

## Approximate Expressions to Evaluate the Performance in Butene-1 Purification Units

Sergio P. Bressa, Nestor O. Ardiaca, Osvaldo M. Martinez and Guillermo F. Barreto\*

-Depto. de Ing. Qca., Fac. de Ing., U. N. L. P., 1 esq. 47 (1900) La Plata, Argentina

-Centro de Investigación y Desarrollo en Procesos Catalíticos (CINDECA), (CONICET-UNLP),  
Calle 47N°257, CC59 (1900) La Plata, Argentina

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

### 1 INTRODUCTION

Selective hydrogenation of small amounts of butynes and butadiene is industrially employed for obtaining high purity butene-1 used as co-monomer in the production of linear low-density polyethylene. For this purpose, the content of vinylacetylene, butyne-1 and 1,3-butadiene present in the process stream should be reduced to a few tens of ppm.

A mathematical model for simulating selective hydrogenation of butyne-1 and 1,3-butadiene on Pd based catalysts in industrial trickle bed reactors was recently presented in this journal<sup>[1]</sup>. This model accounts for the reaction net displayed in Table 1. Mass transfer limitations at vapor-liquid interface and at the catalyst external surface were included in the formulation.

Design features were evaluated with the aid of this model in terms of the minimum (critical) weight of catalyst to achieve the operation target with minimum losses of 1-butene. Provided that the actual catalyst loading is larger than this critical amount, the operation can be effectively conducted with minimum losses of 1-butene if H<sub>2</sub> is depleted in the process stream just when the purity specification is reached, thus avoiding further hydrogenation and hydroisomerization of 1-butene (Table 1) in the remaining of the bed. The input flow rate of H<sub>2</sub> to meet this condition,  $F_{H_2,asymp}^0$ , is conveniently expressed as

$$R_{asymp}^0 = F_{H_2,asymp}^0 / (F_{BD}^0 + F_{BY}^0) \quad (1)$$

The model was then employed in Ref. [1] to analyse the effect of relevant variables such as feed composition, catalyst selectivity and the level of butene-1 purity on  $R_{asymp}^0$  and the loss of 1-butene, expressed as

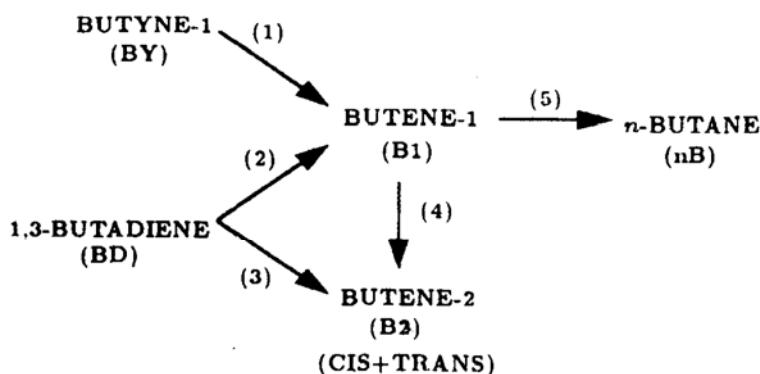
$$\Delta_{B1} = (F_{B1}^0 - F_{B1}^{exit}) / F_{B1}^0 \quad (2)$$

$R_{asymp}^0$  and  $\Delta_{B1}$  are directly related to the selectivity of the process. Ideally,  $R_{asymp}^0$  should be close to one and  $\Delta_{B1}$  should remain close to zero.

Received 1998-02-18, accepted 1998-06-28.

\* To whom correspondence should be addressed. E-mail address: onmartin @ volta. ing. unlp. edu. ar.

Table 1 Reaction network and kinetic expressions



$$r_1 = k_{BY,B1} x_{BY} x_{H_2} / DEN$$

$$r_2 = k_{BD,B1} x_{BD} x_{H_2} / DEN$$

$$r_3 = k_{BD,B2} x_{BD} x_{H_2} / DEN$$

$$r_4 = k_{B1,B2} x_{B1} x_{H_2} / DEN$$

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

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

The purpose of this communication is to present approximate expressions to relate the composition of the process stream in terms of catalyst selectivity ratios. These approximations are based on a homogeneous approach ignoring external mass transfer limitations. It will be shown that they can be conveniently employed to estimate the relevant magnitudes  $R_{asymp}^0$  and  $\Delta_{B1}$  for properly designed units. In a more wider context, these expressions will be useful as a complement to the rigorous model described in Ref. [1], as they provide an explicit insight into the relations between feed composition, catalyst properties and purity specification, and limiting values for  $R_{asymp}^0$  and  $\Delta_{B1}$ .

## 2 APPROXIMATE EXPRESSIONS

Approximate relations between the molar flows of the individual species will be derived here. It is assumed that:

- (1) The liquid flows in plug flow along the catalytic bed;
- (2) The amount of  $C_4$  species in the vapor phase are negligible or they are present in the same ratio as in the liquid phase;
- (3) Isothermal operation or similar values of activation energy for the different reactions are assumed;
- (4) Mass transfer resistances to the catalyst surface can be neglected.

From assumptions (1) and (2), the ratio of variations in total molar flow of butyne-1 and 1,3-butadiene in a differential bed length can be written as the ratio of net reaction rates

$$dF_{BY}/dF_{BD} = r_{BY}/r_{BD} \quad (1)$$

according to the kinetic expressions in Table 1, the r.h.s. is proportional to liquid molar fractions on the catalyst surface, which recalling assumptions (1), (2) and (3) can be expressed as

$$dF_{BY}/dF_{BD} = \frac{k_{BY} F_{BY}}{k_{BD} F_{BD}} \quad (2)$$

where  $k_{BD} = k_{BD,B1} + k_{BD,B2}$ . Integrating this expression [with a constant ratio ( $k_{BY}/k_{BD}$ ), following assumption (3)] from the bed inlet up to a generic bed section

$$F_{BY} = F_{BY}^0 \delta^Y \quad (3)$$

where  $\delta = F_{BD}/F_{BD}^0$ ;  $Y = k_{BY}/k_{BD}$ .

Similarly, the differential relation between butene-1 and 1,3-butadiene is

$$dF_{B1}/dF_{BD} = \frac{k_{B1}F_{B1} - k_{BY}F_{BY} - k_{BD,B1}F_{BD}}{k_{BD}F_{BD}}$$

where  $k_{B1} = k_{B1,B2} + k_{B1,nB}$ . It can be integrated after replacing  $F_{BY}$  from Eq. (3)

$$F_{B1} = F_{B1}^0 \delta^X + \frac{F_{BY}^0 Y}{Y - X} (\delta^X - \delta^Y) - \frac{F_{BD}^0}{1 - X} \left( \frac{k_{BD,B1}}{k_{BD}} \right) (\delta - \delta^X) \quad (4)$$

where  $X = k_{B1}/k_{BD}$ . Repeating the procedure between *n*-butane and 1,3-butadiene

$$F_{nB} = F_{nB}^0 - \frac{k_{B1,nB}}{k_{BD}} \left[ F_{B1}^0 \frac{\delta^X - 1}{X} + \frac{F_{BY}^0 Y}{Y - X} \left( \frac{\delta^X - 1}{X} - \frac{\delta^Y - 1}{Y} \right) + \frac{F_{BD}^0}{1 - X} \left( \frac{k_{BD,B1}}{k_{BD}} \right) \left( \frac{\delta^X - 1}{X} - \delta + 1 \right) \right] \quad (5)$$

Eqs. (3) to (5) apply at any section in the bed, but specifically they are useful at the bed exit. In practice, butyne-1 is hydrogenated with high selectivity ( $Y \gg 1$  and  $Y/X \gg 1$ ) and 1,3-butadiene starts to react once butyne-1 has been almost completely depleted<sup>[1]</sup>. In normal operations,  $F_{BY}^{\text{exit}} \cong 0$  and  $\delta_{\text{exit}} = F_{BD}^{\text{exit}}/F_{BD}^0 \ll 1$ . Eqs. (4) and (5) can then be written at the exit

$$F_{B1}^{\text{exit}} = (F_{B1}^0 + F_{BY}^0) \delta_{\text{exit}}^X - \frac{F_{BD}^0}{1 - X} \left( \frac{k_{BD,B1}}{k_{BD}} \right) (\delta_{\text{exit}} - \delta_{\text{exit}}^X) \quad (6)$$

$$F_{nB}^{\text{exit}} = F_{nB}^0 - \frac{k_{B1,nB}}{k_{BD}} \left[ (F_{B1}^0 + F_{BY}^0) \frac{\delta_{\text{exit}}^X - 1}{X} + \frac{F_{BD}^0}{1 - X} \left( \frac{k_{BD,B1}}{k_{BD}} \right) \left( \frac{\delta_{\text{exit}}^X - 1}{X} - \delta_{\text{exit}} + 1 \right) \right] \quad (7)$$

The molar flows of butene-2 and  $H_2$  can be written directly by balancing

$$F_{B2}^{\text{exit}} = F_{B2}^0 + F_{B1}^0 + F_{BD}^0 + F_{BY}^0 + F_{nB}^0 - F_{B1}^{\text{exit}} - F_{BD}^{\text{exit}} - F_{nB}^{\text{exit}} \quad (8)$$

$$F_{H2}^{\text{exit}} = F_{H2}^0 - (F_{BD}^0 - F_{BD}^{\text{exit}}) - F_{BY}^0 - (F_{nB}^{\text{exit}} - F_{nB}^0) \quad (9)$$

An expression for  $R_{\text{asympt}}^0$  [see Eq. (1)] can be found from Eq. (7) by taking  $F_{H2}^{\text{exit}} = 0$  and assuming that the tolerance has been reached for 1,3-butadiene ( $F_{BD}^{\text{exit}} = F_{BD}^{\text{tol}}$ )

$$R_{\text{asympt}}^0 = 1 - \frac{F_{BD}^{\text{tol}} + F_{nB}^{\text{exit}} - F_{nB}^0}{F_{BD}^0 + F_{BY}^0} \quad (10)$$

where  $F_{nB}^{\text{exit}}$  is obtained from Eq. (4) with  $F_{BD} = F_{BD}^{\text{exit}} = F_{BD}^{\text{tol}}$ .

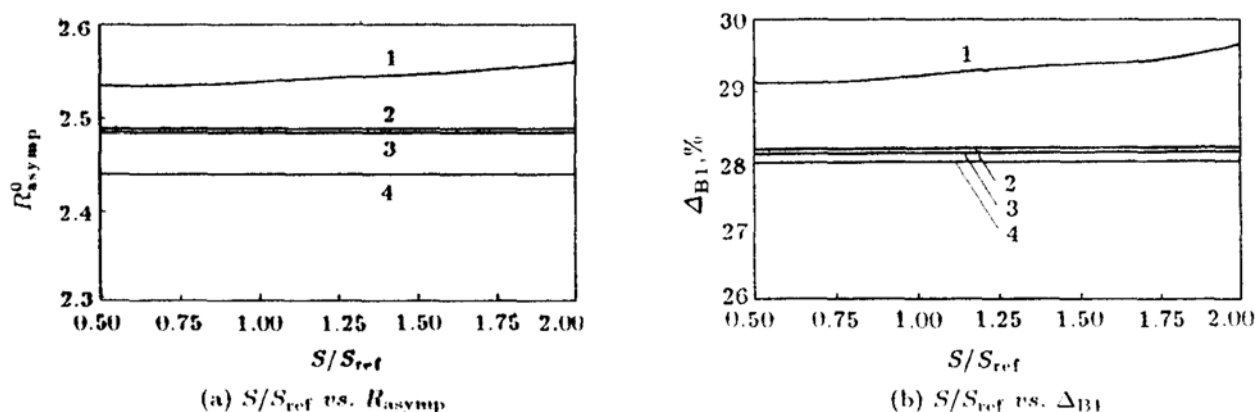
### 3 DISCUSSION AND CONCLUSION

Assumptions (1) to (3) made to develop Eqs. (3)–(8) have been discussed in Ref. [1]. They are most likely to hold under usual operating conditions and, therefore, they will not introduce any significant error.

As regards assumption (4), the results discussed in Ref. [1] reveals that mass transfer limitations to the external catalyst surface can not be neglected. It is important then to investigate the effect of variables likely to modify the ratios of reaction rates to mass transfer rates on the accuracy of the approximate expressions.

The effect of bed section area ( $S$ ) for a fixed rate of the process stream will be analysed next (equivalent to analyse variations in total feed rate for a fixed  $S$ ). The value of  $S$  changes the liquid and gas linear velocities and, hence, mass transfer coefficients for both, gas-liquid transport and liquid-solid transport. It should be born in mind that the gas-liquid resistance only affect in practice the level of  $H_2$  dissolved in the liquid<sup>[1]</sup> and, hence, the magnitude of the different reaction rates, but not the selectivity of the process (see the reaction rate expressions in Table 1). On the contrary, mass transfer resistance to the catalyst surface produces an adverse effect on selectivity, as the concentration of the diluted impurities butyne-1 and 1, 3-butadiene on the catalyst surface will decrease.

The effect of  $S$  on  $R_{asymp}^0$  and  $\Delta_{B1}$  is shown in Figs. 1 (a) and (b) for operating conditions specified in Table 3 of Ref. [1], employing a commercial catalyst with kinetic parameters given in Table 2 in Ref. [1], and for a 1,3-butadiene tolerance of 100 ppm. Curves 1 correspond to the numerical results obtained with the mathematical model developed in Ref. [1]. Curves 2 were obtained similarly, but neglecting liquid/solid resistance, and for curves 3 both resistances, liquid/solid and gas/liquid, were neglected.



**Figure 1** Effect of bed section  $S$  on  $R_{asymp}^0$  and  $\Delta_{B1}$  for 100 ppm of 1,3 butadiene at the exit

( $S_{ref} = 0.28 m^2$  is the value employed in Ref. [1])

- 1—results from the model in Ref. [1]; 2—same as curve 1, but neglecting liquid-solid mass transfer limitations; 3—same as curve 1, but neglecting liquid-solid and gas-liquid mass transfer limitations; 4—results from approximated expressions (6), (7) and (10)

Comparison of curves 2 and 3 confirms that  $R_{asymp}^0$  and  $\Delta_{B1}$  do not practically depend on gas/liquid mass transfer, as explained above.

It can be appreciated by comparing curves 1 and 2 that the effect of gas/solid resistance on  $R_{asymp}^0$  and  $\Delta_{B1}$  is mild for the catalyst under consideration. Also, it is evident that the value of  $S$  has little influence. Although mass transfer coefficients varies as  $S$  is modified, the final effect on the concentration drop of impurities across the liquid-solid film is quite moderate. This is favoured by the type of kinetic expressions, which not only depend on the molar fraction of hydrocarbons, but also on  $X_{H_2}$ , and  $H_2$  also suffers a concentration drop in the liquid-solid film.

As expected from the previous discussion, the results from the approximate Eqs. (4) and (8), curves 4 in Figs. 1 (a) and (b) are very good estimates of the values given by the rigorous model. The small differences with respect to curves 2 are mostly due to the fact that in the rigorous model calculations  $F_{H_2}^{exit}$  is not taken as 0, but a small value is allowed ( $F_{H_2}^{exit} \cong F_{BD}^{tol}$ )<sup>[1]</sup>.

Other variables which affect the ratios of reaction rates to mass transfer rates are the total pressure (due to an increase in  $H_2$  partial pressure) and reaction rates constants. At  $p = 1.5$  MPa, the value of hydrogen partial pressure is twofold the value corresponding to 1 MPa (case in Figs. 1) However,  $\Delta_{B1}$  only increases slightly (up to 29.9%) above the value in Fig. 1(b) (29.3%). Increasing the values of all kinetic constants in 100% makes  $\Delta_{B1}$  increases slightly up to 30.0%. The estimate from Eq. (6), (the value in Fig. 1(b), 28%) keeps on being fairly accurate.

It can be concluded that the effect of mass transfer limitations to the catalyst surface is moderate over relatively large variation of operating conditions and kinetic parameters. This feature stems in a suitable level of catalytic activity. Actually, a catalyst showing much higher activities (*i.e.* one order of magnitude) than the ones tested in Ref. [1] should not be employed, as there will be not proper operating conditions to reduce the external mass transport limitations and, therefore, to obtain an adequate selectivity.

As a consequence, it will be also valid to ascertain that once a unit is installed with a suitable catalyst, variations in operating conditions (temperature, feedstock composition, catalyst deactivation, *etc.*) will not usually affect to a large extent the achievable selectivity. As a consequence, the approximate expression developed here will be applicable.

An important practical use of these expressions is that they can be employed to estimate  $R_{asymp}^0$  if appropriate records of operating practice have been collected in a given industrial unit. Thus, having measures of the reactor input ( $F_{B2}^0, F_{B1}^0, F_{BD}^0, F_{BY}^0, F_{uB}^0$ ) and output ( $F_{B2}^{exit}, F_{B1}^{exit}, F_{BD}^{exit}, F_{uB}^{exit}$ ), Eqs. (6)–(8) allow to evaluate the three relevant ratios of kinetic constants,  $X = (k_{B1}/k_{BD}), (k_{BD,B1}/k_{BD})$  and  $(k_{B1,uB}/k_{BD})$ . Then, Eq. (10) may be employed as a handy tool for setting  $R_{asymp}^0$  when changes in the feedstock or operating conditions are expected.

A final comment should be made about the significance of mass transfer limitations. Although with a proper catalytic activity their effect on selectivity has been shown to be almost negligible, they can not be ignored when the amount of catalyst should be evaluated. For the catalysts tested in Ref. [1], mass transfer limitations increase in the order of 20% the necessary catalyst mass.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) and the University of La Plata, Argentina.

## NOMENCLATURE

- $F_j$  molar flow of species  $j$ , kmol·s<sup>-1</sup>
- $K_j^a$  adsorption equilibrium constant for species  $j$
- $k$  kinetic constant, kmol·kg<sup>-1</sup>·s<sup>-1</sup>
- $R$  ratio between hydrogen and impurities molar flows Eq. (1)
- $r$  reaction rate per unit catalyst mass, kmol·kg<sup>-1</sup>·s<sup>-1</sup>
- $S$  bed section, m<sup>2</sup>
- $X$  ratio between kinetic constants ( $k_{B1}/k_{BD}$ )

$x$	molar fraction in liquid phase
$Y$	ratio between kinetic constants ( $k_{BY}/k_{BD}$ )
$\delta$	ratio between molar flows ( $F_{BD}/F_{BD}^0$ )
$\Delta_{B1}$	loss of butene-1 [Eq. (2)]

**Superscripts**

exit	at the reactor exit
tol	tolerance
0	feed conditions

**Subscripts**

asyp	asymptotic value
BD	1,3-butadiene
B1	butene-1
B2	butene-2 (cis and trans)
BY	butyne
exit	at the reactor exit
H <sub>2</sub>	hydrogen
nB	<i>n</i> -butane

**REFERENCES**

- 1 Bressa, S. P., Ardiaca, N. O., Martinez, O. M., Barreto, G. F., Chinese J. of Chem. Eng., **6** (2), 103 (1998)