

# Selective hydrogenation of 1,3-butadiene: improvement of selectivity by using additives

J.A. Alves<sup>a,b</sup>, S.P. Bressa<sup>a,b</sup>, O.M. Martínez<sup>a,b</sup>, G.F. Barreto<sup>a,b,\*</sup>

<sup>a</sup> Centro de Investigación y Desarrollo en Ciencias Aplicadas (CINDECA), UNLP-CONICET, Argentina

<sup>b</sup> Programa de Investigación y Desarrollo en Ingeniería de Reactores (PROIRO), Facultad de Ingeniería UNLP, Argentina

Received 28 March 2003; accepted 16 September 2003

## Abstract

The objective of this work is to evaluate the behavior of isoprene as an additive to improve selectivity in the selective hydrogenation of 1,3-butadiene from 1-butene-rich cuts.

To this end, the liquid-phase hydrogenation of 1,3-butadiene, 1-butene and isoprene on a commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst of the eggshell type at 313 K was studied in a batch system. It was found that the adsorption strength of isoprene is between those of 1,3-butadiene and 1-butene. Thus, in the presence of isoprene, 1-butene concentration remains practically constant even when the liquid is almost depleted from 1,3-butadiene.

The improvement of the selectivity of an industrial reactor for 1-butene purification by adding isoprene was evaluated. To this end, a kinetic model was fitted to the experimental results and a simplified model of an industrial unit was adopted. It was found that adding 1% of isoprene can reduce 1-butene losses by a factor between 1.3 and 10 for H<sub>2</sub> partial pressures ranging 100–500 kPa, respectively.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Selective hydrogenation; 1-Butene; 1,3-Butadiene; Isoprene; Pd catalyst; Kinetics

## 1. Introduction

1-Butene (1BE) is used as monomer in the production of polybutene and as comonomer in the production of linear-low-density polyethylene. Polymerization-grade 1BE is obtained from 1BE-rich cuts after selective hydrogenation of 1,3-butadiene (BD) and acetylenic compounds up to about 10 ppm. The process is industrially carried out in fixed catalytic beds with the liquid hydrocarbon mixture and H<sub>2</sub> flowing concurrently either in down or up flow. Process temperature ranges between 300 and 330 K and total pressure must be high enough to maintain the hydrocarbons in liquid phase [1].

Pd-based catalysts are universally employed in selective hydrogenation due to the high intrinsic selectivity of Pd to adsorb acetylenics and BD instead of 1BE [2], thus preventing 1BE from adsorbing and reacting. Commercial catalysts for selective hydrogenation are manufactured by impregnating with Pd an external layer ranging 50–250 μm (eggshell

catalysts). Low-loaded Pd eggshell catalysts are employed to reduce mass transport resistances.

Acetylenic compounds are so selectively adsorbed by Pd that they cover essentially all active sites blocking the access of BD and 1BE. BD is the second compound as ranked by its adsorption strength. When the concentration of acetylenics becomes low enough, BD covers the active sites inhibiting 1BE reactions. Once BD has been almost completely hydrogenated, the hydrogenation and hydroisomerization of 1BE takes place.

It can be concluded from the just outlined process that acetylenics are not likely to affect selectivity and that the essential problem is to achieve a high conversion of BD with a minimum loss of 1BE. Hence, the presence of acetylenic compounds will not be considered in this work.

The simplified sketch of overall reactions presented in Fig. 1 has been proven enough to capture the essential features of the system [3–5]. As indicated in Fig. 1, 1BE can be hydrogenated to *n*-butane (BA) or, mainly, hydroisomerize to *cis*-2-butene and *trans*-2-butene, considered as a lump of 2-butene (2BE). The hydrogenation of 2BE is ignored because it proceeds always more slowly than that of 1BE [6]. The hydrogenation reactions are essentially irreversible at process temperatures. The hydroisomerization of 1BE,

\* Corresponding author. Present address: CINDECA, 47 No. 257, C.C. 59, B1900AJK-La Plata, Argentina. Tel./fax: +54-221-4211353.  
E-mail address: barreto@dalton.quimica.unlp.edu.ar (G.F. Barreto).

### Nomenclature

$C_T$	total molar concentration (mol/m <sup>3</sup> )
$D$	effective diffusion coefficient (m <sup>2</sup> /s)
$F_T$	hydrocarbon total molar flow rate (mol/s)
$H$	Henry's constant of H <sub>2</sub> (kPa <sup>-1</sup> )
$k_i$	rate coefficients of reaction $i$ in Fig. 1 (mol/kg <sub>active layer</sub> s)
$K^{\text{ad}}$	adsorption constant (-)
$L$	length of the active layer (m)
$M_{\text{cat}}$	mass of catalyst (kg)
$N_T$	total mole number
$p_{\text{H}_2}$	hydrogen partial pressure (kPa)
$P_T$	total pressure (kPa)
$r_i$	intrinsic rate of reaction $i$ in Fig. 1 per unit mass of active layer (mol/kg <sub>active layer</sub> s)
$r_j$	intrinsic consumption rate of compound $j$ per unit mass of active layer (mol/kg <sub>active layer</sub> s)
$\bar{r}_j$	observed consumption rate of compound $j$ per unit mass of catalyst (mol/kg s)
$S_{\text{cat}}$	external area of the catalyst pellet (m <sup>2</sup> )
$t$	time (min)
$t_{\text{BD}}$	time at which $x_{\text{BD,bulk}} = x^*$ (min)
$t_{\text{IP}}$	time at which $x_{\text{IP,bulk}} = x^*$ (min)
$x$	mole fraction inside the active layer (-)
$x_{\text{BD,tol}}$	specified BD tolerance at the exit of the reactor (-)
$x_{j,\text{bulk}}$	mole fraction of compound $j$ in the liquid bulk (-)
$x^*$	mole fraction defined in Eq. (2) (-)
$z$	dimensionless coordinate inside the active layer, $z = z'/L$ (-)
$z'$	coordinate inside the active layer (m)
$z_{\text{H}_2}^0$	molar ratio between H <sub>2</sub> and hydrocarbon inputs to the industrial reactor (-)

### Greek letters

$\kappa$	liquid–solid mass transport coefficient (m/s)
$\rho_{\text{cat}}$	catalyst density (kg/m <sup>3</sup> )
$\tau$	modified time ( $M_{\text{cat}}t/N_T$ ) in the experimental batch reactor or modified space–time ( $M_{\text{cat}}/F_T$ ) in the simulated fixed bed reactor (kg s/mol)
$\chi$	conversion (-)

### Subscripts and superscripts

BD	1,3-butadiene
1BE	1-butene
2BE	2-butene
H <sub>2</sub>	hydrogen
HC	hydrocarbons
$i$	reaction $i$ in Fig. 1
IP	isoprene
$j$	compound $j$
sat	saturation
0	initial condition in the experiments or condition at the inlet of the industrial reactor

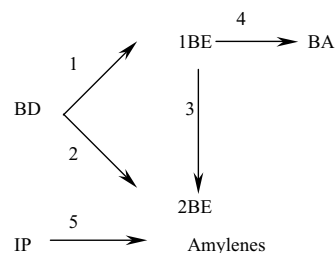


Fig. 1. Overall reaction network.

which occurs only in the presence of H<sub>2</sub>, should only proceed to small degree, so it can also be regarded as being irreversible. Reactions 1 and 2 in Fig. 1 are the purification reactions whereas Reactions 3 and 4, which consume 1BE, are the undesirable reactions.

Contrary to expectation from the use of low-loaded Pd eggshell catalysts, we found that, under typical operating conditions of industrial reactors, strong diffusion limitations severely impair the observed selectivity [7,8]. It is worth to mention that 1BE losses observed in industrial reactors raise up to 20–30%.

The reason for poor selectivity lies in the fact that at high BD conversions its diffusion capability inside the active layer becomes less than that of H<sub>2</sub>. At these conditions, BD is depleted inside the catalyst and H<sub>2</sub> will diffuse deeper inside the active layer bringing about the reactions of 1BE [7,8].

It can be argued that the design of commercial catalysts should not introduce such diffusion limitation. However, a lower initial activity (using less Pd content) would surely shorten the time of the catalyst under continuous service without regeneration or replacing, as these catalysts are known to loose activity by the growth of heavy residues [9]. A daily loss of 1% in activity would lead after 2 years to about (1/1000) of the fresh catalyst activity.

A way to improve selectivity consists in including an additive in the process stream. Partial deactivation with CO was studied, but it did not yield satisfactory results [9].

The objective of this contribution is to study the effect of introducing an additional unsaturated compound in the feed to diminish the impact of the diffusion limitations on the observed selectivity. The additive should present an adsorption strength intermediate between those of BD and 1BE. If so, we can expect that the additive rather than 1BE will consume the excess of H<sub>2</sub> inside the catalyst when the concentration of BD has dropped enough. Elimination of H<sub>2</sub> inside the catalyst is of paramount importance to suppress 1BE hydrogenation and, more important, to stop 1BE hydroisomerization. The additive should fulfil at least an extra condition: it and its hydrogenation products should be easily separated from the C<sub>4</sub> stream after the selective hydrogenation unit.

The compound chosen for this study is isoprene (IP). As shown in Fig. 1, its hydrogenation products are amylenes. The conjugate double bonds of IP suggest that it should be adsorbed more strongly than 1BE. Besides, it is known that the increase either in the carbon number or in the skeletal

hydrocarbon branching weakens the adsorption strength. So, IP should be adsorbed less strongly than BD.

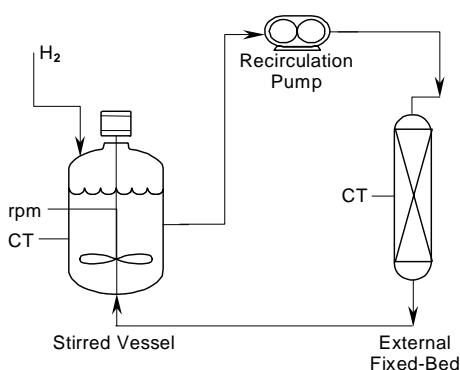
The effluent from the 1BE purification unit is fed to a fractionation column to separate 1BE from the less volatile 2BE and BA [1]. The ratios of the vapor pressure of BA and 2BE with respect to that of 1BE at 313 K are about 0.80. In the case of IP that ratio is 0.27, indicating that IP will not be present in the polymerization-grade 1BE stream at any significant extent and that IP can also be easily separated from 2BE and BA.

We carried out an experimental study in a batch laboratory reactor to verify the foreseen behavior of IP and to fit a kinetic model for the reaction set in Fig. 1. A simplified model of an industrial 1BE purification unit will then be used to show how the operating variables can be chosen, including the amount of IP added in the feed, to eliminate BD without significant 1BE losses.

## 2. Experimental

We used a commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst of the eggshell type containing Pd at 0.2% on an overall weight basis. Specific surface area of the catalyst is 71 m<sup>2</sup>/g. The structure of the pellets, with a mean diameter of 2.34 mm, consists in a 230 μm external layer of Pd/Al<sub>2</sub>O<sub>3</sub> and an Al<sub>2</sub>O<sub>3</sub> inert core.

The experimental reaction system consists of a 100 cm<sup>3</sup> stirred vessel and an external 0.00635 m tube holding the catalyst sample, as sketched in Fig. 2. The liquid solution is recirculated between the stirred vessel and the catalytic bed by a gear pump. The recirculating flow rate was high enough to minimize external transport effects and to operate the catalytic bed at nearly uniform composition. The stirred vessel, which contains most of the liquid mixture in the loop, is used for maintaining the solution saturated with H<sub>2</sub> and for temperature control. The operating pressure,  $P_T$ , is maintained constant by feeding H<sub>2</sub> through a pressure regulator. Catalytic pellets in its original size were packed in the external tube. The catalyst samples were treated for reduction



CT: Temperature Control  
rpm: Agitation Speed Control

Fig. 2. Experimental set-up.

finishing in the same bed before reaction. Some other details concerning the experimental system were described in [7].

Batch type experiments with respect to the hydrocarbon mixture were carried out. *n*-Hexane was used as a solvent and some quantities of propane were employed to regulate independently the total pressure and H<sub>2</sub> partial pressure,  $p_{H_2}$ , which were kept constant during the run [7]. Hence, the saturation mole fraction of H<sub>2</sub>,  $x_{H_2,sat}$ , remained nearly constant throughout each experiment.

Liquid samples were analyzed by gas chromatography at room temperature employing a column packed with 0.19% picric acid on Graphpac and employing a FID detector.

## 3. Experimental results

Four tests were performed at 313 K. The experimental settings of the four runs are detailed in Table 1. The relevant variable changed for the three tests that include isoprene in the initial mixture; runs 2, 3 and 4 in Table 1; was the hydrogen partial pressure, which was set at about 110, 300 and 59 kPa.

The results of the tests without IP at  $p_{H_2} = 97$  kPa, run 1 in Table 1, and that with IP at  $p_{H_2} = 59$  kPa, run 4, are plotted in Fig. 3a and b. Symbols correspond to measured mole fractions,  $x_{j,bulk}$ , and the continuous curves result from the model described later on.

Fig. 3a shows that BD reacts at nearly zeroth order regime up to about reaction time  $t_{BD}$ . This is the reaction time at which the diffusion capabilities of H<sub>2</sub> and BD inside the active layer become equal, i.e.

$$D_{H_2}x_{H_2,sat} = D_{HC}x_{BD,bulk} \quad (1)$$

where  $D_{H_2}$  and  $D_{HC}$  are the effective diffusion coefficients of H<sub>2</sub> and hydrocarbons, respectively. We adopted a single value  $D_{HC}$  for the hydrocarbons because negligible differences were found among them.

Calling  $x^*$  the value of  $x_{BD,bulk}$  that satisfies Eq. (1) and expressing  $x_{H_2,sat} = Hp_{H_2}$ , we can write  $x^* = (D_{H_2}/D_{HC})Hp_{H_2}$ , where  $H$  is the Henry's constant for H<sub>2</sub>. For the hydrocarbon composition in the experimental runs  $D_{H_2}/D_{HC} = 3.82$  and  $H = 9.7 \times 10^{-6} \text{ kPa}^{-1}$  were evaluated as described in [7]. Then,  $x^*$  is related to  $p_{H_2}$  by

$$x^* = 3.7 \times 10^{-5} p_{H_2} \quad (2)$$

At  $t < t_{BD}$ ,  $x_{1BE,bulk}$  increases because of the hydrogenation of BD, Reaction 1 in Fig. 1, whereas the hydrogenation and

Table 1  
Experimental settings (temperature = 313 K)

Run	$10^2 x_{BD}^0$	$10^2 x_{1BE}^0$	$10^2 x_{IP}^0$	$p_{H_2}$ (kPa)	$P_T$ (kPa)
1	1.55	5.64	–	97	240
2	1.32	6.95	0.61	110	250
3	0.89	9.29	1.30	300	390
4	0.85	8.75	1.19	59	210

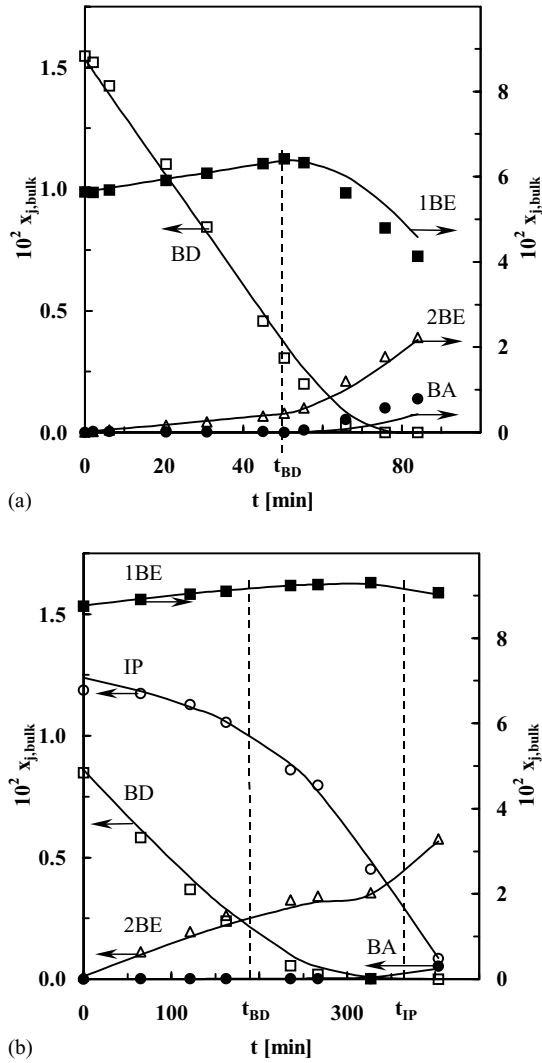


Fig. 3. Results from experimental tests: (a)  $x_{BD,bulk}^0 = 1.55 \times 10^{-2}$ ,  $x_{1BE,bulk}^0 = 5.64 \times 10^{-2}$ ,  $x_{IP,bulk}^0 = 0$ ,  $p_{H_2} = 97$  kPa. (b)  $x_{BD,bulk}^0 = 0.85 \times 10^{-2}$ ,  $x_{1BE,bulk}^0 = 8.75 \times 10^{-2}$ ,  $x_{IP,bulk}^0 = 1.19 \times 10^{-2}$ ,  $p_{H_2} = 59$  kPa.

hydroisomerization of 1BE, Reactions 3 and 4, are evidently impaired. At  $t > t_{BD}$  there will be  $H_2$  inside the active layer in excess to the amount needed for hydrogenating BD. Then, 1BE will start to react irrespective of the intrinsic inhibitory effect of BD. In effect, we can see from Fig. 3a that consumption of 1BE becomes evident soon after  $t_{BD}$ . Therefore, the production rate of 2BE and BA increases because of Reactions 3 and 4, respectively.

The effect of IP can be appreciated in Fig. 3b. It is evident that at  $t < t_{BD}$  the IP hydrogenation is impaired by the presence of BD, although some extent of reaction is observed, showing that the adsorption strength of BD is higher than that of IP. At  $t > t_{BD}$ , an  $H_2$  excess inside the catalyst is available and the consumption of IP is neatly accelerated. It can also be appreciated that 1BE is not consumed to any significant extent until  $t$  exceeds the value  $t_{IP}$ . This value is defined similarly to  $t_{BD}$ , i.e. the reaction time for which  $x_{IP,bulk} = x^*$ , Eq. (2). From these results, it is evident that IP adsorption

strength is higher than that of 1BE. Therefore, we conclude that IP satisfies the expected behavior. No further qualitative insight is provided by the remaining two tests, which were also employed to estimate the kinetics parameters.

#### 4. Kinetic model and data analysis

The experimental data were fitted to a model considering the diffusion and reaction problem inside the active layer. The intrinsic reaction rate expressions have been taken from a general mechanistic model proposed in [8,10]. This model has been proven successful to describe the liquid-phase hydrogenation of 1,3-butadiene in the presence of *n*-butenes [8] and the vapor-phase hydrogenation and hydroisomerization of *n*-butenes [10] on commercial Pd catalysts. The reliability of the kinetic model was validated over a wide range of experimental conditions including those close to the industrial operating conditions. A kinetic expression for the liquid-phase hydrogenation of isoprene in presence of 1,3-butadiene and *n*-butenes over Pd catalysts was not found in literature. Hence, the adoption of a rate equation for isoprene hydrogenation analogous to that of 1,3-butadiene and *n*-butenes was considered a reasonable approach. As shown later, the adopted kinetic expression for the hydrogenation of isoprene was satisfactorily fitted to the experimental data. Considering some simplifications as in [8], we obtained the kinetic expressions presented in Table 2.

Recalling that the experimental catalytic bed operates under essentially uniform bulk liquid composition, the conservation equations employed for the unsaturated species during each run were

$$\frac{dx_{j,bulk}}{d\tau} = -\bar{r}_j \quad (3a)$$

with initial condition

$$x_{j,bulk}(\tau = 0) = x_j^0 \quad (3b)$$

where  $\tau = M_{cat}t/N_T$ ,  $N_T$  is the total number of moles,  $M_{cat}$  the catalyst mass, and  $\bar{r}_j$  the observed consumption rate of species  $j$  per unit mass of catalyst sample.  $\bar{r}_j$  is evaluated from

$$\bar{r}_j = \frac{\left[ \int_0^1 r_j dz \right] L S_{cat} \rho_{cat}}{M_{cat}} \quad (4)$$

Table 2

Kinetic expressions<sup>a</sup>

$$r_i = \frac{k_i (K_{BD}^a / K_{IP}^a) x_{BD} x_{H_2}}{DEN}, \quad i = 1, 2$$

$$r_3 = \frac{k_3 (K_{1BE}^a / K_{IP}^a) x_{1BE} \sqrt{x_{H_2}}}{DEN}$$

$$r_4 = \frac{k_4 (K_{1BE}^a / K_{IP}^a) x_{1BE} x_{H_2}}{DEN}$$

$$r_5 = \frac{k_5 x_{IP} x_{H_2}}{DEN}$$

<sup>a</sup> DEN =  $(K_{BD}^a / K_{IP}^a) x_{BD} + x_{IP} + (K_{1BE}^a / K_{IP}^a) x_{1BE}$ .

where  $z$  is the dimensionless coordinate inside the active layer,  $z = z'/L$ ,  $r_j$  the net consumption rate of  $j$  per unit mass of active layer evaluated at  $z$ ,  $L$  the thickness of the active layer,  $S_{\text{cat}}$  the external area of the catalyst sample and  $\rho_{\text{cat}}$  the catalyst density. The consumption rates  $r_j$  are stoichiometrically related to the reaction rates  $r_i$  in Fig. 1; e.g. for 1BE  $r_{\text{BE}} = r_1 - r_3 - r_4$ .

The field of  $r_j$  needed in Eq. (4) is obtained by solving the following conservation balances inside the active layer

$$D_j C_T \frac{d^2 x_j}{dz^2} = L^2 \rho_{\text{cat}} r_j \quad (5a)$$

with boundary conditions

$$D_j \frac{dx_j}{dz} = L \kappa_j (x_j - x_{j,\text{bulk}}) \quad \text{at } z = 0 \text{ (catalyst surface)} \quad (5b)$$

$$\frac{dx_j}{dz} = 0 \quad \text{at } z = 1 \text{ (end of the active layer)} \quad (5c)$$

where  $x_j$  is the mole fraction of  $j$  at  $z$ ,  $C_T$  the total molar concentration of the liquid,  $D_j$  the effective diffusivities of  $j$  inside the active layer and  $\kappa_j$  the mass transport coefficient between the catalyst external surface and the liquid bulk.

In writing Eqs. (5a) and (5b), we considered that  $L$  is small enough to ignore the curvature effect and that liquid–solid and intraparticle mass transport can be described by a Fick type expression.

Details about evaluation of  $D_j$ ,  $\kappa_j$ , vapor–liquid equilibrium and the numerical procedure employed to solve Eqs. (5) are given in [7]. The regression analysis and the integration of Eqs. (3) have been performed by using the codes GREG and DDASAC, respectively, included in GREGPAK [11] (the codes GREG and DDASAC have been superseded by the codes GREGPLUS and DDAPLUS included in Athena Visual Workbench described at <http://www.athenavisual.com>).

Table 3 shows the intrinsic values of rate coefficients  $k_i$  and adsorption constant ratios obtained from experimental data fitting. The experiments did not allow to estimate  $K_{\text{1BE}}^a/K_{\text{IP}}^a$  with a satisfactory precision. However, the very low modal value of this ratio indicates that Pd selectively adsorbs isoprene instead of 1-butene, inhibiting the adsorption and reaction of the later.

Table 3  
Values of kinetic parameters,  $k_i$  (mol/kg<sub>active layer</sub> s)

$k_1 = (3.73 \pm 0.36) \times 10^1$
$k_2 = (2.09 \pm 0.18) \times 10^1$
$k_3 = 2.983 \pm 0.65$
$k_4 = (6.49 \pm 1.48) \times 10^1$
$k_5 = (1.08 \pm 0.16) \times 10^2$
$\frac{K_{\text{BD}}^a}{K_{\text{IP}}^a} = (1.53 \pm 0.46) \times 10^1$
$\frac{K_{\text{1BE}}^a}{K_{\text{IP}}^a} = (1.19 \pm 0.75) \times 10^{-3}$

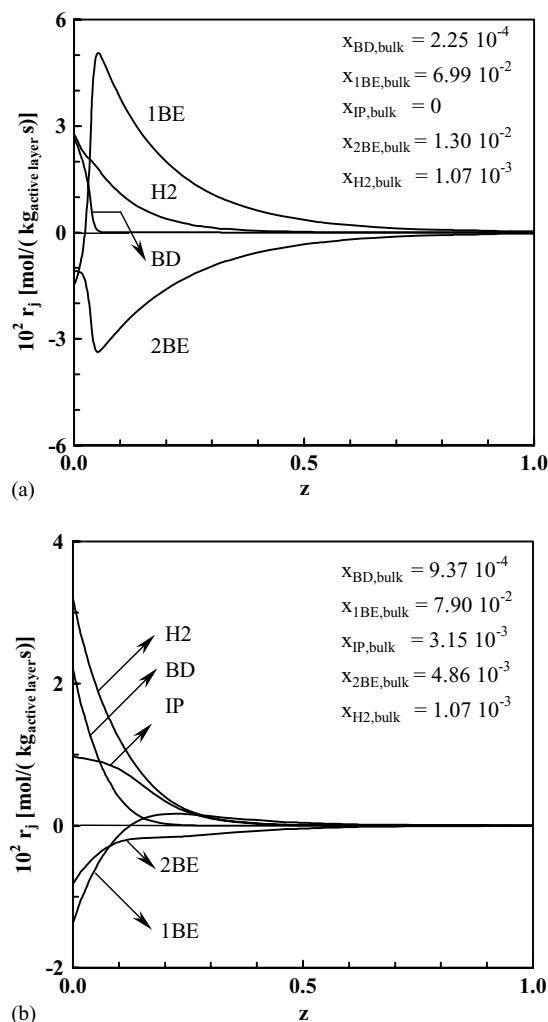


Fig. 4. Profiles inside the catalytic layer of net consumption rates: (a) without IP,  $x_{\text{BD,bulk}} < x^*$  and (b) with IP, ( $x_{\text{BD,bulk}} + x_{\text{IP,bulk}} < x^*$ ).

Fig. 3a and b reveals that the fitting model captures all the essential features shown by the experimental data. A similar fit is achieved for the other two tests. The average of relative differences in  $x_{j,\text{bulk}}$  between model and data is 13.2%.

Fig. 4a and b show calculated consumption rate profiles inside the active layer for two bulk compositions. In 4a,  $x_{\text{BD,bulk}} < x^*$  holds and  $x_{\text{IP,bulk}} = 0$ . Due to the excess of H<sub>2</sub> a large consumption of 1BE is predicted (the observed net consumption rate,  $\bar{r}_j$ , is given by the area under the  $r_j$  curve).

In 4b the relevant composition difference with respect to 4a is that IP is present in the reaction mixture and ( $x_{\text{BD,bulk}} + x_{\text{IP,bulk}} = x^*$ ). This condition states that the amount of H<sub>2</sub> is just enough to deplete both diolefins. As shown in 4b, 1BE only reacts slowly inside the active layer between  $0.1 < z < 0.5$  and IP consumes almost all the excess H<sub>2</sub> after BD depletion. The shield effect of IP as regards the consumption of 1BE is clearly shown. 4a and b indicate the existence of

the asymptotic regime inside the catalyst, i.e. all reactions cease before the end of the active layer.

### 5. Effect of isoprene on process selectivity

A simple model of an industrial trickle-bed reactor for 1BE purification will be used to analyze the effect of adding IP in the feed. This model includes the kinetic expressions given in Table 2.

In a previous work, a complete model to represent the behavior of an actual industrial unit was developed [5]. We concluded that the plug-flow hypothesis is suitable for both fluid phases and that isothermal operation can be safely considered. For the purpose of this work, we will assume that catalyst pellets are completely wetted and that vapor and liquid are in thermodynamic equilibrium. Under usual temperature and pressure conditions, 313 K and about  $10^3$  kPa, almost the total amount of hydrocarbons remains in the liquid-phase, whereas  $H_2$  is slightly soluble. Then, the liquid-phase molar flow rate is nearly the same as the total molar flow rate of the hydrocarbons [12].

With these simplifying assumptions, the concentration profile of hydrocarbons along the reactor are evaluated as for a single phase with piston flow. Then Eq. (3a) applies to the liquid-phase with  $\tau = M_{cat}/F_T$ , where  $F_T$  is the total molar flow rate of hydrocarbons. Inlet conditions are those expressed in Eq. (3b).

The growth of heavy residues during operation impairs catalyst activity [9]. Hence, an excess of catalyst is usually loaded in order to extend the time of the catalyst bed under continuous service.

The  $H_2$  input should be carefully adjusted to reach the final BD tolerance with a negligible amount of residual BD. If so, Bressa et al. [5] proved that the vapor-phase extinguishes at a certain depth of the bed.

When the vapor-phase still exists,  $x_{H_2,bulk} = x_{H_2,sat}$  results from the assumption of vapor-liquid equilibrium. After vapor-phase extinguishes  $x_{H_2,bulk}$  must be obtained from stoichiometric relationships. Then, for the whole bed we can write  $x_{H_2,bulk} = \min\{x_{H_2,sat}, z_{H_2}^0(1 - \chi_{H_2})\}$ , where  $x_{H_2,sat} = 9.7 \times 10^{-6} p_{H_2}$ ,  $z_{H_2}^0$  is the overall mole fraction of  $H_2$  at the inlet and  $\chi_{H_2}$  the  $H_2$  conversion. The value of  $z_{H_2}^0$  is the minimum input to reach BD tolerance,  $x_{BD,tol}$ , with minimum 1BE losses.

The effect of  $x_{IP}^0$  on 1BE conversion,  $\chi_{1BE}$ , at different values of  $p_{H_2}$  is shown in Fig. 5a and b. Calculations were made with  $x_{BD}^0 = 1\%$ ,  $x_{1BE}^0 = 20\%$  and  $x_{BD,tol} = 10$  ppm at the exit.

Results shown in Fig. 5a were obtained for the kinetic parameters given in Table 3. It is evident that  $p_{H_2}$  level severely affects the process selectivity. Variations of  $p_{H_2}$  might be accomplished by modifying the total operating pressure. However, total pressure cannot be freely manipulated because it

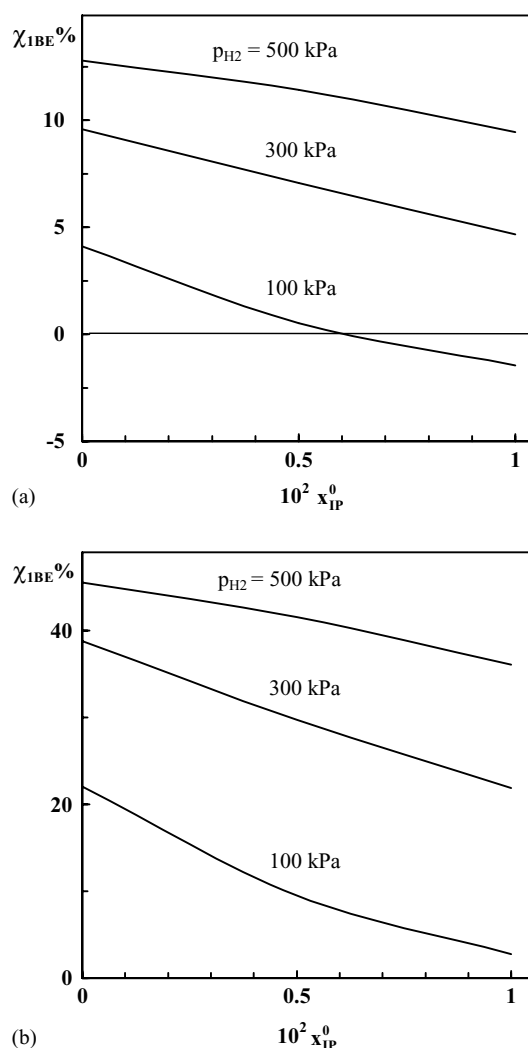


Fig. 5. 1BE losses for kinetic values in Table 3 (a) and after selective deactivation (b).

also affects upstream and downstream operations. 5a clearly shows that adding IP significantly reduces 1BE losses. Feeding 1% of IP causes an effect similar to a decrease of  $p_{H_2}$  in 200 kPa.

In 5b, the kinetic coefficients of all hydrogenation reactions were reduced to a quarter of their values in Table 3, whereas the isomerization coefficient  $k_3$  was left unchanged. These conditions intend to simulate the effect of catalyst aging that selectively reduces the hydrogenation rates as observed in industrial records and laboratory results. Losses of 1BE increase by about 3–5 times respect to those obtained with the fresh catalyst in 5a. To explain these results, we should mention that the asymptotic regime holds inside the active layer in both cases, 5a and b. In the latter case, 1BE consumes the excess of  $H_2$  inside the active layer more slowly. Hence, the hydroisomerization of 1BE, which maintains the same reaction rate, takes place along a larger fraction of active layer increasing 1BE losses.

However, the relative effect of  $p_{H_2}$  and  $x_{IP}^0$  in 5b remains nearly the same as in 5a, since the drop of 1BE losses caused by adding 1% of IP is similar to that obtained by a decrease of  $p_{H_2}$  in 200 kPa. To achieve acceptable levels of 1BE losses at conditions in 5b (say less than 5%), values of  $p_{H_2}$  as low as 100 kPa and  $x_{IP}^0$  as high as 1% should be employed.

## 6. Conclusions

The experimental procedure, the proposed kinetic model and the analytical tools employed in this study have been found suitable to quantitatively characterize the kinetic behavior of eggshell type commercial Pd catalysts in the simultaneous hydrogenation of isoprene, 1,3-butadiene and 1-butene, including isomerization of the latter.

It was verified that isoprene adsorption strength is lower than that of 1,3-butadiene, but higher than that of 1-butene. Therefore, isoprene is a good candidate as additive to increase the selectivity in 1-butene purification processes.

From the developed kinetic model and employing a simplified description of an industrial unit the influence on process selectivity of  $p_{H_2}$ , isoprene amount fed to the reactor, and catalyst activity was analyzed. It is concluded that  $p_{H_2}$  level is crucial to process selectivity. Calculations made without isoprene showed that the 1-butene loss at  $p_{H_2} = 500$  kPa is three times the value at  $p_{H_2} = 100$  kPa for a fresh catalyst and it is twice the value at  $p_{H_2} = 100$  kPa for an aged catalyst. Adding in the process stream low amounts of isoprene can significantly reduce those 1-butene losses. For example, when 1% of isoprene is added in the feed, 1-butene losses at  $p_{H_2} = 300$  kPa decrease from about 10 to 5% for a fresh catalyst and from about 40 to 20% in the case of an aged catalyst. The relative effect of  $p_{H_2}$  and the amount of isoprene in the feed for the fresh catalyst remains nearly the same as in the case of the aged catalyst. In both cases, feeding 1% of isoprene causes an effect similar to a decrease of  $p_{H_2}$  in 200 kPa.

The previous summary remarks that the amount of isoprene added in the feed must be changed according to catalytic activity decay and the operating pressure.

## Acknowledgements

The financial assistance of ANPCyT, CONICET and UNLP is acknowledged. JAA, OMM and GFB are members of CONICET. SPB is member of CIC PBA.

## References

- [1] M.L. Derrien, Selective hydrogenation applied to the refining of petrochemical raw materials produced by steam cracking, *Stud. Surf. Sci. Catal.* 27 (1986) 613–666.
- [2] S. Hub, L. Hilaire, R. Touroude, Hydrogenation of but-1-yne and but-1-ene on palladium catalyst. Particle size effect, *Appl. Catal.* 36 (1988) 307–322.
- [3] J.-P. Boitiaux, J. Cosyns, M. Derrien, G. Léger, Proper design of butadiene hydrogenation process for maximum 1-butene yield by using comprehensive kinetic modeling, in: *Proceedings of the AIChE Spring National Meeting*, Paper No. 1453, Houston, USA, 1985.
- [4] C. Vergel, J.P. Euzen, P. Trambouze, J.P. Wauquier, Two-phase flow catalytic reactor. Influence of hydrodynamics on selectivity, *Chem. Eng. Sci.* 50 (1995) 3303–3312.
- [5] S.P. Bressa, N.O. Ardiaca, O.M. Martínez, G.F. Barreto, Analysis of operating variables in the catalytic purification of butene-1 in a trickle bed, *Chin. J. Chem. Eng.* 6 (2) (1998) 103–115.
- [6] S.P. Bressa, J.A. Alves, O.M. Martínez, G.F. Barreto, Analysis of operating variables on the performance of a reactor for total hydrogenation of olefins in a C3–C4 stream, *Chem. Eng. J.* 92 (1–3) (2003) 41–54.
- [7] N.O. Ardiaca, S.P. Bressa, J.A. Alves, O.M. Martínez, G.F. Barreto, Experimental procedure for kinetic studies on egg-shell catalysts. The case of liquid-phase hydrogenation of 1,3-butadiene and *n*-butenes on commercial Pd catalysts, *Catal. Today* 64 (3–4) (2001) 205–215.
- [8] N.O. Ardiaca, S.P. Bressa, J.A. Alves, O.M. Martínez, G.F. Barreto, Kinetic study of the liquid-phase hydrogenation of 1,3-butadiene and *n*-butenes on a commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, *Stud. Surf. Sci. Catal.* 133 (2001) 527–534.
- [9] J.-P. Boitiaux, J. Cosyns, M. Derrien, G. Léger, Newest hydrogenation catalysts, *Hydrocarb. Process.* 64 (4) (1985) 51–59.
- [10] S.P. Bressa, O.M. Martínez, G.F. Barreto, Kinetic study of the hydrogenation and hydroisomerization of the *n*-butenes on a commercial palladium/alumina catalyst, *Ind. Eng. Chem. Res.* 42 (2003) 2081–2092.
- [11] W.E. Stewart, M. Caracotsios, J.P. Sørensen, Parameter estimation from multiresponse data, *AIChE J.* 38 (1992) 641–650.
- [12] S.P. Bressa, N.O. Ardiaca, O.M. Martínez, G.F. Barreto, Approximate expressions to evaluate the performance in butene-1 purification units, *Chin. J. Chem. Eng.* 6 (3) (1998) 271–276.