

## Analysis of Operating Variables in the Catalytic Purification of Butene-1 in a Trickle Bed

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**Abstract** A mathematical model for analyzing and simulating selective hydrogenation of butyne-1 and 1,3-butadiene in industrial trickle bed reactors operated to obtain high purity butene-1 is presented in this work. From the analysis of typical operating conditions, only the relevant phenomena are finally retained in the model formulation. The model is then employed to analyze the effect of operating variables and catalyst selectivity in process performance. In particular, the search for the minimum hydrogen flow rate necessary to fulfil butene-1 purity specifications is undertaken.

**Keywords** selective hydrogenation, butene-1, 1,3-butadiene, trickle bed reactor

### 1 INTRODUCTION

Selective hydrogenation is industrially employed in the preparation of high purity butene-1 for co-monomer use in the production of linear low-density polyethylene (LLDPE). Impurities of acetylenic compounds (vinyl acetylene, butyne-1) and 1,3-butadiene are selectively hydrogenated to reach concentrations of about 10 ppm in the final product.

The purification of butene-1 is carried out in one or more fixed bed catalytic reactors. Palladium supported on low porosity  $Al_2O_3$  is the usual catalyst, although other transition metals can be included in the formulation to improve selectivity<sup>[1-3]</sup>. Operating temperatures with Pd based catalysts are in the range 290-330 K, while pressure is raised up to at least 1 MPa to operate with the  $C_4$  cut in liquid phase. According to Boitiaux *et al.*<sup>[4]</sup>, the liquid phase acts as a solvent to avoid the accumulation of oligomers on the catalyst surface, reducing in this way the catalyst deactivation rate.

As the necessary amount of  $H_2$  is usually higher than the absorption capacity of the  $C_4$  cut, a vapor/liquid mixture flows downwards through the catalytic beds. Trickle flow develops under typical operating conditions.

Butene-1 can be lost by hydrogenation to *n*-butane and by hydroisomerization to *cis*-butene-2 and *trans*-butene-2. The term hydroisomerization is used to recall the fact that the presence of  $H_2$  is necessary for the isomerization of butene-1 on Pd catalysts. Ideally, these reactions should be inhibited by the presence of alkynes or diolefins. It is then of paramount importance for the efficiency of the process to choose adequately the operating

conditions to reduce the losses to a minimum, while satisfying the specification for the purity of butene-1. This task can be greatly simplified if a tuned mathematical simulator of the unit is available. Also, if the catalyst has to be replaced, the selection from different marketed catalysts will be conveniently assisted by coupling experimental tests from laboratory with a mathematical simulator of the industrial unit.

Modelling the behaviour of selective hydrogenation units is not an obvious task, owing to the complexity of the series-parallel reaction network<sup>[5]</sup> and to hydrodynamic and mass transfer effects encountered in trickle bed reactors<sup>[6]</sup>. It is one of the objective of this work to identify the main factors affecting the performance of selective hydrogenation units and propose a mathematical model for usual ranges of operating conditions.

The mathematical model will be employed to analyse the effect of the relevant variables in selective hydrogenation such as feed composition, selectivity ratios and, mainly, the minimum hydrogen input necessary to accomplish the purity specification.

Although the essential features of the global catalytic mechanism have been described in the open literature<sup>[7-9]</sup>, we have not found a complete set of needed kinetic parameters in liquid phase to perform a quantitative treatment. Therefore, catalytic tests for the evaluation of reaction rate parameters have been carried out and will be also described here.

## 2 KINETIC MODEL

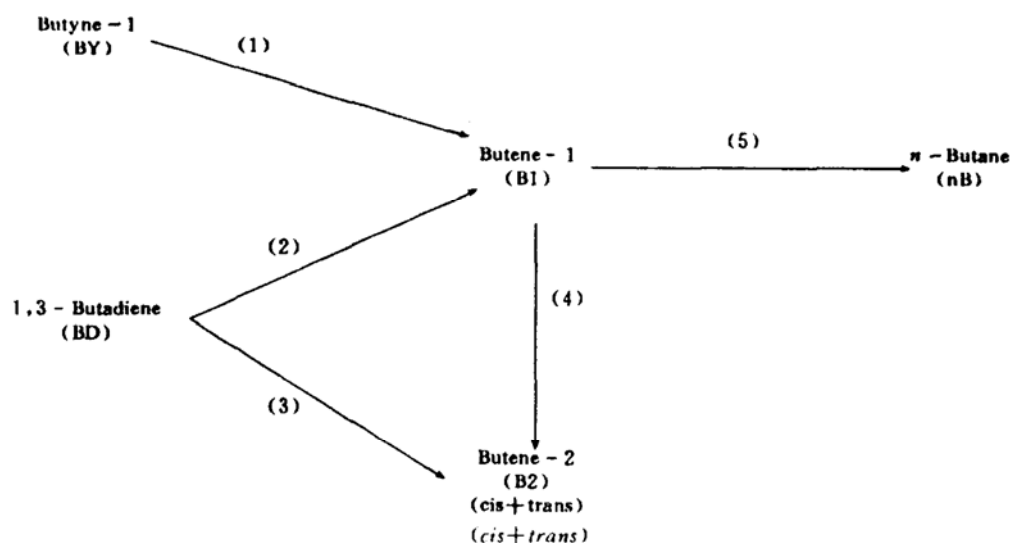
The global reaction network for unsaturated compounds in C<sub>4</sub> streams and their kinetic expressions, as suggested by Boitiaux *et al.*<sup>[1,4]</sup> and Vergel *et al.*<sup>[10]</sup>, are displayed in Table 1. It is known that alkynes likely to be present (*e. g.*, butyne-1, vinyl acetylene) strongly inhibits the reactions of butene-1 and to a lesser degree the hydrogenation of 1,3-butadiene<sup>[5]</sup>. For simplicity, only butyne-1 is considered in the reaction network, as a more detailed discrimination among acetylenic compounds will not bring any appreciable difference in the selectivity of the process.

The hydrogenation reactions are essentially irreversible at the low operation temperatures (290—330K), while the formation of *cis*- and *trans*-butene-2 from butene-1 is thermodynamically favoured. Since the isomerization of butene-1 should only proceed to a small degree, the isomerization reactions can also be regarded as being irreversible (Table 1).

It has been found that the rates of hydrogenation of *cis*- and *trans*-butene-2 are very low at process conditions<sup>[2]</sup>. Therefore, these reactions have not been included in the reaction network. Reactions (1), (2) and (3) in Table 1 are the purification reactions, while reactions (4) and (5), consuming butene-1, are the undesirable reactions.

The behaviour of several commercial Pd-catalysts has been studied in a laboratory stirred reactor with a 100 ml vessel operated in discontinuous mode. The experiments were conducted at a constant temperature of 323 K and total pressure of 1 MPa. The initial composition (molar fraction) was around 10% of butene-1, 0.6% of 1,3-butadiene and *n*-hexane was employed as inert solvent. The catalysts were crushed and the fraction sized between 0.6—0.9 mm was used in the tests. The samples (around 0.2 g) were directly suspended in

Table 1 Reaction network and kinetic expressions



$$r_1 = k_{BY,B1} x_{BY} x_{H_2} / \text{DEN} \quad r_2 = k_{BD,B1} x_{BD} x_{H_2} / \text{DEN}$$

$$r_3 = k_{BD,B2} x_{BD} x_{H_2} / \text{DEN} \quad r_4 = k_{B1,B2} x_{B1} x_{H_2} / \text{DEN}$$

$$r_5 = k_{B1,nB} x_{B1} x_{H_2} / \text{DEN}$$

$$\text{DEN} = (K_{BY}^a x_{BY} + K_{BD}^a x_{BD} + K_{B1}^a x_{B1}) (1 + K_{H_2}^a x_{H_2})$$

Catalyst M

$$k_{BY,B1} = 0.545 \text{ kmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1} \quad k_{BD,B1} = 8.929 \times 10^{-3} \text{ kmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$$

$$k_{BD,B2} = 3.65 \times 10^{-2} \text{ kmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1} \quad k_{B1,B2} = 2.878 \times 10^{-3} \text{ kmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$$

$$k_{B1,nB} = 8.878 \times 10^{-4} \text{ kmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$$

$$K_{BY}^a = 1462; \quad K_{BD}^a = 89.0; \quad K_{B1}^a = 1(\text{fixed}); \quad K_{H_2}^a = 77.0$$

where  $k$  is the kinetic constant per unit catalyst mass.

the reacting mixture.

The tested catalysts showed significant differences in selectivity. We will present here the results obtained for a catalyst [with Pd at 0.3% (wt)] showing a medium selectivity, as evaluated from the ratio between the specific reaction rates of butene-1 and 1,3-butadiene,  $S = (k_{B1,B2} + k_{B1,nB}) / (k_{BD,B1} + k_{BD,B2})$ . This catalyst, identified as Catalyst M, is originally available in 3mm spheres showing a 0.1mm thick layer impregnated with Pd. The internal transport limitations, eventually existing inside these spheres, will be nearly the same as those in the kinetic experiments, as the size (0.6–0.9mm) of the tested particles is considerable larger than thickness of the active layer. Thus, the results reported here correspond to effective reaction rates.

External transport limitations were taken into account to analyse the experimental data. The expression given by Levins and Glastonbury<sup>[14]</sup> was adopted.

The kinetic model parameters for the reactions of 1,3-butadiene and butene-1 were evaluated with the multi-response regression package GREG<sup>[12]</sup>. The results are displayed in

Table 1 (except for the parameters concerning butyne-1,  $k_{BY,B1}$  and  $K_{BY}^a$ , and hydrogen,  $K_{H_2}^a$ ). Although the production of *cis*- and *trans*-butene-2 from either 1,3-butadiene or butene-1 was discriminated in the regression analysis, it is enough for the purpose of this paper to consider the global production of both isomers as quantified by the rate constants  $k_{BD,B2}$  and  $k_{B1,B2}$ .

The comparison between the experimental composition as a function of time and the values predicted from the evaluated reaction rates is shown in Fig. 1. It is clear that a good fitting was obtained.

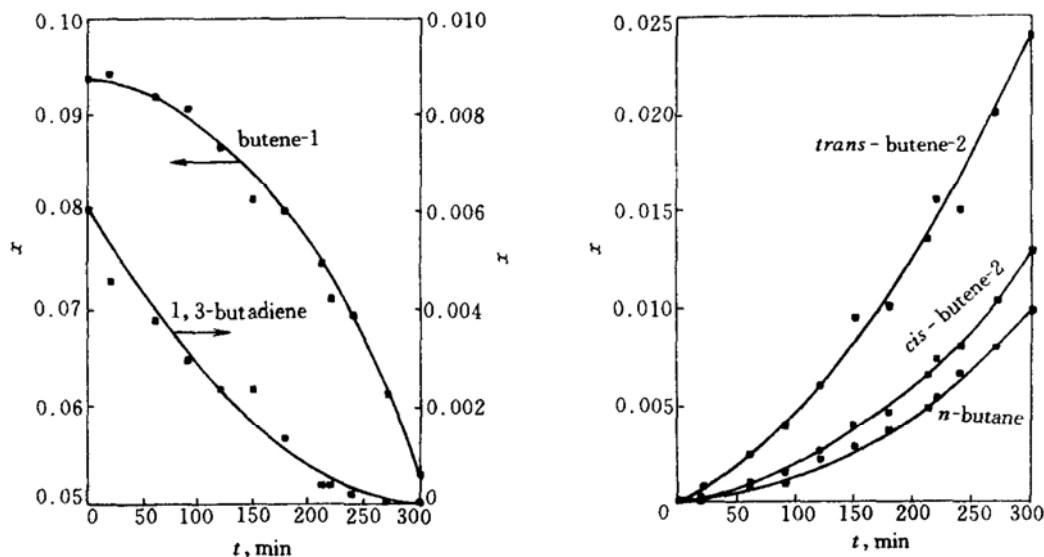


Figure 1 Comparison between experimental and predicted composition as a function of reaction time

■ experimental value; — model values

A similar analysis was carried out for the resulting best catalyst, identified as Catalyst B. The comparison between the selectivity ratios  $S_{B2} = k_{B1,B2} / (k_{BD,B1} + k_{BD,B2})$  and  $S_{nB} = k_{B1,nB} / (k_{BD,B1} + k_{BD,B2})$  for Catalysts M and B are displayed in Table 2, where a significant difference in favour of Catalyst B can be appreciated.

The parameters concerning butyne-1,  $k_{BY,B1}$  and  $K_{BY}^a$  (Table 1), were evaluated from the study of simultaneous hydrogenation of butyne-1 and 1,3-butadiene presented by Vasudevan<sup>[5]</sup>. The adsorption constant  $K_{H_2}^a$  was obtained by fitting the data from Boitiaux *et al.*<sup>[1]</sup>.

Table 2 Selectivity for Catalysts M and B

Catalyst	$S_{B2} = k_{B1,B2} / (k_{BD,B1} + k_{BD,B2})$	$S_{nB} = k_{B1,nB} / (k_{BD,B1} + k_{BD,B2})$
M	$6.30 \times 10^{-2}$	$1.95 \times 10^{-2}$
B	$1.64 \times 10^{-2}$	$0.051 \times 10^{-2}$

### 3 REACTOR MODEL

To describe the model adopted for selective hydrogenation of C<sub>4</sub> cuts in trickle bed reactors, it is convenient to keep in mind typical operating conditions. The values displayed in Table 3 correspond to nominal operating conditions and design variables for an actual industrial

plant.

For the model proposed here, it will be assumed that the hydraulic design of the unit is appropriate to ensure uniform flow distribution. It has been verified<sup>[13]</sup> that the hydrodynamic regime corresponding to conditions given in Table 3 is the trickle flow (low interaction regime), axial dispersion effects can be neglected in both, vapor and liquid, and particles remain completely wet. Therefore, the hypothesis of plug flow for both phases was employed.

Table 3 Typical operating conditions for selective hydrogenation

Parameter	Compound	Molar percent of the C <sub>4</sub> cut, %	
temperature	323 K	butyne-1	0.42
pressure	1 MPa	1,3-butadiene	0.58
pellet diameter	0.0030 m	butene-1	21.00
reactor diameter	0.60 m	butene-2 ( <i>cis+trans</i> )	49.00
molar flow rate	0.275 kmol·m <sup>-2</sup> ·s <sup>-1</sup>	<i>n</i> -butane	29.00

### TEMPERATURE RISE AND PRESSURE DROP

Selective hydrogenation is carried out adiabatically since the relatively small concentration of impurities leads to mild temperature rises. The energy balance included in the mathematical model reveals that temperature rises 10–15°C for the feed composition given in Table 3. The most important consequence of this variation could be its effect on selectivity, which in turn would depend on differences in activation energies for the reactions. However, up to our knowledge there is no evidence in the literature of significant changes in selectivity within the usual range of temperatures. Our own experiments with Catalyst B (Section 2) suggest a negligible effect between 313K and 323K. Therefore, and because the main concern in this contribution is to discuss the operation in terms of selectivity, temperature was assumed uniform along the bed for the results discussed in the next sections. It should remain clear, however, that for a comprehensive simulation, temperature changes and variation of kinetic parameters with temperature should be considered.

Pressure drop along the bed has been evaluated by the correlation proposed by Larkins *et al.*<sup>[14]</sup> For the conditions in Table 3 and with properties of Catalyst M (Table 1), a catalyst depth of about 15 m is needed, as described later. The predicted pressure drop is acceptably low, about 73kPa, indicating suitable values of the superficial velocities.

### MASS TRANSFER STEPS

Commercial catalysts are of the so-called egg-shell type, obtained by depositing the active metals within a thin layer from the particle external surface. In this way, intra-particle concentration gradients, which would severely impair the selectivity, are minimized. It is recalled that the reported results (Tables 1 and 2) for the tested catalysts include possible mass transfer effects inside the particles. For this reason, internal transport limitations have not been explicitly included in the model.

The three external mass transport limitations have been considered in the model:

- (1) Vapor bulk/vapor-liquid interface;
- (2) Vapor-liquid interface/liquid bulk;

## (3) Liquid bulk/catalyst external surface.

The molar fluxes  $N_j$  across the vapor-liquid interface were evaluated from the Stefan-Maxwell expressions, as described elsewhere<sup>[13]</sup>. Binary mass transfer coefficients and interfacial area  $a_v$  were estimated from correlations presented in Dhingra *et al.*<sup>[15]</sup> and Fukushima and Kusaka<sup>[16]</sup>.

Only the dilute components (impurities and dissolved hydrogen) are likely to undergo mass transfer limitations between the liquid bulk and the catalyst surface. Therefore, the expressions for low mass transfer rates were directly employed for this step, with mass transfer coefficients evaluated from the formulation given by Rao and Drinkenburg<sup>[17]</sup>.

**MATERIAL BALANCES**

The differential mass conservation equations for the individual components in the liquid phase on the basis of the plug flow hypothesis are

$$dL_j/dM_c = a_v N_j / \rho_c + \sum_{i=1}^{N_R} a_{ij} g_i(x_1^s, \dots, x_N^s) \quad j=1, \dots, N \quad (1)$$

where  $g_i$  are effective reaction rates based on a set of stoichiometrically independent reactions. For the global reaction scheme (Table 1), the hydrogenation reactions are taken as the independent set. Then,  $g_1=r_1$ ,  $g_2=r_2-r_5$ ,  $g_3=r_3+r_5$ ,  $g_4=r_4$ . The extents of reaction are defined as

$$dX_i/dM_c = g_i(x_1^s, \dots, x_N^s) \quad i=1, \dots, N_R \quad (2)$$

Integral expressions can be written for the vapor molar flows

$$V_j = F_j^0 - L_j + \sum_{i=1}^{N_R} a_{ij} X_i \quad j=1, \dots, N \quad (3)$$

The physical equilibrium condition at the vapor-liquid interface was evaluated by using de RKS equation of state modified by Graboski and Daubert<sup>[18]</sup> for mixtures containing hydrogen.

Mass transfer from the liquid bulk to catalyst surface is expressed by

$$k_j^*(a_p/\rho_c)(x_j^s - x_j) = \sum_{i=1}^{N_R} a_{ij} g_i \quad j=1, \dots, N \quad (4)$$

The initial conditions for the set of differential equations (1)–(2) are established from known values of  $F_j^0$  and the assumption of vapor/liquid equilibrium at the reactor inlet. The code described by Mascuzzini *et al.*<sup>[19]</sup> was used for numerical integration.

The numerical results and the analysis made in Ref. [13] indicate that the vapor side does not introduce significant limitations to interfacial mass transfer, but the resistance for  $H_2$  transfer in the liquid phase should be taken into account. This result can be employed to simplify the set of material balance equations and their numerical solution, as detailed in Ref. [13].

**4 RESULTS AND DISCUSSION****4.1 General behaviour of the mathematical model**

Some general features of selective hydrogenation will be considered first. The results dis-

cussed in this section are evaluated with reaction rate parameters in Table 1 and conditions in Table 3, unless otherwise stated. Fig. 2 shows molar fraction profiles in both phases for an inlet  $H_2$  molar flow rate  $F_{H_2}^0 = 2 \text{ mol} \cdot \text{s}^{-1}$ . To analyze the global variations in the hydrocarbon species only the liquid phase need to be considered as the liquid molar rate is 50–100 times the vapor molar rate.

Since butyne-1 is strongly adsorbed on the catalyst surface, it mostly reacts under a zeroth order regime. It can also be appreciated in Fig. 2 that hydrogenation of 1,3-butadiene is significantly inhibited while butyne-1 remains in the system. At the same time, butene-1 does not react to any appreciable degree and its concentration slightly increases during hydrogenation of butyne-1. Once butyne-1 is completely depleted, the rapid hydrogenation of 1,3-butadiene takes place.

It is evident that hydrogenation of butyne-1 in the zeroth order regime is much slower than that of 1,3-butadiene. This is explained by the ratio  $(k_{BD}/K_{BD})/(k_{BY}/K_{BY}) = 13.8$  evaluated from Table 1. As a consequence, the amount of catalyst necessary to carry out the operation will strongly depend on the concentration of butyne-1 in the feed.

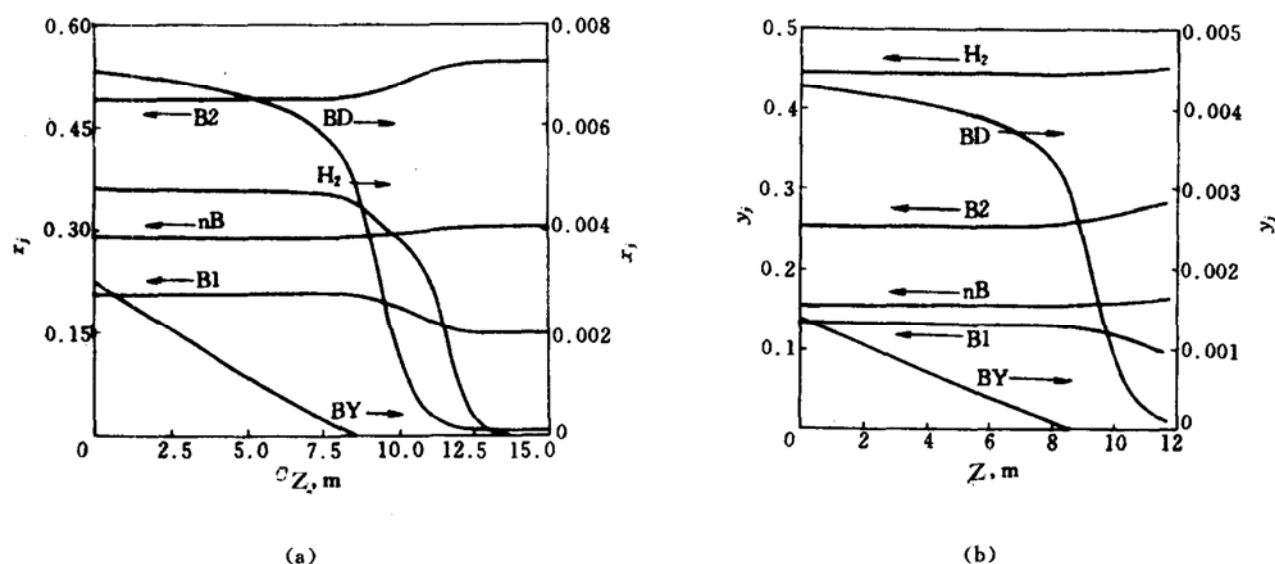


Figure 2 Molar fraction profiles in liquid and (b) vapor phase  
 BY—butyne-1; BD—1,3-butadiene; B1—butene-1; B2—butene-2; nB—*n*-butane

The liquid remains essentially saturated with  $H_2$  while butyne-1 is reacting, but a sudden drop in its molar fraction is observed as a consequence of the fast hydrogenation of 1,3-butadiene. This concentration drop reveals an important effect of mass transfer limitation on the liquid side. At the same time, the  $H_2$  molar fraction in the vapor phase remains practically equal to the equilibrium value ( $y_{H_2} \cong 0.45$ ) (Fig. 2). It is recalled that due to similar volatilities of the hydrocarbon species, the system behaves as one of two components. Hence, at a given pressure and temperature, the equilibrium molar fractions  $x_{H_2,eq}$  and  $y_{H_2,eq}$  remain essentially constants<sup>[13]</sup>.

For adequate hydrogen inputs and provided that the catalyst bed is large enough,  $H_2$  con-

sumption will be nearly completed. Before this happens, the vapor phase extinguishes (at a depth of about 11.7 m for the conditions in Fig. 2). From this point on, the hydrogenation reactions will be sustained only by the amount of hydrogen already absorbed in the liquid phase.

#### 4.2 Variables indexing the reactor performance

In practice, once the reaction unit is installed, the most relevant variable to conduct properly the operation is the rate of  $H_2$  input. For given operating conditions, the minimum inlet rate of hydrogen  $F_{H_2, \min}^0$  to satisfy the impurities tolerance can be evaluated from the proposed model. The resulting values, relative to the total amount of impurities in the feed

$$R_{\min}^0 = F_{H_2, \min}^0 / (F_{BD}^0 + F_{BY}^0) \quad (5)$$

are plotted in Fig. 3 as a function of the reaction modulus  $\tau$  defined as

$$\tau = \frac{M_c}{(F_{BY}^0 / r_{BY}^* + F_{BD}^0 / r_{BD}^*)} \quad (6)$$

where  $r_{BY}^*$  and  $r_{BD}^*$  are rates of reaction of each impurity evaluated at the reactor inlet, but neglecting the presence of the other impurity

$$r_{BY}^* = \frac{k_{BY} x_{BY}^0 x_{H_2}^0}{(K_{BY}^a x_{BY}^0 + K_{B1}^a x_{B1}^0)(1 + K_{H_2}^a x_{H_2}^0)}$$

$$r_{BD}^* = \frac{k_{BD} x_{BD}^0 x_{H_2}^0}{(K_{BD}^a x_{BD}^0 + K_{B1}^a x_{B1}^0)(1 + K_{H_2}^a x_{H_2}^0)}$$

The values of  $R_{\min}^0$  in Fig. 3 correspond to three levels of purity specification, expressed as the residual content of impurities (butyne-1 and 1,3-butadiene). The residual hydrogen flow rate,  $R^{\text{exit}} = F_{H_2}^{\text{exit}} / (F_{BD}^0 + F_{BY}^0)$  is also plotted in Fig. 3

It is observed in Fig. 3 that  $R_{\min}^0$  tends to a limiting value,  $R_{\text{asympt}}^0$ , as  $\tau$  increases. At the same time, there remains a negligible amount of  $H_2$  in the effluent,  $F_{H_2}^{\text{exit}} \approx 0$ . At high values of  $\tau$ , there is a fraction of the bed which is not actually working. A characteristic value of  $\tau$ , which will be denoted by  $\tau_{\text{crit}}$ , can be defined by choosing a small value of  $F_{H_2}^{\text{exit}}$ . This value was taken coincident with the impurity tolerance,  $F_{H_2}^{\text{exit}} = (F_{BY} + F_{BD})_{\text{tol}}$ . The resulting value of  $\tau_{\text{crit}}$  is indicated in Fig. 3 for a tolerance of 10ppm in the exit stream. It can be considered for any practical purpose that  $R_{\min}^0 = R_{\text{asympt}}^0$  when  $\tau > \tau_{\text{crit}}$ .

For  $\tau < \tau_{\text{crit}}$ , the necessary value of  $R_{\min}^0$  increases rapidly. The main effect produced by higher values of  $F_{H_2, \min}^0$  is to diminish the estimated liquid side resistance to mass transfer because of the effect of the vapor flow rate. It is clear that the operation will be feasible for a limited range of values  $\tau < \tau_{\text{crit}}$ , since the  $H_2$  liquid concentration can not rise beyond the saturation value. In actual practice, it will be most difficult to conduct the operation at  $\tau < \tau_{\text{crit}}$  due to the high sensibility shown by  $R_{\min}^0$  in this region. The amount of catalyst in the bed should guarantee that values of  $\tau$  be greater than  $\tau_{\text{crit}}$  during the operating period before catalyst regeneration or replacement.

Values of  $R^0$  higher than  $R_{\min}^0$  will insure the purity specification, but will produce extra losses of butene-1. Bressa<sup>[13]</sup> analyzed the effect of  $R^0$  on the butene-1 loss, expressed as



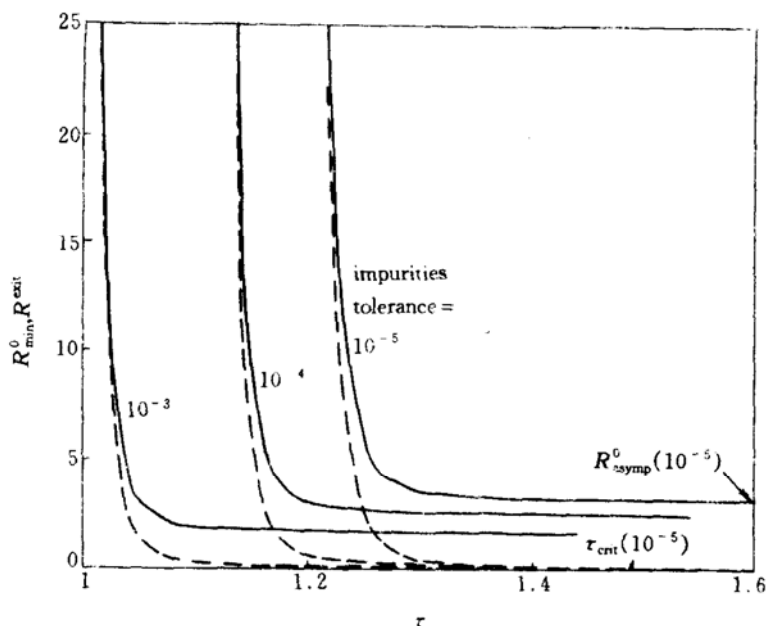


Figure 3 Values of  $R_{\min}^0$  and  $R^{\text{exit}}$  as a function of parameter  $\tau$   
 impurities tolerance (molar fraction) =  $(z_{\text{BY}} + z_{\text{BI}})^{\text{exit}}$ ; —  $R_{\min}^0$ ; - - -  $R^{\text{exit}}$

$$\Delta_{\text{BI}} = (F_{\text{BI}}^0 - F_{\text{BI}}^{\text{exit}}) / F_{\text{BI}}^0 \quad (7)$$

$\Delta_{\text{BI}}$  steadily increases as  $R^0$  is raised beyond  $R_{\min}^0$ . For example, for the kinetic parameters in Table 2, conditions in Table 3 and an impurity tolerance of 100 ppm,  $\Delta_{\text{BI}}$  increases from 30% to 40% as  $R^0$  is raised a 20% from  $R_{\text{asymp}}^0$ . This result stresses the importance of a fine tuning for the operating  $\text{H}_2$  input to reduce the butene-1 loss to a minimum.

So far, the significance of three parameters to identify selective hydrogenation has been stressed.  $\tau_{\text{crit}}$  is a design parameter related to the minimum amount of catalyst,  $R_{\text{asymp}}^0$  is the operating parameter fixing the minimum hydrogen input to achieve the tolerable level of impurities and  $\Delta_{\text{BI}}$  evaluates the selectivity of the operation. The influence of different variables on these parameters will be described next.

#### EFFECT OF IMPURITIES TOLERANCE, CATALYST SELECTIVITY AND COMPOSITION OF THE $C_4$ CUT

The effect of variables which affect directly the selectivity of the operation will be analysed here.

The effect of purity specification can be analysed in Fig. 4. In spite of a wide variation in the level of impurities tolerance,  $\tau_{\text{crit}}$  varies slightly. This is mainly due to the fact that an important fraction of the total amount of catalyst is employed for the slow butyne-1 hydrogenation, while the tolerance becomes in practice related to the residual amount of 1,3-butadiene.

The high values of  $R_{\text{asymp}}^0$  needed for low tolerances are mainly due to  $\text{H}_2$  consumed by butene-1. Consequently,  $\Delta_{\text{BI}}$  increases significantly as the tolerance diminishes. A catalyst more selective than Catalyst M will be necessary to avoid these large butene-1 losses.

The effect of catalyst selectivity, as defined by the ratios  $S_{nB}$  and  $S_{B2}$ , is depicted in Figs. 5 (a) and 5 (b).  $\tau_{crit}$  and  $R_{asymp}^0$  vary with the ratio  $S_{nB}$  [(Fig. 5 (a))], but they are independent of  $S_{B2}$ . In particular,  $R_{asymp}^0$  increases significantly with  $S_{nB}$ , because the higher rate of butene-1 hydrogenation. The simultaneous variation of  $\tau_{crit}$  is a consequence of the changes in  $R_{asymp}^0$ .

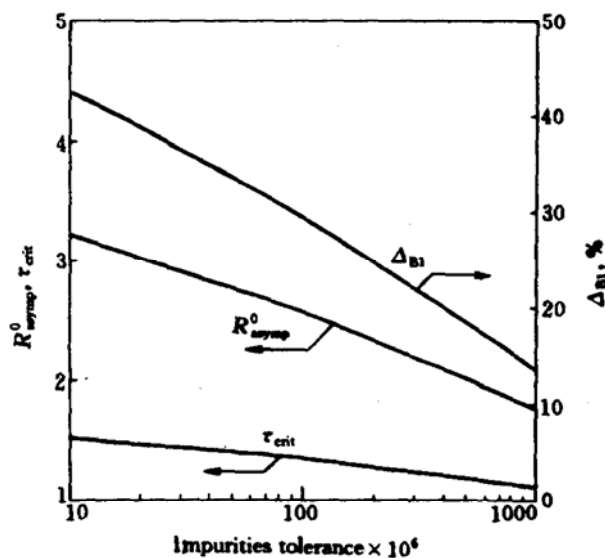


Figure 4 Variation of  $\tau_{crit}$ ,  $R_{asymp}^0$  and  $\Delta_{B1}$  with impurities tolerance (molar fraction)

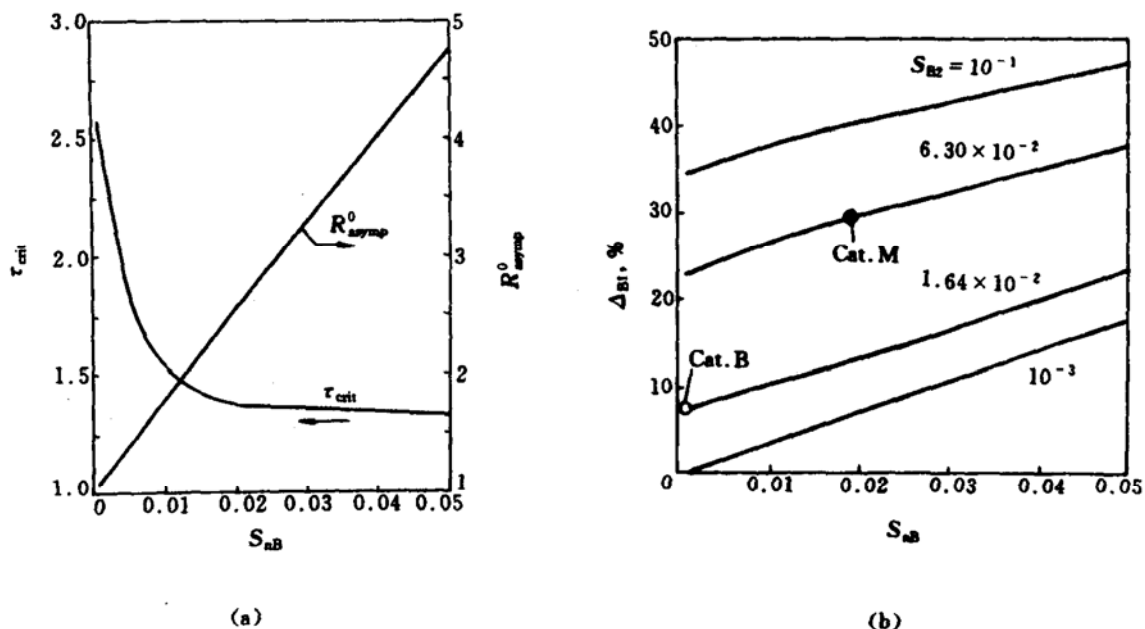


Figure 5 Variations of  $\tau_{crit}$  and  $R_{asymp}^0$  (a) and  $\Delta_{B1}$  (b) with catalyst selectivity for 100 ppm of impurities tolerance

$$S_{B2} = k_{B1,B2} / (k_{BD,B1} + k_{BD,B2}); S_{nB} = k_{B1,nB} / (k_{BD,B1} + k_{BD,B2})$$

The loss in butene-1 is strongly affected by the selectivity ratios. The values of  $\Delta_{B1}$  for catalyst M and Catalyst B are specifically indicated in Fig. 5(b). It is recalled that Catalyst B was the most selective catalyst out of the tested set. The difference in performance with Catalyst M would bring a strong impact in the process efficiency.

The effect of varying the relative amounts of butyne-1 and 1,3-butadiene in the feed, maintaining the total concentration of impurities  $z_{BY}^0 + z_{BD}^0 = 0.010$ , is shown in Fig. 6. The changes in  $R_{asymp}^0$  and  $\Delta_{B1}$  observed in Fig. 6 are significant, and their trends are easily explained by recalling that hydrogenation of butyne-1 is more selective than that of 1,3-butadiene. High concentrations of butyne-1 increases considerably the necessary mass of catalyst.

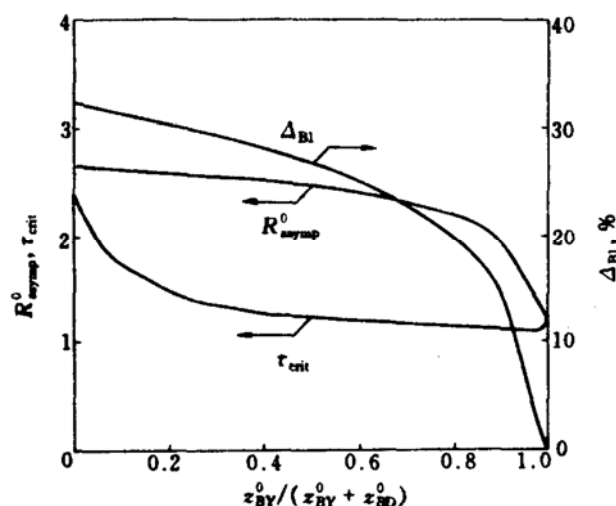


Figure 6 Variation of  $\tau_{crit}$ ,  $R_{asymp}^0$  and  $\Delta_{B1}$  with the relative amounts of butyne-1 and 1,3-butadiene in the feed for 100ppm of impurities tolerance

## 5 CONCLUSIONS

A mathematical model for selective hydrogenation of butyne-1 and 1,3-butadiene for butene-1 purification in a trickle bed reactor has been presented in this work.

Kinetic expressions presented in the literature for the catalytic reaction network taking place over Pd based catalysts have been employed. Kinetic coefficients were adjusted from experiments in a laboratory test reactor for some commercial catalysts. The coefficients for one catalyst showing an intermediate rating of selectivity were chosen as a basis to undertake a parametric analysis of the behaviour of selective hydrogenation units for the purification of butene-1.

Three variables have been selected to identify the system;  $\tau_{crit}$  is the design parameter related to the minimum amount of catalyst necessary to achieve the specification of impurities in the product stream;  $R_{asymp}^0$  is the operating parameter fixing the minimum  $H_2$  input and  $\Delta_{B1}$ ,

the loss of butene-1, measures the process efficiency.

It is shown that  $H_2$  input has to be in practice finely adjusted according to the value of  $R_{\text{asympt}}^0$  to avoid unnecessary losses of butene-1. The mathematical model was then employed to characterize the dependency of  $\tau_{\text{crit}}$ ,  $\Delta_{B1}$  and, in particular,  $R_{\text{asympt}}^0$ . Feed composition, specification of impurities in the product and catalyst selectivity are shown to affect significantly the resulting values of these parameters.

It is believed that the mathematical model presented here introduces the major features likely to affect the behaviour of selective hydrogenation units, while maintaining a reasonable degree of complexity. It has been shown how the model can be employed as an efficient tool to operate industrial units, for catalyst selection or as a guideline for design purpose.

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### NOMENCLATURE

$a_p$	particle area per unit bed volume, $m^2 \cdot m^{-3}$
$a_v$	vapor-liquid interfacial area per unit bed volume, $m^2 \cdot m^{-3}$
$F$	overall molar flow, $kmol \cdot s^{-1}$
$g$	effective reaction rate per unit catalyst mass, $kmol \cdot kg^{-1} \cdot s^{-1}$
$K_j^*$	adsorption equilibrium constant for species $j$
$k$	kinetic constant per unit catalyst mass, $kmol \cdot kg^{-1} \cdot s^{-1}$
$k_j^*$	liquid-catalyst-surface mass transfer coefficients for species $j$ , $kmol \cdot m^{-3} \cdot s^{-1}$
$L$	liquid molar flow, $kmol \cdot s^{-1}$
$M_C$	catalyst mass, $kg$
$N$	number of compounds
$N_j$	molar flux for species $j$ across the gas-liquid interphase, $kmol \cdot m^{-2} \cdot s^{-1}$
$N_R$	number of reactions
$R$	ratio between hydrogen and impurities molar flows [Eq. (5)]
$r$	reaction rate per unit catalyst mass, $kmol \cdot kg^{-1} \cdot s^{-1}$
$S_{B2}$	selectivity $[k_{B1, B2} / (k_{BD, B1} + k_{BD, B2})]$
$S_{nB}$	selectivity $[k_{B1, nB} / (k_{BD, B1} + k_{BD, B2})]$
$t$	reaction time, min
$V$	vapor molar flow, $kmol \cdot s^{-1}$
$X$	extent of reaction, $kmol \cdot s^{-1}$
$x$	molar fraction in liquid phase
$y$	molar fraction in vapor phase
$z$	overall molar fraction
$\alpha$	stoichiometric coefficient
$\Delta_{B1}$	loss of butene-1 [Eq. (7)]
$r$	dimensionless parameter [Eq. (6)]
$\rho_c$	bed density, $kg \cdot m^{-3}$

**Superscripts**

exit	at the reactor exit
s	catalyst surface
0	feed condition

**Subscripts**

asympt	asymptotic value
BD	1,3-butadiene
B1	butene-1
B2	butene-2( <i>cis</i> - and <i>trans</i> -)
BY	butyne-1
crit	critical value
H <sub>2</sub>	hydrogen
<i>i</i>	<i>i</i> th reaction
<i>j</i>	<i>j</i> th species
min	minimum value
nB	<i>n</i> -butane
tol	tolerance

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