanol (WHSV)	
Mean pore diameter	3.75 nm	Reactor mass feed rate, F <sub>m</sub>	3800 kg/h
Particle density, $\rho_p$	$1250 \text{ kg/m}^3$	Feed ethanol molar fraction	0.8
Mass of catalyst	2537 kg	Superficial velocity of the	0.67 m/s
		reaction mixture (feed section)	
Inner tube diameter, d <sub>t</sub>	4 cm	Debitul de Dowtherm vapori	1.53 kg/s
Tube wall thickness	3 mm,	Feed temperature of reaction	673 K
		mixture, T <sub>0</sub>	
Tube wall conductivity	46.5 W/(m	Dowtherm vapor temperature	673 K
	K)	in the intertubular space, $T_{a0}$	
Number of tubes, N <sub>t</sub>	1089	Feed pressure of gaseous	1.5 bar
		mixture, P <sub>0</sub>	
Length of the tube, L	3 m	Tube diameter, D <sub>i</sub>	2,8 m

Table 4.1. Constructive and nominal operation parameters values of the catalytic reactor

The inside diameter of the pipe was chosen so that a pipe diameter to particle diameter ratio greater than 10 could be ensured to limit the influence of the 'wall effect' on the flow of the gas mixture through the catalytic bed (Rase, 1977). The length of the pipes was selected so that the velocity of the gaseous mixture through the catalytic bed was sufficiently high. (for the amount of catalyst and the diameter of the pipes, given).

The concentration of ethanol in the reactor feed mixture and the feed temperature were the same in all simulations (0.80 and 673 K, respectively), representing the upper limits of the range used in the construction of the kinetic model.

The integration of the balance equations (4.1) for different positions of the particles in the catalytic bed allows the calculation of the internal efficiency factor for chemical reactions, using the relation (4.17), as well as the external ethanol concentration and temperature gradients, using the relations (4.18a) and (4.18-b). For the first three reactions of the kinetic model (Table 3.10) the values of the internal efficiency factors are significantly lower than unity, suggesting the significant influence of the internal diffusion of ethanol on the corresponding reaction rates (figure 4.8-A). It should be emphasized that the efficiency factor curves for reactions R1 and R3 overlap quite closely. In the entry neighbourhood, the efficiency factors for reactions R4 to R7 are much greater than unity and close to unity in the rest of the bed (Figure 4.8-B).

These results show that the corresponding reaction rates are favorably influenced by the slow diffusion of the intermediate products, which favors their accumulation inside the particle. The values of the internal efficiency factors and the external concentration and temperature gradients suggest that the analyzed ETB process is characterized by moderate-fast kinetics.

The external gradients of ethanol concentration and temperature, calculated for the minimum gas mixture feed flow rate ( $D_m$ =906 kg/h, corresponding to the minimum WHSV value in the working range) are relatively small throughout the catalytic bed and can be neglected in the reactor simulations (figure 4.9-A). The concentration gradient of ethanol shows a minimum, which corresponds to the minimum point in the temperature evolution, under these conditions.

Simulation calculations of the multitubular reactor, under nominal conditions (Table 4.1) led to a (fractional) ethanol conversion of 0.37 and a 1,3-BD yield of 0.31 (selectivity value in 1,3-BD is 0.84), as can be seen from Figure 4.10-A. These results correspond to a 1,3-BD production of 602 kg/h or a catalyst productivity of 0.237 kg 1,3-BD/(kgcat h).

The axial temperature profile, together with the heat transfer coefficient between the catalytic bed and the tube wall ( $\alpha$ i) are shown in figure 4.10-B. The minimum that appears in the temperature evolution, specific to endothermic transformations inside heated pipes, loaded with catalyst, indicates the appearance of two zones, separated by the minimum point: the first is characterized by high reaction rates, where the heat consumed in the chemical transformation is

greater than the heat transferred to the catalytic bed, and the second zone, characterized by slower transformation speeds, where the heat consumed is less than that transferred to the catalytic bed. The increasing evolution of  $\alpha$ i along the catalytic bed is determined by the change in composition (especially by hydrogen concentration increase). The total pressure drop of the gas phase across the catalytic bed is ~0.07 bar (figure 4.9-B).



Figure 4.8. Effectiveness factors for the reactions R1, R2 and R3 along the catalyst bed (A); Effectiveness factors for the reactions R4 - R7 along the catalyst bed (B).



*Figure 4.9. Evolution of external concentration and temperature gradients along the catalytic layer* (*A*);*Evolution of pressure along the catalytic layer* (*B*)



Figure 4.10 Evolutions of ethanol conversion and butadiene (BD) yield inside the catalyst bed (A); Evolutions of bed temperature and internal heat transfer coefficient,  $\alpha_i$  (B)

### 4.2.3.2. A sensitivity analysis of the multitubular reactor

The main independent variables influencing reactor performance are reaction mixture feed rate ( $D_m$ ), feed gas temperature ( $T_0$ ), feed ethanol concentration ( $y_{Et,0}$ ) and heating fluid inlet temperature ( $T_{a0}$ ). To quantitatively assess their influence on reactor performance, normalized (relative) sensitivities of yield in 1,3-BD ( $\eta_{1,3-BD}$ ) to these variables were calculated using the relationship:

$$S_{\theta}^{y} = \frac{\theta}{y} \frac{\partial y}{\partial \theta} \simeq \frac{\theta}{y} \frac{\Delta y}{\Delta \theta} = \frac{\Delta y/y}{\Delta \theta/\theta}$$
(4.42)

where,  $y=\eta_{1,3-BD}$  is the yield in 1,3-BD and  $\theta$  is an independent variable (D<sub>m</sub>, y<sub>Et,0</sub>, T<sub>0</sub> or T<sub>a0</sub>). The selectivity value given by (4.42) represents the fractional variation of y induced by a given fractional variation of  $\theta$ . For example, considering an increase in the independent variables,  $\Delta\theta/\theta = 0.01$ , the percentage variation of the yield in 1,3-BD at the exit of the catalytic bed, relative to its nominal value, will be identical to the normalized selectivity (the relation (4.43)):

$$100(\Delta \eta_{\rm BD}/\eta_{\rm BD}) = 100 \, \mathrm{S}_{\theta}^{\mathrm{y}} \, \Delta \theta / \theta = \mathrm{S}_{\theta}^{\mathrm{y}} \tag{4.43}$$

The numerical values of the 1,3-BD yield sensitivity, at reactor exit, are presented in Table 4.3, and the corresponding profiles along the catalyst bed, in figures 4.13. As observed, the yield in 1,3-BD is most sensitive to variations in heating fluid temperature and flow rate,

respectively, and less sensitive to variations in ethanol concentration in the feed. The data in Table 4.2 show that an increase in the temperature of the heating agent, by 1 % (~ 6.7 K), leads to an increase in the yield in 1,3-BD of ~ 5.8 % relative to the nominal value ( $\Delta \eta_{1,3BD}$  ~0.018). Increasing the feed rate of the reaction mixture (D<sub>m</sub>) leads to a decrease in the 1,3-BD yield (negative sensitivity values), due to the decrease in the reaction time.



Figure 4.13. Normalized sensitivity of 1,3-BD yield in respect with feed temperature and feed ethanol molar fraction respectively (A); Normalized sensitivity of 1,3-BD yield in respect with inlet temperature of heating fluid and feed rate of reaction mixture respectively (B)

#### 4.2.3.3.Correlation of reaction efficiency factors with bed temperature

In order to simplify the mathematical model of the catalytic reactor by reduceing the calculation time, which is important in applications that require a large number of iterations, such as optimization calculations, temperature-dependent correlations of the efficiency factors have been proposed for reactions R.1 - R3 (Table 3.10), including three parameters, a, b and c:

$$\mathbf{f}_{i} = \frac{\tanh(\varphi_{i})}{\varphi_{i}} \tag{4.44}$$

$$\varphi_{i} = a_{i} \left( k_{i} + c_{i} \right)^{b_{i}}$$
 (4.45)

Where  $\phi$  is a variable analogous to the Thiele modulus, specific to single reactions; fi- internal effectiveness factor, for reaction i.

For reactions R.4 -R.7 (Table 3.10), where the efficiency factors are above unity, they were considered equal to 1 (fi=1, i=4,..7), a value that predominates along the length of the catalytic

bed (Figure 4.8). The values of the coefficients a,b,c for the estimation of the efficiency factors of the three reactions are shown in Table 4.4.

#### 4.4 Optimization studies

In the following, some optimization problems will be formulated and solved for the analyzed reactors, for the synthesis of butadiene from ethanol, in order to determine the most appropriate structure of the multibed reactor and the optimal values of some working parameters, in relation to different objective functions.

### 4.4.1 Optimization of the adiabatic multibed reactor

The objective of this study was to determine the constructive and operating parameters of fixed-bed reactors, which lead to the maximization of some objective functions directly related to the performance of the reactor: 1,3-BD yield ( $F_{ob}$ ), butadiene flow rate ( $F_{ob1}$ ) and an economic function ( $F_{ob2}$ ):

$$F_{OB} = \eta_{BD} = X_A \sigma_{BD} \tag{4.46}$$

$$F_{OB1} = Dm_A \frac{\eta_{BD} M_{BD}}{2M_A}$$
(4.47)

$$F_{OB2} = Dm_A p_{BD} \left( \frac{\eta_{BD} M_{BD}}{2M_A} - \frac{(1 - X_A) C_{sep}}{p_{BD}} \right)$$
(4.48)

Where:  $Dm_A$ = Mass flow rate of fed ethanol;  $M_A$  = molar mass of ethanol;  $M_{BD}$  = molar mass of 1,3-BD; X = ethanol conversion;  $C_{sep}$ =cost of separation of untransformed ethanol;  $p_{BD}$  = sale price of 1,3-BD;  $\eta_{BD}$  = yield in 1,3-BD.

The optimization was performed for the same mass of catalyst, distributed in several beds operated adiabatically. For the direct heating variant, the decision variables are: the flow fractions injected between the catalytic beds ( $f_{bk}$ , k=1,2...), the total mixture flow and the lengths of the catalytic beds. The optimization of the indirectly heated reactor considers as decision variables the total mixture flow, the temperatures of the mixture fed to each catalytic bed ( $T_{0,k}$ , k = 1,2...) and the lengths of the catalytic beds.

### Optimisation study with yield as objective function

The optimization problem was solved for two constructive variants (direct heating and indirect heating respectively) in order to evaluate their efficiency in maximizing the yield in 1,3-BD.

### i) Direct heat adiabatic reactor

The ranges of decision variables considered in our study are:

- Flow fractions:  $0 \le f_{bk} \le 1$ . In the first bed, the restriction is  $0.2 \le f_{b1} \le 1$ , to avoid excessively small flow rates in this bed, which lead to calculation difficulties.

- Length of catalytic beds:  $0.2 \leq Z_i \leq 3$ , (m)

- Feed mixture flow rate:  $870 \le D_m \le 7355$ , kg/h.

A minimum length of the catalytic beds was proposed, in order to maintain the validity of the hypothesis of neglecting the axial mixing ( $Z_i/d_p>50$ ). Optimization calculations were carried out, where the catalyst is divided into 2, 3 or 4 beds. The results showed that the distribution of the catalyst on several beds is not favorable, because the reduction of the reaction time has a decisive effect on the performance of the reactor. Table 4.7 (the first two lines) shows the results obtained for the optimization of the reactor with direct heating, with 2 beds and respectively a single adiabatic bed, imposing the injection temperature between beds equal to the maximum allowed (673 K).

From the calculations presented in the first line, it follows that the first bed has the minimum allowed length, the last one has a length close to the total length, most of the fed flow being distributed on the first bed (88%). The results presented in the second line of Table 4.7, for a reactor with a single adiabatic bed, are slightly superior, which shows that it is more advantageous for the reaction to be conducted in a single bed, the optimal values being 31.39 % for yield, respectively 39.63% for ethanol conversion. One way to increase the yield in 1,3-BD in the direct-heated multibed reactor is to increase the temperature of the reactant injected between the beds. This must be done with caution, in order to limit exceeding the maximum allowed temperature on the catalytic beds. The third line of Table 4.7 shows the results of some optimization calculations, where the temperature of the injected mixture (693 K) is higher than the maximum temperature allowed in the catalytic beds. The temperature of the feed mixture (673 K), over a portion of ~0.1 m. As expected, the ethanol conversion (42.09 %) and the yield to 1,3-BD (34.05

%) at the exit from the reactor, are higher, compared to those obtained for the case where the flow injected between the beds has a temperature of 673 K.

Z,[m]	$T_a$ ,[K]	fb	η <sub>1,3-BD</sub> ,	X,[%]	D <sub>m</sub>	D <sub>1,3-BD,</sub>
			[%]		[kg/h]	[kg/h]
$Z_1 = 0.2$	673	$fb_1 = 0,88$	31.32	39.59	877	140
$Z_2 = 2.8$		$fb_2 = 0,13$				
$Z_1 = 3$	673	$fb_1 = 1$	31.39	39.63	877	140
$Z_1 = 0.2$	693	$fb_1 = 0.20$	34.05	42.09	877	152.7
$Z_2 = 2.8$		$fb_2 = 0.80$				

*Table 4.7. Results obtained from the optimization of the direct heat multibed reactor - optimization of the number and lengths of the catalytic bed (catalyst mass and feed rate are given in Table 4.1)* 

 $Z_i$  - length of layer i;  $f_{bi}$ - flow fraction fed between beds i și i+1; X = ethanol conversion;  $\eta_{1,3-BD} = 1,3-BD$  yield;  $T_a$ = temperature of flow fraction injected between beds;  $D_m$ = Total mass flow;  $D_{1,3-BD}$ = Butadiene flow rate

### ii) Indirect heat adiabatic reactor

Table 4.9 shows the results obtained from the optimization of the indirect heating reactor. As in the case of the direct heating reactor, simulations were carried out where the catalyst is distributed in 2, 3 or 4 beds.

In this case, it is more advantageous to distribute the catalyst in 4 beds, with increasing lengths towards the exit of the reactor, because with number of beds increase, the reaction temperature is maintained at higher values, which makes the values obtained for yield and conversion to grow. Figure 4.18 shows the results obtained following the optimization of the reactor with indirect heating (values of conversion, selectivity and efficiency.), corresponding to the optimal parameters given in Table 4.9.

The results presented in the last line of Table 4.9, for a reactor with 4 adiabatic beds, are slightly superior, which shows that it is more advantageous for the reaction to be conducted in a reactor divided into 4 catalytic beds, the optimal values being 61.32 % for yield, respectively 70.12% for ethanol conversion.

Z,[m]	$T_{in\_str,}[K]$	η <sub>1,3-BD</sub> , [%]	X, [%]	D <sub>m</sub>	D <sub>1,3-BD</sub> ,
				[kg/h]	[kg/h]
$Z_1 = 1.37$	$T_1 = 673$	47.31	56.14	877	211
$Z_2 = 1.63$	$T_2 = 673$				
$Z_1 = 0.768$	$T_1 = 673$	56.07	64.98	877	251
$Z_2 = 0.951$	$T_2 = 673$				
$Z_3 = 1.281$	$T_3 = 673$				
$Z_1 = 0.531$	$T_1 = 673$	61.32	70.12	877	274
$Z_2 = 0.643$	$T_2 = 673$				
$Z_3 = 0.786$	$T_3 = 673$				
$Z_4 = 1.040$	$T_4 = 673$				

Table 4.9. Results obtained from the optimization of the multibed reactor with indirect heating

 $Z_i$  - length of layer i;  $\overline{T_{in\_strat}}$  = inlet temperature i bed; X = ethanol conversion;  $\eta_{1,3-BD}$  = 1,3-BD yield;  $D_m$ = Total mass flow;  $D_{1,3-BD}$  = Butadiene flow rate

### Maximizarea debitului de butadienă în reactorul multistrat adiabat

Considering the previous results, the direct heating multibed reactor is no longer considered, the optimization problem being solved only for the case of the indirect heating reactor. The ranges of the decision variables considered in the study are:

- Feed temperature on beds:  $473 \leq T_i \leq 673$ , K
- Length of catalytic beds:  $0.2 \leq Z_i \leq 3$ , (m)
- Feed mixture flow rate:  $870 \le D_m \le 7355$ , kg/h.

Table 4.10 shows the results obtained following the optimization of the adiabat reactor for the objective function  $F_{OB1}$  (butadiene flow rate) compared to the results obtained following the maximization of the yield in 1,3-BD ( $F_{OB}$ ).

As can be seen, when the mixing flow rate is considered as decision variable and it is desired to maximize the yield in 1,3-BD, the optimum corresponds to a small mixing flow rate, to ensure a high reaction time, which ensures obtaining yield values high (61.31 %). The disadvantage in this case is obtaining a low flow rate of 1,3-BD (274 kg/h). On the other hand, maximizing the flow rate of 1,3-BD (objective function  $F_{OB1}$ ) requires feeding a 5 times higher

mixture flow rate to obtain a flow rate of 1,3-BD only 2 times higher than that obtained in the case of yield maximization. This is because the yield in 1,3-BD is much lower (~24%, for 28% ethanol conversion). This results in a large flow of unconverted ethanol, which is normally separated and recycled along with the inert. It should also be emphasized that high flow rates of reactant mixture implicitly imply high flow rates of inert, which is separated and recirculated.

	Z,[m]	T <sub>in_strat</sub> , [K]	η <sub>1,3-BD</sub> ,	X, [%]	$D_m [kg/h]$	D <sub>1,3-BD</sub> ,
			[%]			[kg/h]
$F_{OB} =$	$Z_1 = 0.531$	$T_1 = 673$	61.32	70.12	877	274
$\eta_{BD}$	$Z_2 = 0.643$	$T_2 = 673$				
	$Z_3 = 0.786$	$T_3 = 673$				
	$Z_4 = 1.040$	$T_4 = 673$				
F <sub>OB1</sub> =D <sub>BD</sub>	$Z_1 = 0.649$	$T_1 = 673$	24.01	28.05	4896	599
	$Z_2 = 0.668$	$T_2 = 673$				
	$Z_3 = 0.756$	$T_3 = 673$				
	$Z_4 = 0.927$	$T_4 = 673$				

*Table 4.10. Results obtained from the optimization of the adiabatic fixed-bed reactor with indirect heating - total reaction mixture flow rate is the decision variable* 

 $Z_i$  - length of layer i;  $T_{in\_strat}$  = inlet temperature i bed; X = ethanol conversion;  $\eta_{1,3-BD}$  = 1,3-BD yield;  $D_m$ = Total mass flow;  $D_{1,3-BD}$  = Butadiene flow rate

### Optimisation study with an economic function as objective function

Also in this case the optimization problem was solved only for the adiabatic multibed reactor with indirect heating. The ranges of the decision variables considered in the study are:

- Feed temperature on beds:  $473 \leq T_i \leq 673$ , K
- Length of catalytic beds:  $0.2 \leq_{Zi} \leq 3$ , (m)
- Feed mixture flow rate:  $870 \le D_m \le 7355$ , kg/h.

Table 4.11 shows the results obtained following adiabat reactor optimization using economic objective function ( $F_{OB2}$ ) for different values of separation cost and the selling price

of 1,3-BD ratio,  $(0.05 \le \frac{C_{Sep}}{p_{But}} \le 0.375)$ . For the ratio  $\frac{C_{Sep}}{p_{But}} = 0.375$ , the optimal conversion value

66.39%, respectively the 1.3 BD yeld value 57.99%, are obtained for a feed rate 1016 kg/h.

*Tabelul 4.11. Rezultatele obținute în urma optimizării reactorului multistrat adiabat cu încălzire indirectă – funcție obiectiv de natura economica* 

$C_{\scriptscriptstyle Sep}$	Z,[m]	$T_{in\_str,}[K]$	η <sub>1,3-BD</sub> ,	X, [%]	D <sub>m</sub> [kg/h]	D <sub>1,3-BD</sub> ,
$p_{But}$			[%]			[kg/h]
0,05	$Z_1 = 0.687$	$T_1 = 673$	31.63	37.35	3323	535
	$Z_2 = 0.697$	$T_2 = 673$				
	$Z_3 = 0.746$	$T_3 = 673$				
	$Z_4 = 0.868$	$T_4 = 673$				
0,125	$Z_1 = 0.658$	$T_1 = 673$	40.74	47.40	2146	445
	$Z_2 = 0.697$	$T_2 = 673$				
	$Z_3 = 0.757$	$T_3 = 673$				
	$Z_4 = 0.888$	$T_4 = 673$				
0,25	$Z_1 = 0.633$	$T_1 = 673$	51.29	59.07	1337	350
	$Z_2 = 0.683$	$T_2 = 673$				
	$Z_3 = 0.768$	$T_3 = 673$				
	$Z_4 = 0.916$	$T_4 = 673$				
0,375	$Z_1 = 0.579$	$T_1 = 673$	57.99	66.39	1016	301
	$Z_2 = 0.664$	$T_2 = 673$				
	$Z_3 = 0.779$	$T_3 = 673$				
	$Z_4 = 0.978$	$T_4 = 673$				

 $Z_i$  - length of layer i;  $T_{in\_strat}$  = inlet temperature i bed; X = ethanol conversion;  $\eta_{1,3-BD}$  = 1,3-BD yield;  $D_m$ = Total mass flow;  $D_{1,3-BD}$  = Butadiene flow rate

On the other hand, a ratio value  $\frac{C_{Sep}}{p_{But}} = 0.05$  (low cost of butadiene separation) leads to an

optimal conversion 31.63% and a yield 37.37% values, corresponding to a higher flow rate of feed mixture (3323 kg/h) and a higher flow rate of butadiene at the reactor exit. Thus, with the decrease in the cost of separation (the energy consumed for separation), the flow rate of 1,3-BD

obtained increases, as a result of a higher feed flow rate and, consequently, obtaining smaller values for conversion of ethanol, respectively a 1,3-BD yield.

### 4.4.2. Optimization study of the multitubular reactor

The ranges of the decision variables considered in the study are:

- Heat agent temperature:  $473 \leq T_a \leq 673$ , K
- Feed mixture flow rate:  $870 \le D_m \le 7355$ , kg/h.

Two constructive variants of the intertubular space were taken into account: continuous and respectively zoned space (4 zones). in segments with separate circulation of the Dowtherm liquid thermal agent. Table 4.12 shows the results obtained following the optimization of the multibed reactor with one zone (unzoned) and zoned (four zones) intertubular space, respectively. Comparing the results obtained for yield maximization, it can be seen that in the case of the zoned intertubular space reactor, higher values of conversion and yield in 1,3-BD are obtained, but the differences are not very significant. The difference is due to zone heating of the thermal agent which maintains the reaction temperature at higher values (Figures 4.20-A and 4.20-B). In the case of the zoned extratubular space reactor, it can be observed that the first bed has a lower temperature drop compared to the other beds. This is due to the exothermicity of the DEE formation reaction which is predominant over the first length of the catalytic beds.

	T <sub>ag,</sub>	η <sub>1,3-BD</sub> ,	Х,	D <sub>m</sub>	D <sub>1,3-BD</sub> ,			
	[K]	[%]	[%]	[kg/h]	[kg/h]			
	Unzoned multitubular reactor							
$F_{OB} = \eta_{1,3-BD}$	673	74	83	906	343			
$F_{OB} = \eta_{1,3-BD}$	673	75	84	906	346			
F <sub>OB1</sub> =D <sub>1,3DB</sub>	673	20	25	7278	737			
$F_{OB2} = C_{sep} / p_{BD} = 0.05$ 673 32 38 4137					667			
$F_{OB2}=C_{sep}/p_{BD}=0.37$	75 673	66	75	1262	423			

*Tabele 4.12. Results obtained from the optimization of the multitubulart reactor with one zone and 4 zones extratubular space respectively* 



*Figure 4.19. Maximising 1,3-BD yield. Variation of ethanol conversion, 1,3-BD yield and 1,3-BD selectivity in the multibed reactor with unzoned intertubular space A) respectively zoned B)* 



*Figure 4.20. Variation of reaction temperature and thermal agent temperature in multibed reactor with one zone intertubular space A) respectively four zones B).* 

### 5. GENERAL CONCLUSIONS

Due to the economic importance of 1,3-BD, the study of its synthesis from ethanol has been resumed in the last decades, efforts being directed especially in the field of developing new catalysts with improved performance. As pointed out in the first chapter of the thesis, important progress has been made in this field, catalytic materials with much higher activity and selectivity being discovered, compared to those used in the first technologies, industrially exploited until the 1960s. However, almost all of the studies published in the last decades are limited to working conditions at laboratory scale, missing the investigations related to the behavior of the new catalysts in industrial working conditions, as well as the aspects related to the manufacturing costs. A much smaller number of published studies deal with ETB process engineering aspects (process kinetics on different catalysts, deactivation and regeneration of catalysts under industrial conditions, integrated design of catalytic reactors and separation plants, optimization studies, etc.).

The objective of this PhD thesis was to analyze the process of converting ethanol into 1,3-BD, in a single step (Ledev Process), in order to develop a design procedure for catalytic reactors usable for this process. Next, the research carried out within the thesis, on this catalytic process, the results obtained and the main conclusions are listed.

1. A rigorous thermodynamic analysis of the transformation process of ethanol into 1,3-BD was carried out, based on the chemical species involved in this transformation, identified in published experimental studies, physico-chemical data and specific calculation relationships, existing in literature. The main results of this analysis are the following:

(a) the analysis of the spontaneity of the ETB transformation, based on a chemical equation, characterizing its global stoichiometry, revealed that the conventional rules for its evaluation, according to which the interval of spontaneity corresponds to negative values of the standard enthalpy variation (or over unit value of the equilibrium constant,  $K_a$  ), leads to an underestimation of the temperature range over which the transformation is spontaneous. Significant values of ethanol conversion at equilibrium (over 70 %) are obtained at temperatures for which the equilibrium constant of the global reaction,  $K_a=K_p$ , is under unity.

(b) rigorous calculations of the equilibrium composition were performed, using both the equilibrium constant method (based on reaction schemes proposed in published studies of the transformation mechanism) and the Gibbs method. The results of these calculations show practically total ethanol conversions at steady state and very low 1,3-BD yields (well below those currently obtained experimentally). This demonstrates that transformations of practical importance are kinetically controlled (they occur at states far from chemical equilibrium), the main factor influencing practical yields being the activity and selectivity of the catalyst.

2. A kinetic model of the one-step ETB process was developed for a modified MgO-SiO<sub>2</sub> catalyst using experimental data published by Da Ros et al. (2017-b). The expressions of the reaction rates are of the power law type of the partial pressures and include terms that express the reversibility, for the reactions in which the equilibrium constants on the working interval have

relatively small values ( $K_p$ <30). The estimation of the parameters of the kinetic model was carried out with an own calculation program, developed in the Matlab language.

3. The kinetic model developed in this work was used to formulate some mathematical models of the ETB process for the modified MgO-SiO<sub>2</sub> catalyst, at the level of the catalyst particle and respectively of the fixed bed of catalytic particles. A heterogeneous mathematical model was used to describe the process at the level of the catalytic bed, which includes the steps of heat and mass transfer between the gaseous and solid phases, respectively the diffusion-reaction steps in the catalytic particle. The simulation of the catalytic process at two levels (particle and respectively catalytic bed) was carried out with calculation programs developed during the PhD stage, also using the Matlab scientific calculation language.

4. The simulation of the ETB process at the level of the catalyst particle highlighted interesting particularities of its development, determined by the complexity of the chemical reactions that define the transformation and the interaction between the chemical kinetics and the diffusional transport kinetics in the porous structure of the particle. Among them, it is mentioned: (a) the shapes of radial evolutions in the spherical particle, for the rates of ethanol consumption and 1,3-BD formation, respectively, depend on the particle 's position in the catalytic bed (curves with a maximum in the particles placed in the feed neighbouring zone, and continuously increasing/decreasing curves for particles placed in the rest of the bed).

(b) average values per particle volume of rates of ethanol consumption and 1,3-BD formation, respectively, as well as the selectivity of conversion to 1,3-BD, are dependent on particle size. Under usual working conditions, the dependences of the two rates show a maximum in respect with the particle diameter, while the selectivity in 1,3-BD increases continuously with the grain size. The knowledge of these dependencies is important in the selection of the particle size, as well as in optimization calculations for the particle size distribution along the catalytic bed.

(c) The diffusion steps of ethanol and reaction products are influencing significantly the overall kinetics of the process, with a negative (limiting) effect for ethanol transformation reactions (to acetaldehyde and secondary products respectively) and a positive effect for reactions transforming intermediate products. These effects are expressed quantitatively by means of the internal effectiveness factors of the chemical reactions.

5. The simulation of the ETB process at the level of the fixed catalyst bed led to the following results:

(a) The temperature and ethanol concentration gradients external to the catalyst particle have negligible values along the catalytic bed, which highlights an insignificant influence of the gasparticle heat transfer, respectively of the mass transfer of ethanol from the convective zone of the gas towards the external surface of the particle. So, the only physical step that significantly influences the overall kinetics of the process is internal diffusion.

(b) The influence of internal diffusion for ethanol consumption reactions (R1, R2 and R3 from Table 3.10) is important along the entire length of the catalytic bed, while for reactions R4-R7 it is limited to the area near to the feed section of the bed (the first 0,5 m of the bed).

(c) Empirical correlations of effectiveness factors for reactions R1, R2 and R3 as a function of reaction temperature have been developed, which ensure good accuracy of the calculation of these effectiveness factors. The correlations are useful for simplifying the simulation calculation of the catalytic reactor, by eliminating the need to integrate the balance equations at the grain level. The simulation of the catalytic reactor with the simplified mathematical model, which includes the effectiveness factors, led practically identical results to those obtained by including the balance equations at the granule level in the reactor model. It is emphasized that this test was performed for the multitube reactor, while the data used in the effectiveness factor correlation were obtained from the adiabatic reactor simulation.

(d) A parametric sensitivity study of the yield in 1,3-BD obtained in the multitubular reactor was carried out, which showed that the operating parameters to which it is most sensitive are the temperature of the heat agent and the flow rate of the reactant mixture, respectively.

(e) The performance of adiabatic multibed and multitubular fixed-bed reactors, operated under identical conditions, were compared through numerical simulation. The results showed that the adiabatic multibed reactor with interbed heating by hot reactant injection is the least performing in terms of 1,3-BD yield and ethanol conversion. The result is explained by the reduction of the reaction time, due to the bypassing of some catalytic beds by the hot reactant injected to heat the mixture. The adiabatic multibed reactor with interbed heating using heat exchangers provides slightly lower performance than the multitube reactor, if the number of beds is limited (maximum 5). With a number of 6 catalytic beds, this reactor provides the same conversion performance as the multitubular reactor. The result is explained by the increase in the average temperature level in the reactor, along with the increase in the number of beds.

(f) A study was carried out to optimize the operation of the adiabatic and multitubular multibed reactors, which sought to determine the working parameters that maximize three objective functions: the yield of transformation into 1,3-BD, the flow rate of 1,3-BD and respectively a simplified expression of the economic efficiency of reactor operation. The results of the optimization calculations highlighted possibilities to orient the operation in the sense of achieving one of these three objectives.

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### SUGGESTIONS FOR FURTHER RESEARCH

Taking into account both the published studies and the results obtained during the current PhD stage, the following possible research developments are proposed:

- Experimental research of the ETB process kinetics for high-performance catalysts, in order to develop high-accuracy kinetic models of this process.
- Continuation of the theoretical studies of the comparative performances for other types of reactors, in achieving the transformation of ethanol into butadiene (fluidized bed reactors operated in different hydrodynamic regimes, circulating bed reactors, monolithic type reactors).
- Analysis, by modeling and simulation, of the reactors integrated in the industrial installation, taking into consideration the interaction between the reactor and the separation plant.
- Analysis of the development of the ETB process in grains having other geometries (cylinders, rings, etc.), in order to select the most advantageous geometric shape and its dimensions.
- Studies of the kinetics of catalyst deactivation under conditions specific to industrial operation and the development of equations characterizing the activity's dependence on working conditions and time. Such equations are necessary in more complete calculation for simulation and optimization of the ETB process; these describe the behavior of the catalyst and the evolution of the process throughout the operation period between two successive bed regenerations.