Simulation and optimization of a fixed bed reactor operating in coking–regeneration cycles

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y = controlled variable

Greek Symbols

α = exponential constant
γ = interaction parameter
λ = uncertainty parameter
θ = delay
$\tilde{\theta}$ = nominal delay
τ = lag

Subscripts

C = controller
d = disturbance
I = integral
P = primary
S = secondary

Superscripts

AB = AB criterion
* = unfiltered value
CL = closed loop
OL = open loop

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Simulation and Optimization of a Fixed Bed Reactor Operating in Coking–Regeneration Cycles

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The optimization of the operation of a fixed bed catalytic reactor operating in deactivation–regeneration cycles for the dehydrogenation of butene into butadiene has been carried out. Unlike previous optimizations, in this work the influence of the regeneration stage has been taken into account by means of a detailed model which predicts the transient temperature profiles developed in the process. Also, maximum temperature restrictions during the regeneration stage were considered in the optimization scheme. The optimum values of the feed composition, duration of the production stage, and residual coke level at the end of a coking–regeneration cycle have been obtained. The results of the optimization show that the different regeneration parameters (such as the maximum temperature allowable, the oxygen concentration, and the extent of the regeneration), strongly influence the global process optimum.

Introduction

Catalyst deactivation by coke affects a large number of heterogeneous catalytic processes and poses important problems in industrial operation. Generally speaking, the activity of a catalyst will decrease with increasing coke deposition. Thus, in order to restore at least partially the catalytic activity, coke must be removed from deactivated catalysts after a certain time on stream, which varies for each process, and that is determined by economic considerations. There are several alternatives for coke removal, including the gasification of the coke deposits with mixtures containing steam, hydrogen, carbon dioxide, or oxygen. The last method, termed oxidative regeneration, involves the combustion of the coke deposits by mixtures of oxygen and a diluent. The implications of catalyst coking and of the subsequent regeneration on the behavior of single particles and of catalytic reactors have attracted a great deal of attention, as evidenced in recent years by reviews covering these subjects (e.g., Doraiswamy and Sharma, 1984; Butt, 1984; Hughes, 1984; Lee, 1985; Butt and Petersen, 1988; Froment and Bischoff, 1990).

Catalyst regeneration can be carried out either continuously or periodically, this being mainly determined by the active life of the catalyst. Thus, when the catalyst deactivates very rapidly (e.g., in the fluid catalytic cracking process), continuous regeneration is required, and moving bed reactors or fluidized bed reactors with continuous catalyst replacement are usually employed for the process. On the other hand, when catalysts with a sufficiently long active life are employed, periodic regeneration is an alternative to consider. The catalyst can then be unloaded and regenerated in a separate installation or regenerated in situ. This latter case is the subject of this work, which is concerned with operation cycles consisting of a production–deactivation period followed by a regeneration stage in the same reactor.

The optimization of a catalytic reactor subjected to cyclic operation requires sufficiently detailed simulation models for both the deactivation and the regeneration stages. Concerning the first stage, a review of the works published on simulation of catalytic systems undergoing deactivation by coke is well beyond the scope of this introduction. As an example, the subject has been extensively addressed by Froment in several reviews (e.g., Froment, 1976, 1981, 1984, 1991) concerning both kinetic modeling and reactor operation aspects.

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On the other hand, the main effort in the modeling of the oxidative regeneration of fixed bed reactors has been directed toward the prediction of the transient temperature profiles developed during the exothermic combustion of the coke deposits. These studies were aimed to the development of operating procedures capable of avoiding excessive temperature rises which could damage the catalyst and/or reaction equipment. The evolution of the modeling studies starts from the early works of Van Deempter (1953, 1954), Johnson et al. (1962), and Schulman (1963), followed by more sophisticated models (Olson et al., 1968; Sampath et al., 1975) and, more recently, by the works of Byrne et al. (1985, 1989), who studied the influence of operating and coke-related variables upon the regeneration process. Also, in the work of Santamaria et al. (1991), different regeneration strategies were analyzed in view of the regeneration rate achieved and of the magnitude of the high-temperature zone generated in the reactor. Finally, in two recent works (Blasco et al., 1991, 1992), the extent of sintering at different positions in a fixed bed reactor after several production–regeneration cycles was studied experimentally and related to the thermal history of different bed regions.

One of the main aspects in the optimization of the cyclic operation is the relative duration of the production–regeneration cycles. The total amount of the reaction product obtained in a given cycle increases with reaction (production) time. Also, a longer reaction time results in a larger amount of coke accumulation, which causes a reduction of the rate of production and increases the time required for regeneration. As a result, an optimum reaction time exists, which can be calculated for the particular conditions of each process. An example of such an analysis is given by Kunugita et al. (1976), for the dehydrogenation of butane over a chromia–alumina catalyst in a perfectly mixed reactor. These authors discussed several schemes for the determination of the optimum duration of the operation stage, including maximizing the production rate, minimizing the production costs, and maximizing the gross profit.

Arandes and co-workers (Arandes et al., 1984, 1985; Arandes and Bilbao, 1986) optimized the esterification of 1-butanol with acetic acid and also the dimerization of acetaldehyde in fixed bed reactors. In these works, the different stages of the system are considered with some detail, and the possibility of partial regeneration is contemplated. However, the simplification of isothermality is introduced for both the deactivation and the regeneration periods.

Dumez and Froment (1976) optimized the production of an industrial reactor for the dehydrogenation of 1-butene to 1,3-butadiene on a chromia–alumina catalyst. In this work, a rigorous transient simulation was carried out for the production–deactivation stage, which allowed for the existence of strong temperature variations along the bed during this period. The simulation of the regeneration was avoided by assuming a linear relationship between the average coke content in the bed and the duration of the decoking process. A detailed simulation of the operation–deactivation stage for this system based on Dumez and Froment kinetics was carried out by Acharya and Hughes (1990), who were able to predict with good accuracy the experimental coke deposition profiles determined by means of a neutron attenuation technique.

Due to catalyst deactivation, when the dehydrogenation of 1-butene is carried out industrially, operation times are usually limited to about 15 min (Dumez and Froment, 1976). This means that regeneration times are of com-parable duration, and often may be higher. Therefore, the regeneration stage has an obvious influence on the optimum operating conditions for the system. As shown above, a considerable effort has been devoted to developing reliable models for the operation–deactivation stage of fixed bed catalytic reactors in general, and for those dealing with the dehydrogenation of butane and butene in particular. In these works, however, the regeneration stage has been simulated with strong simplifications. Also, to our knowledge, none of the works on optimization of fixed bed reactors under cyclic operation has contemplated the fact that oxidative regeneration is a very exothermic process, which is in practice subjected to important maximum temperature restrictions.

With the above considerations, the present work is an optimization study of the dehydrogenation of 1-butene in a fixed bed reactor subjected to maximum temperature restrictions during regeneration. To this end, a relatively detailed regeneration model has been used which predicts the transient temperature profiles developed in the process. The optimum values of the duration of the production stage, feed composition (in the deactivation and regeneration stages), and activity level at the start of each cycle have been obtained with the objective of maximizing the total amount of butadiene produced per cycle.

Model Development

The production–deactivation and the regeneration stages have been simulated with different models. These are then used in the process optimization algorithm.

Simulation of the Production–Deactivation Stage. The simulation has been carried out under the general kinetic scheme proposed by Dumez and Froment (1976). The following assumptions have been made:

(i) Coke formation occurs in parallel and in series to the main reaction, according to the following scheme:

$$C_4H_8 \xrightarrow{\ r_H\ } C_4H_6 + H_2 \qquad (1)$$

$$\underset{r_{C1}}{\searrow} \qquad \underset{r_{C2}}{\swarrow}$$

$$\text{coke}$$
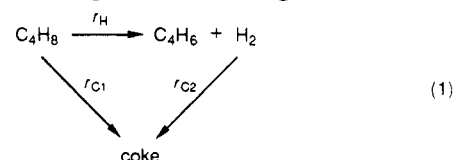
(ii) External transport resistances are neglected. The intraparticle mass-transfer restrictions are accounted for by the use of an effectiveness factor (Dumez and Froment, 1976).

(iii) Reactor operation is plug flow and adiabatic. The change in gas density due to a variation in the number of moles is accounted for.

(iv) The catalyst bed is diluted with inert particles of known thermal properties.

(v) At the start of the reaction, the reactor may be exempt from coke deposits or it may be only partly regenerated. In this case, the coke distribution along the reactor resulting from the previous regeneration must be known.

(vi) Coking is the only cause of catalyst deactivation. Therefore any activity losses due to sintering are not considered. This is reasonable since the maximum temperature allowed during the regeneration stage in most of the simulations carried out in this work was 900 K. The effect of sintering may be taken into account by incorporating the kinetics of thermal aging (Blasco et al., 1992).

With these assumptions, the following conservation equations can be written for the different species:

butene

$$\epsilon \frac{\partial C_B}{\partial t} = -\frac{\partial}{\partial z}(u C_B) - \rho_{b,cat}\left(r_{He} + \frac{r_{C1}}{\psi_{CB} M_B}\right) \qquad (2)$$

butadiene

$$\epsilon \frac{\partial C_D}{\partial t} = -\frac{\partial}{\partial z}(uC_D) + \rho_{b,cat}\left(r_{He} - \frac{r_{C2}}{\psi_{CD}M_D}\right) \quad (3)$$

hydrogen

$$\epsilon \frac{\partial C_H}{\partial t} = -\frac{\partial}{\partial z}(uC_H) + \rho_{b,cat}r_{He} \quad (4)$$

coke

$$\frac{\partial C_C}{\partial t} = r_{C1} + r_{C2} \quad (5)$$

where

$$r_{He} = \eta r_H \quad (6)$$

and r_H, r_{C1}, and r_{C2} are the rates of the main reaction and of coke formation from butene and butadiene. The values for these reaction rates were taken from the work of Dumez and Froment (1976).

The energy balance can be written as

$$\rho_{b,T}C_{p,s} \frac{\partial T}{\partial t} = -\frac{\partial}{\partial z}(u\rho_g C_{p,g}T) + \rho_{b,cat}(-\Delta H_R)r_{He} \quad (7)$$

The initial and boundary conditions for the above equations were defined as follows:

at $t = 0$: $C_B(0,z) = C_{B0}$ for $z = 0$

$C_B(0,z) = 0$ for $z \neq 0$

$C_D(0,z) = 0$

$C_H(0,z) = C_{H0}$ for $z = 0$

$C_H(0,z) = 0$ for $z \neq 0$

$C_C(0,z) = C_{Ci}(z)$

$T(0,z) = T_0$ (constant)

at $z = 0$, for any time: $C_B(t,0) = C_{B0}$

$C_D(t,0) = 0$

$C_H(t,0) = C_{H0}$

$T(t,0) = T_0 \quad (8)$

The values of the parameters and operating conditions employed in the simulation are given in Table I. The model was discretized using a second-order backward finite difference scheme, and the resulting systems of ordinary differential equations was integrated using a Gear routine. Computation test runs using discretization by orthogonal collocation gave very similar results.

Simulation of the Regeneration Stage. A sharp interface model for the catalyst particle has been used to simulate the regeneration. This models takes into account the influence of the chemical composition (hydrogen content) of the coke upon the rate of heat generation (Santamaria et al., 1991). The following supplementary assumptions have been made:

(i) The internal temperature gradients in the catalyst particle are neglected, as well as those at the gas–solid boundary. The coke combustion kinetics were taken from the work by Hughes and Shettigar (1971).

(ii) The coke distribution profile along the bed corresponds to that obtained from the production–deactivation model after a given reaction time. This is generally nonuniform.

(iii) Reactor operation is plug flow and adiabatic.

Table I. Production Stage. Reactor Characteristics and Operating Conditions

length (L)	0.8 m
cross-sectional area	1.0 m²
diam of catalyst particles	0.0046 m
diam of inert particles	0.0046 m
catalyst bed density	400 kg of catalyst/m³ of reactor volume
inert bed density	900 kg of inert/m³ of reactor volume
total pressure	25.325 kPa
total molar feed rate	4.1667 mol/(m²·s)
feed composition	pure butene or butene/hydrogen mixtures
feed temp (T_0)	873 K
initial bed temp	873 K

Table II. Simulation Parameters Used in the Regeneration Stage

effective diffusivity (D_e)	1×10^{-6} m²/s
feed composition	N_2/O_2 mixtures
total molar feed rate	4.1667 mol/(m²·s)
total pressure	101.3 kPa
inlet gas temp (T_0)	773 K
initial bed temperature (T_i)	773 K
coke composition	$CH_{0.5}$

With the above assumptions, the following equations can be written:

oxygen balance

$$\epsilon \frac{\partial C_A}{\partial t} = -r_v - u \frac{\partial C_A}{\partial z} \quad (9)$$

where

$$r_v = \frac{1-\epsilon}{V_p}\left(\frac{\rho_{b,cat}}{\rho_{b,T}}\right)\left(-\frac{dN_A}{dt}\right) \quad (10a)$$

$$-\frac{dN_A}{dt} = 4\pi r_c^2 k C_{A,c} \quad (10b)$$

$$C_{A,c} = \frac{C_A}{1 + \left(\dfrac{k}{k_m}\right)\left(\dfrac{r_c}{r_p}\right)^2 + \left(\dfrac{kr_c}{D_e}\right)\left(1 - \dfrac{r_c}{r_p}\right)} \quad (10c)$$

variation of the unreacted core radius

$$\frac{dr_c}{dt} = -\frac{M_C k(1-\epsilon)}{\rho_{b,T}C_{Ci}}C_{A,c} \quad (11)$$

coke consumption

$$\frac{dX_C}{dt} = \frac{M_C(1-\epsilon)}{\rho_{b,T}C_{Ci}V_p}\left(-\frac{dN_A}{dt}\right) \quad (12)$$

heat balance

$$\rho_{b,T}C_{p,s} \frac{\partial T}{\partial t} = -u\rho_g C_{p,g} \frac{\partial T}{\partial z} + (-\Delta H_R)r_v \quad (13)$$

where

$$\rho_{b,T} = \rho_{b,cat} + \rho_{b,I} \quad (14)$$

The initial and boundary conditions are

at $t = 0$: $C_A(0,z) = C_{A0}$ for $z = 0$

$C_A(0,z) = 0$ for $z \neq 0$

$C_C(0,z) = C_{Ci}(z)$

$T(0,z) = T_0$

at $z = 0$, for any time: $C_A(t,0) = C_{A0}$

$T(t,0) = T_0 \quad (15)$

The values of the parameters used in the simulation are given in Table II. Other values are as in Table I. The

method used for the numerical solution was the same as in the previous case.

The results of the model were checked against those of a more sophisticated simulation (Santamaria et al., 1991), in which the conservation equations were solved at the particle level and both internal and external heat- and mass-transfer resistances were taken into account. For a similar set of conditions, a satisfactory agreement was found between the results of both models concerning the transient temperatures and coke profiles during regeneration.

Process Optimization. The optimization problem studied in this work consists in obtaining the maximum production of butadiene per unit mass of catalyst in a given cycle, while at the same time observing a maximum temperature restriction. Different operating parameters such as the duration of the production–deactivation stage (t_D), the mole fraction of oxygen in the reactor feed during regeneration (Y_{A0}), or the hydrogen content of the feed during the production stage (Y_{H0}), have been used as optimization variables. The values of some operation variables such as Y_{H0} and Y_{A0} can, in practice, be modified during the operation and regeneration stages respectively. In this work, however, they have been taken as constants for a given run.

The objective function to be maximized is defined as

$$F_{obj}(\mathbf{X}) = \frac{\int_0^{t_D} F_D(t)\ dt}{W_{cat}(t_D + t_p + t_e + t_R)}$$

[kmol of D/(h of cycle time·kg of catalyst)]   (16)

subjected to $T_{max} \leq T_{MALL}$. In eq 16, two out of the three variables mentioned were used simultaneously as optimization variables ($\mathbf{X}$).

The purge and evacuation times (t_p and t_e, respectively) were assumed to be constant and equal to 150 s each. These periods are intended to remove hydrocarbon vapors or oxygen before the regeneration and production stages, respectively. Given their short duration, the purge and evacuation periods are not expected to have any significant effect on the coke content of the bed. The duration of the regeneration stage, t_R, which is another possible choice for an optimization variable, was obtained in this case as a result of the simulation. A different value of t_R was obtained for each specified level of activity regained at the end of the regeneration (or, equivalently, for each level of residual coke, CC_f).

The optimization case dealt with in this work is a nonlinear programming problem. The solution used a quasi-Newton method (a variable metric method), with penalty functions to account for the temperature restrictions. The method requires in each step the simulation of the production and regeneration stages. The coke profiles in the reactor at the end of each of these stages define the initial condition for the next stage. The gradients of the objective function and of the restrictions were evaluated numerically, as part of the solution algorithm.

Results and Discussion

Results Obtained in the Simulation of the Production and Regeneration Periods. The results obtained in the optimization depend on the simulation models employed in the deactivation and regeneration stages. Therefore, some of these results will be shown next in order to illustrate the general trends obtained for the evolution with time of the main process variables.

Figure 1a shows the coke profiles obtained in the reactor during the production stage for an initially coke-free bed,
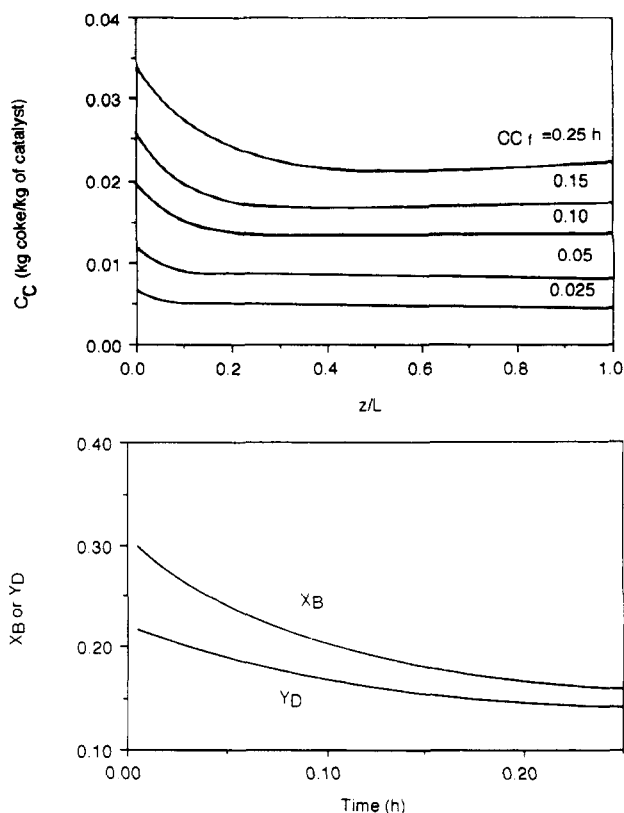

Figure 1. Simulation of catalyst deactivation during the dehydrogenation of 1-butene at 873 K. (a, top) Evolution of the coke profiles along the bed. (b, bottom) Butene conversion (X_B) and butadiene yield (Y_D) as a function of time.

using a pure butene feed at an initial temperature of 873 K. The total duration of the run was in this case of 900 s (0.25 h). It can be observed that a decreasing coke profile along the bed is obtained in this case, which, at the end of the production stage, presents a slight minimum, as a consequence of the low-temperature wave that propagates through the reactor due to the endothermic nature of the dehydrogenation reaction (Dumez and Froment, 1976). The coke deposits cause the deactivation of the catalyst, and consequently, the production rate drops with time on stream. This is shown in Figure 1b, where the conversion of butene and the butadiene yield are plotted as a function of time.

Figure 2 shows the main results obtained for the regeneration stage using the coke profile given by the last curve (0.25 h) in Figure 1a as the initial coke profile at the start of the regeneration. In this case, the regeneration was simulated using a feed containing 8% oxygen, and the simulation was allowed to proceed up to a reaction time of 3960 s (1.1 h). It can be observed that a high-temperature zone develops and travels along the bed during regeneration. This causes a faster depletion of the coke profiles in the region where the maximum temperature is located. The temperature maxima increase in magnitude as the high-temperature zone moves down the bed, which gives rise to important temperature increments. This would require the interruption of the regeneration process or the modification of the operating conditions (e.g., oxygen concentration in the feed) toward less severe values.

Figure 2c shows the evolution of the oxygen conversion at the bed exit. Under the conditions used in this run, the conversion of oxygen was never higher than about 76%. A maximum in the curve can be observed due to the increase in regeneration rate caused by the increase in temperature, followed by a decreasing period as the coke de-
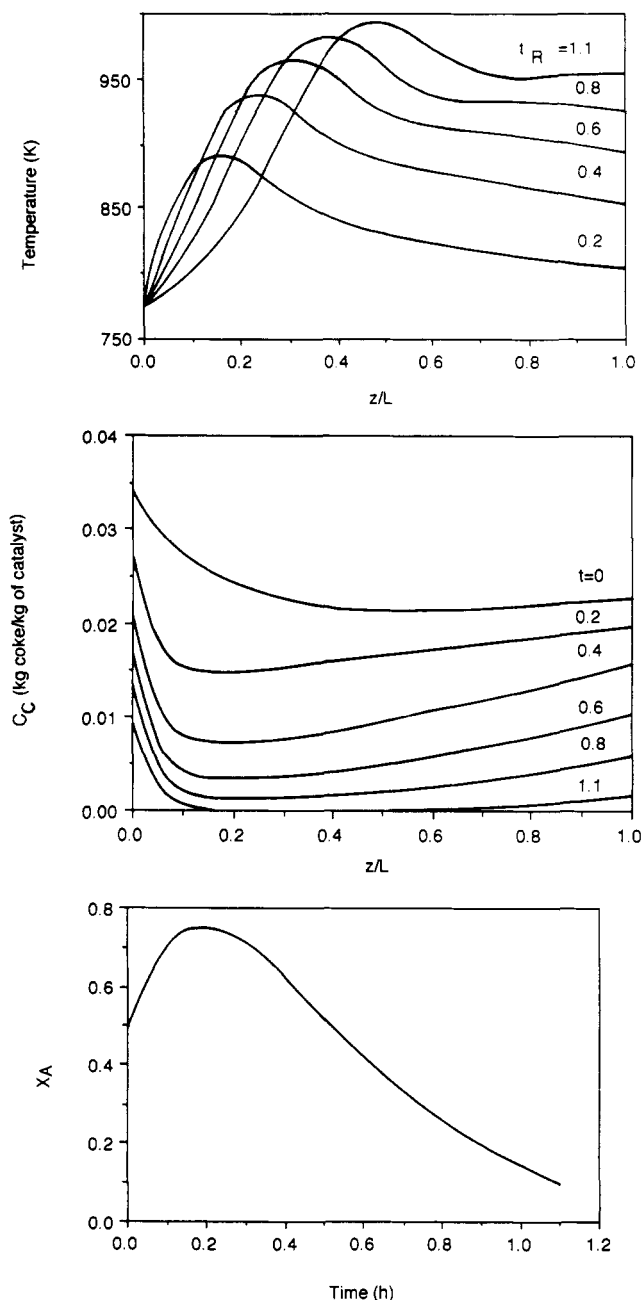
Figure 3. Objective function versus molar concentration of oxygen in the feed during regeneration, for different values of production time.

the maximum temperature restriction imposed on the system. This value of Y_{A0} depends on the total amount and on the distribution of coke in the reactor. These are in turn determined by the duration of the production stage.

For a given value of the target average coke concentration in the bed after regeneration, both t_D and Y_{A0} were used simultaneously as optimization variables. It was found that, irrespective of the initial values of t_D and Y_{A0} employed, the optimum value of the concentration of oxygen during regeneration always converged to 21%, which was the maximum concentration considered. The influence of the oxygen concentration is illustrated in Figure 3, where the values of the objective function have been calculated for different values of Y_{A0} and durations of the production stage. All the cases shown in the figure were calculated for a coke content after regeneration of 0.6%. The coke content before regeneration in each case depended on the value of t_D. All the results presented in this figure satisfied the condition of maximum temperature (T_{max}) equal to or less than 900 K. However, when higher values of t_D were used, e.g., 0.16 h, which would result in a higher amount of coke to eliminate), the maximum temperature restriction was usually violated if high oxygen concentrations were employed. For the conditions of Figure 3, the optimum values of t_D and Y_{A0} were 0.1128 h and 21%, leading to a maximum value of the objective function equal to 2.5282.

From the results presented in Figure 3, it seems likely that higher values of the objective function could have been obtained if higher oxygen concentrations had been considered. Thus, 21% would not be the optimum oxygen concentration overall, but the optimum within the range investigated. However, it does not seem likely that oxygen concentrations higher than that of air would be used in industrial practice, and therefore this was the highest oxygen concentration considered.

The above results show that the optimal regeneration procedure involves regenerating the catalyst at the maximum possible rate. Since this means a very fast rate of heat release and, given the fact that the objective function is severely penalized in case of violation of the maximum temperature restriction, the optimization algorithm reacts by interrupting the regeneration when the temperature reaches the maximum value allowed. A second course of action for the limitation of the temperature increases involves decreasing the value of t_D. This decreases the total amount of coke to eliminate and, therefore, the total heat released during coke burnoff. The optimization algorithm uses the combination of both procedures thus minimizing the duration of the regeneration period while observing

Figure 2. Simulation of the regeneration of a fixed bed reactor with an initial coke profile given by the last curve of Figure 1a. Regeneration with 8% oxygen concentration in the reactor feed. (a, top) Temperature profiles along the bed. (b, middle) Coke conversion profiles. (c, bottom) Oxygen conversion at the reactor exit as a function of time.

posits are exhausted. It is interesting to note that the coke oxidation rate reaches a maximum at a time when a large proportion of the initial coke still remains in the reactor. Also, the maximum temperature in the bed still increases considerably after the maximum reaction rate is reached.

Optimization with Two Variables: t_D and Y_{A0}. As indicated above, the duration of the production stage t_D is a typical optimization variable for systems with cyclical operation. On the other hand, the mole fraction of oxygen during the regeneration stage, Y_{A0}, directly determines the duration of the regeneration for a given set of operating conditions. Both t_D and Y_{A0} are related. Thus, for a given degree of regeneration (e.g., a complete regeneration, elimination of 50% of the coke deposits), there will be a maximum value of the oxygen concentration (and hence a maximum rate of regeneration), which is compatible with
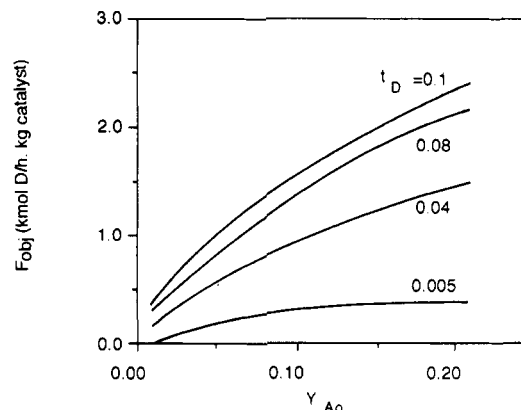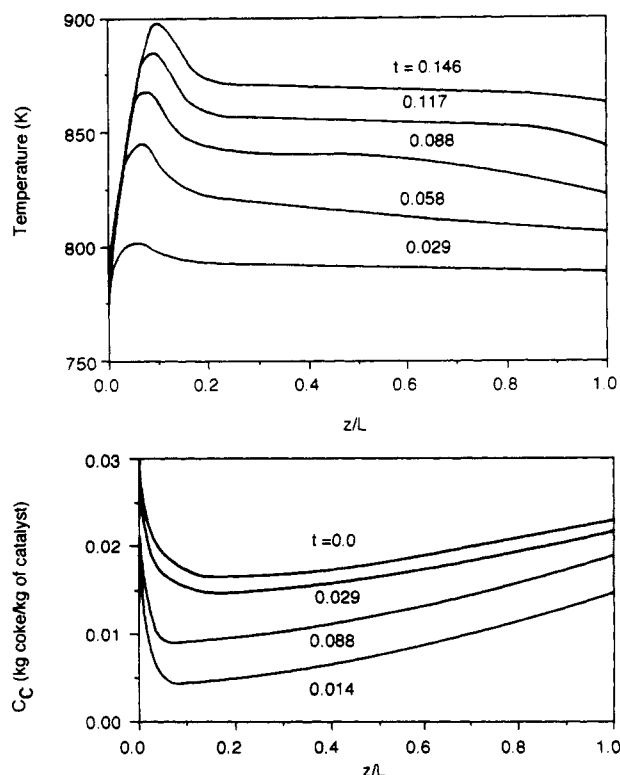
Figure 4. Simulation of catalyst regeneration under optimum operating conditions. (a, top) Evolution of the temperature profiles. (b, bottom) Evolution of the coke profiles.

the temperature limitations.

Figure 4 shows the evolution of the temperature and coke profiles along the bed for the optimum operating conditions (t_D = 0.1159 h and Y_{A0} = 21%), obtained in the case of T_{MALL} equal to 900 K and a remaining average coke concentration after regeneration (CC_f) equal to 1%. A much sharper temperature rise can be observed in this case compared to the results shown in Figure 2a. The corresponding coke profiles also show a steep decrease near the reactor inlet, and thus, most of the coke depletion to the required final value of CC_f is carried out in this region. In this particular case, the initial values used for the optimization were a relatively long production period and a low (2%) value for Y_{A0}. The response of the optimization algorithm was to decrease t_D and to increase Y_{A0} until the above optimum values were obtained. Optimization runs started with different initial values led to the same optimum.

Influence of the Maximum Temperature Restriction. The optimization problem has been solved for several values of the maximum temperature allowable, T_{MALL}, using simultaneously t_D and Y_{A0} as optimization variables. Thus,

$$\mathbf{X}^t = (t_D, Y_{A0}) \qquad (17)$$

subject to the restrictions

$$T \le T_{MALL} \quad \text{and} \quad Y_{A0} \le 0.21 \qquad (18)$$

Several values were considered for the maximum temperature restriction, between 850 and 950 K. The optimization was carried out for three different residual coke levels, namely 0.0005, 0.01, and 0.05 kg of coke/kg of catalyst. The results are shown in Figure 5, where the values of the objective function at the optimum and the duration of the production and regeneration stages are respectively plotted as a function of the maximum temperature restriction. Again, the optimum value found for the oxygen concentration was 21%. It can be noticed that
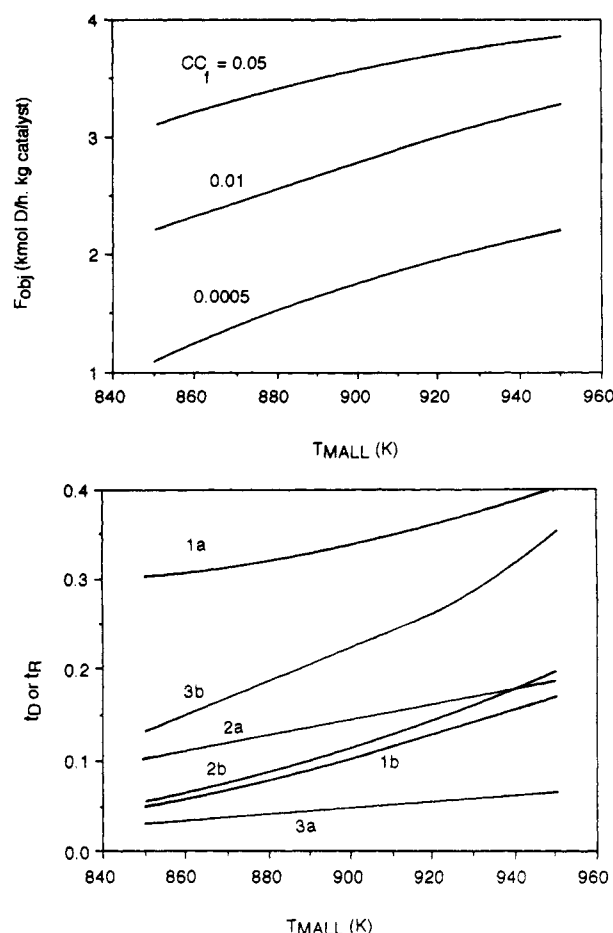

Figure 5. Influence of residual coke level. (a, top) Objective function versus T_{MALL} for different levels of CC_f. (b, bottom) Duration of the production and regeneration stages as a function of T_{MALL} for different levels of CC_f. Curves 1a, 2a, and 3a: duration of the regeneration stage for CC_f equal to 0.0005, 0.01, and 0.05, respectively. Curves 1b, 2b, and 3b: duration of the production stage for CC_f equal to 0.0005, 0.01, and 0.05, respectively.

the maximum temperature restriction has a strong influence upon the value of the objective function at the optimum. For each value of CC_f considered, the objective function increases as T_{MALL} is increased. Also, the optimum duration of both the production and regeneration stages increases if a more severe regeneration can be tolerated. However, it is worth noticing that the economic value implied in an increase of the objective function (i.e., an increase in the butadiene production per cycle) may be offset by the permanent loss of activity of the catalyst, which results in an earlier catalyst replacement. The solution of this problem requires the knowledge of the sintering kinetics of the catalyst and is not addressed in this work.

Influence of the Residual Coke Level, CC_f. As shown in Figure 5a, the residual coke level after regeneration also has a strong influence upon the value of the objective function F_{obj}. In fact, over the range studied, the objective function increases between 2 and 3 times for a given value of T_{MALL} when the value of CC_f is increased from 0.0005 to 0.05. The variation of the objective function is related to the durations of the production and regeneration stages, t_D and t_R, which are plotted as a function of T_{MALL} in Figure 5b for different residual coke levels. In all the cases studied, the values of t_D and t_R increase as T_{MALL} is increased. It can be seen, however, that, for a given value of T_{MALL}, the value of the regeneration time greatly increases when the desired value of the residual coke level
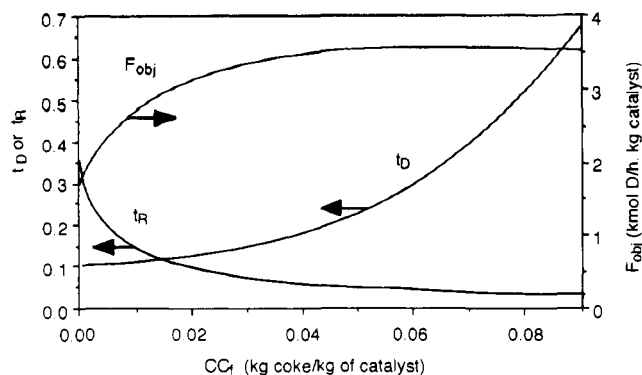
Figure 6. Optimum values of the objective function, and of the durations of the production and regeneration stages, as a function of the residual coke level.

Figure 7. Influence of addition of hydrogen to reactor feed. Objective function versus the residual coke concentration. 1, pure butene feed; 2, reactor feed containing the optimal hydrogen concentration.

is decreased. The reason for this is that the last traces of coke in the reactor are removed at a considerably lower rate, due to the fact that both the coke concentration and the temperature are lower at this stage of the process. Thus, the requirement of complete or almost complete coke removal greatly increases the duration of the nonproductive stage, therefore decreasing the value of the objective function, as shown in Figure 5a.

The influence of the value chosen for the residual coke level is clearly observed in Figure 6, where the optimum values of F_{obj} and of the duration of both stages have been plotted as a function of CC_f. Expressions 17 and 18 again apply to this case. It can be observed that in this case the objective function presents a maximum around $CC_f = 0.07$. Since this value represents the highest of all the optimizations carried out for different residual coke levels, it can be considered the overall system optimum. This means that the optimal operation corresponds to a noncomplete regeneration. This result is in agreement with the analysis carried out by Arandes and co-workers (1984, 1985) for the isothermal case.

As for the optimal duration of the operation and regeneration stages, a stronger influence of the duration of the regeneration stage, t_R, can be appreciated as CC_f is decreased. For low levels of residual coke, ($CC_f \leq 0.014$), the regeneration becomes dominant regarding the cycle time, and $t_R > t_D$. In this case, the long regeneration periods give rise to a decrease in the production per cycle. On the other hand, for relatively high residual coke levels the reactor operates at a relatively low activity during the dehydrogenation period, and thus t_D increases considerably. This is partly compensated by the corresponding decrease in regeneration times, as shown in Figure 6.

Influence of the Reactor Feed Composition. The optimization of the feed composition during the production stage was carried out under the assumption that the regeneration would be performed with a 21% oxygen concentration. This is reasonable, since as shown above, the optimal regeneration was obtained at the maximum possible oxygen concentration in all the cases studied. Thus, Y_{A0} was eliminated as an optimization variable and the hydrogen mole fraction in the reactor feed during dehydrogenation Y_{H0} was included instead. The optimization problem is therefore stated as

$$\mathbf{X}^t = (t_D, Y_{H0}) \tag{19}$$

subjected to the restrictions

$$T \leq T_{MALL} = 900 \text{ K} \quad \text{and} \quad Y_{A0} = 0.21 \tag{20}$$

The injection of hydrogen in the butene feed allowed an important improvement in the production of butadiene per cycle, as compared to the previous case of pure butene
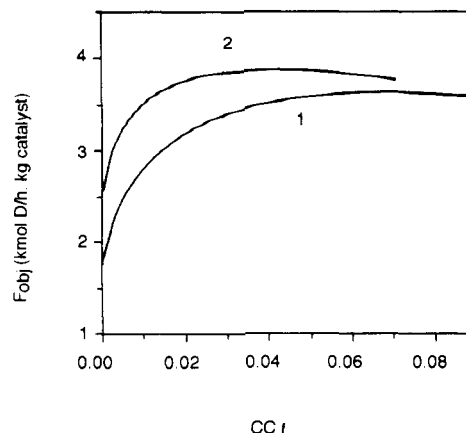
feed. Thus in Figure 7 the objective function is represented versus the residual coke concentration after regeneration for different cases. Curve 2 represents the value of F_{obj} when butene plus hydrogen at the optimal concentration for a given residual coke level is fed to the reactor. The comparison with the case of pure butene feed (curve 1) shows that the optimal residual coke level is lower when hydrogen is introduced. Also, the production rate is higher over all the range of CC_f, with improvements between 10 and 25%. This result is not obvious, since although the presence of hydrogen reduces the rate of coke formation, it also hinders the main reaction (Dumez and Froment, 1976).

The optimum value of the hydrogen concentration in the feed depends strongly on the value of CC_f required. Generally speaking, it was found that the optimum hydrogen mole fraction in the reactor feed decreased when the value of CC_f was increased. At the same time, the regeneration time required to reach the desired final value of CC_f decreased.

The improvement in the levels of butadiene production when hydrogen is introduced in the feed is illustrated in Figure 8a, where the evolution of the butene and butadiene molar flow rates at the reactor exit are represented for a 60/40 butene/hydrogen feed and for a pure butene feed, respectively. In both cases, the same total molar feed rate of 15 kmol/h was employed. The figure shows that, in spite of a 40% lower butene feed rate, the production of butadiene at the reactor exit is comparable in both cases. This is explained by the higher yield to butadiene obtained with the mixed feed, as shown in Figure 8b. The yield to coke is correspondingly lower, which allows a longer production period while keeping low regeneration times. The predicted shape of the coke profiles is considerably modified, as shown in Figure 8c, where it can be observed that the coke deposition under mixed feed operation is much more uniform than when pure butene is fed to the reactor.

Conclusions

The results presented above show the importance of a careful consideration of the regeneration stage when carrying out the optimization of the operation of fixed bed reactors under cyclic operation. In fact, in many instances the regeneration stage becomes dominant in the total duration of the operation cycle. It is also important to note that the strongly exothermic nature of the regeneration process requires a careful selection of operating conditions so as to limit the maximum temperatures reached in the process. Auctioneering control of the oxygen concentration
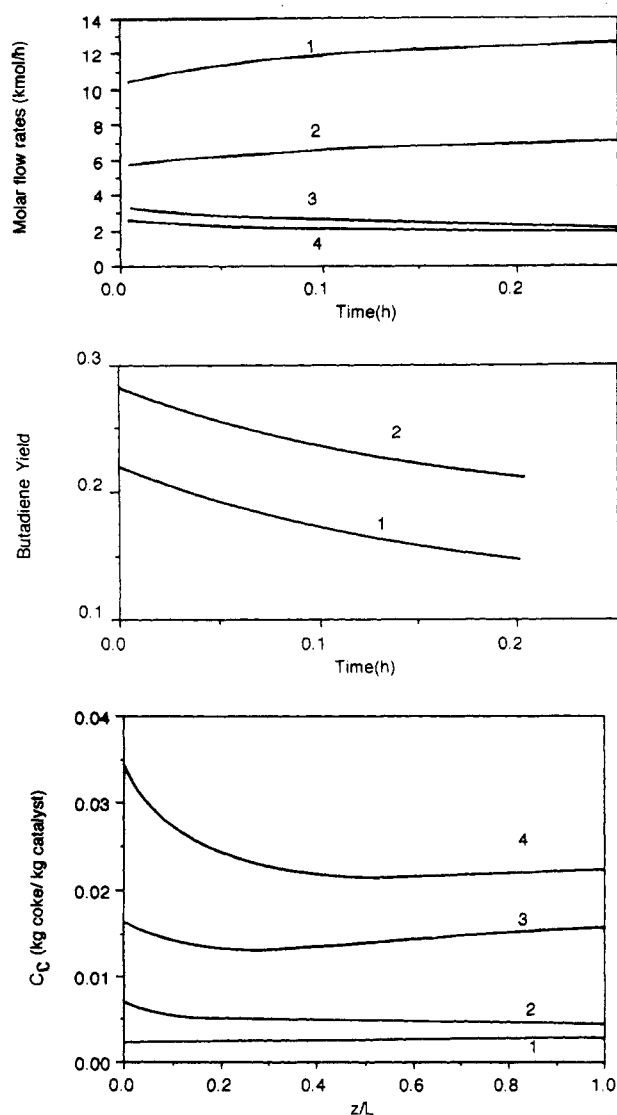
Figure 8. Influence of addition of hydrogen to reactor feed. (a, top) Curves 1 and 2: evolution of the butene molar flow rate at the reactor exit as a function of time, for a 100% butene feed and for a 60/40 butene/hydrogen feed, respectively. Curves 3 and 4: evolution of the butadiene molar flow rate at the reactor exit as a function of time, for a 100% butene feed and for a 60/40 butene/hydrogen feed, respectively. (b, middle) Butadiene yield as a function of time for a 100% butene feed (curve 1) and for a 60/40 butene/hydrogen feed (curve 2), respectively. (c, bottom) Curves 1 and 2: coke profiles along the bed after 0.025 h for a 60/40 butene/hydrogen feed and for a pure butene feed, respectively. Curves 3 and 4: coke profiles along the bed after 0.25 h of production time for a 60/40 butene/hydrogen feed and for a pure butene feed, respectively.

in the regeneration feed is a good example of industrial practice regarding this issue. The optimization has shown that the choice of maximum temperature allowable has a strong influence on the overall performance of the process, as defined by the objective function.

The optimal operation conditions lead to an incomplete regeneration in all the cases studied. This extends previous results considering isothermal regeneration. Also, optimal operation would include admixing hydrogen to the butene feed, in order to diminish coke formation, thus allowing longer production periods and shorter regenerations.

Finally, the optimal operation procedure under the conditions studied (keeping a constant oxygen feed during regeneration) involved a short, very fast regeneration, at the maximum oxygen concentration considered (21%), which is stopped when the temperature restriction is reached. This is far from the usual regeneration practice,

which consists in gradually stepping up the oxygen concentration from a low initial value (e.g., Fulton, 1988). It is clear that the current operating procedure during regeneration arises from safety rather than from process economics considerations. However, the high optimization potential represented by a short, high-oxygen-concentration regeneration which still abides by the maximum temperature restriction should be investigated. Experimental confirmation of the model predictions in laboratory regeneration reactors would be a necessary step before any change in current regeneration strategies is implemented.

Acknowledgment

Nomenclature

A = oxygen
B = butene
C = coke
C_A = concentration of oxygen in the gas phase, $kmol/m^3$
$C_{A,c}$ = concentration of oxygen at the unreacted core, $kmol/m^3$
C_B = concentration of butene in the gas phase, $kmol/m^3$
C_C = coke concentration in the catalyst particle, kg of coke/kg of catalyst
CC_f = average coke concentration in the bed after regeneration, kg of coke/kg of catalyst
C_D = concentration of butadiene in the gas phase, $kmol/m^3$
C_H = concentration of hydrogen in the gas phase, $kmol/m^3$
$C_{p,s}$ = specific heat of the solid, kJ/(kg of solids in the bed·K)
$C_{p,g}$ = specific heat of the gas, kJ/(kg·K)
D = butadiene
D_e = effective diffusivity of oxygen, m^2/h
F_D = molar flow of butadiene at the reactor exit, kmol/h
F_{obj} = objective function, as defined by eq 16, kmol/(h·kg)
ΔH_R = heat of reaction, kJ/kmol
k = kinetic constant for coke combustion, m/h
k_m = external mass-transfer coefficient, m/h
L = reactor length, m
M_i = molecular weight of component I, kg/kmol
r_c = radius of the unreacted core, m
r_{C1} = reaction rate for coke formation from butene, kmol/(kg of catalyst·h)
r_{C2} = reaction rate for coke formation from butadiene, kmol/(kg of catalyst·h)
r_H = reaction rate for dehydrogenation, kmol/(kg of catalyst·h)
r_{He} = effective reaction rate for dehydrogenation, kmol/(kg of catalyst·h)
r_p = particle radius, m
r_v = reaction rate for oxygen consumption, as defined by eq 10a, kmol/(m^3 h)
t = time, h
t_D = duration of the dehydrogenation (production) period, h
t_e = duration of the evacuation period, h
t_p = duration of the purge period, h
t_R = duration of the regeneration period, h
T = temperature, K
T_{max} = maximum temperature reached during regeneration, K
T_{MALL} = maximum temperature allowable during regeneration, K
u = linear gas velocity, m/h
V_p = volume of a catalyst particle, m^3
X = vector containing the optimization variables
X_C = coke conversion
Y_{A0} = oxygen mole fraction in the reactor feed
Y_{H0} = hydrogen mole fraction in the reactor feed

Greek Letters

ϵ = void fraction in the reactor

η = effectiveness factor

$\rho_{b,cat}$ = catalyst bulk density, kg of catalyst/m^3 of reactor

$\rho_{b,I}$ = inert bulk density, kg of inert/m^3 of reactor

$\rho_{b,T}$ = solids bulk density, (kg of catalyst + inert)/m^3 of reactor

ρ_g = density of the gas phase, kg/m^3

ψ_{CB} = coke yield factor, kg of coke/kg of butene

ψ_{CD} = coke yield factor, kg of coke/kg of butadiene

Registry No. 1-Butene, 106-98-9; 1,3-butadiene, 106-99-0.

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