The energy requirements for the two processes are evaluated by making energy balances around the stripping tower. Most of the energy required in the aqueous alkanolamine process is used to evaporate the water which leaves the stripping column. In our design scheme for the mixed-solvent process, the rich-solvent solution is regenerated by stripping with inert gas (flue gases) at elevated temperatures. In this case, most of the energy is needed to provide the heat of reaction to dissociate the amine-acid gas complexes.

ACKNOWLEDGMENT

The authors are grateful to A. Van Aken for helpful discussions, to S. Lynn for advice concerning process-design economics and to Fluor Engineers and Constructors, Irvine, Calif., for suggesting that diglycolamine may be a useful chemical solvent; to the National Science Foundation and to the Venezuelan Fund for Research in Hydrocarbons (FONINVES) for financial support; and to the Computer Center, University of California, Berkeley, for the use of its facilities.

NOTATION

A = Margules constant
a = activity
B = second virial coefficient
f = fugacity
H = Henry's constant
K = chemical equilibrium constant
N = number of moles in solubility apparatus
n = number of moles in the equilibrium liquid
P = pressure
R = gas constant
T = temperature
V = volume
v = molar volume
$\overline{v}$ = partial molar volume
x = mole fraction in liquid
y = mole fraction in vapor
z = true mole fraction
α = fraction of initial number of moles that have reacted
ϕ = vapor-phase fugacity coefficient
γ = liquid-phase activity coefficient

Subscripts

g = gas phase
i = component
l = liquid phase
M = mixture
o = initial conditions, prior to reaction
t = total
1, 2, 3, . . . = components
I, II = complex

Superscripts

o = standard state
L = liquid phase
sat = saturation
$*$ = unsymmetric convention
∞ = infinite dilution

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The Influence of the Freeboard Region in a Fluidized Bed Catalytic Cracking Regenerator

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A model is developed for a fluidized bed reactor with the dense phase region treated by conventional two-phase models. Conversion in the freeboard is obtained based on particle trajectories predicted from drag considerations. The model is applied to an industrial-scale catalytic cracking regenerator. It is shown that the freeboard region can have an important influence on the overall conversion in the unit.

SCOPE

Although fluidized beds are applied as reactors for many industrial heterogeneous and catalytic reactions, design and scale-up of fluidized bed reactors continues to be a difficult undertaking. Considerable effort has been devoted in the past two decades to models which describe the bubbling region of fluidized beds. Recent work shows that end effects may also be important. A significant portion of the reaction can take place in the grid region at the bottom of a fluidized bed, and in the freeboard region above the bed proper.

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Our first objective here is to propose a realistic model to predict reaction rates in the freeboard region. Because freeboard reaction can play an important role in industrial-scale catalyst regenerators (Ford et al. 1977), we make calculations for a regenerator whose properties have been chosen to match those of an operating regenerator. Based on these calculations, we are then able to realize our second objective, to show the importance of the freeboard region relative to the dense bed and to determine the factors upon which reaction in the freeboard depends.

CONCLUSIONS AND SIGNIFICANCE

The overall reaction rate in a large scale fluidized bed depends not only on what goes on in the bed proper, but also on reaction occurring in the freeboard region, into which particles are ejected by bubbles bursting at the bed surface. The freeboard region is especially important for shallow dense beds and for particles which are close to the critical size at which their terminal velocity is equal to the superficial velocity of the upflowing gas. For the cracking catalyst regenerator studied here, the influence of the freeboard is due to additional gas-solid contacting in the freeboard region. The freeboard also has an influence in terms of establishing a steady state temperature level in the bed proper, which would differ from the equilibrium temperature if freeboard effects are neglected.

Our work demonstrates an important industrial case in which bubbling fluidized bed reaction models are unable to give an adequate description of the reactor behavior. End effects should be considered in the design and scale-up of fluidized bed processes, and this may be more important than using sophisticated bubble models. The present work also has implications for the placement, internal or external, of cyclones to return particles which are carried over from fluidized beds. For the present case, we suggest that internal cyclones give higher coke conversions than external ones, because of reduced heat losses.

Although fluidized beds continue to be applied in many industrial processes, modeling and scale-up remain difficult, due to the complexity of gas and particle flow patterns in fluidized bed reactors. Attention in the past two decades has been largely directed at two-phase models which recognize that gas-solid contacting tends to be much better in the dense phase regions of a fluidized bed than in the bubbles which pass through heterogeneous fluidized beds. For reviews of these two-phase models see Grace (1971), Yates (1975) and Horio and Wen (1977).

Recent experimental work (Chavarie and Grace 1975, Furusaki et al. 1976, Ford et al. 1977, Pereira and Beer 1978) shows the need to consider regions other than the bubbling bed in modeling fluidized bed reactors. Behie and Kehoe (1973) modeled the grid jet entry region at the bottom of fluidized beds. This work was extended by Errazu et al. (1979) to a non-isothermal heterogeneous reaction, and by Grace and de Lasa (1978) to more realistic grid jet models. At the same time, Miyauchi (1974), Miyauchi and Furusaki (1974) and Yates and Rowe (1977) proposed models for the freeboard region above a fluidized bed reactor. From the above studies, it is clear that reaction upstream and downstream of the bubbling bed can play a significant role in determining the overall conversion and selectivity in fluidized bed reactors.

Miyauchi (1974) and Miyauchi and Furusaki (1974) were the first to specifically include the freeboard in a fluidized bed reactor model. Their model requires experimental determination of the concentration profile of dilute phase solids and makes no allowance for recycling of entrained particles.

In the present study, we propose a somewhat different model for reaction in the freeboard. The effect of recirculation of particles through the cyclones is included. Solids concentrations are predicted based on the work of Do et al. (1972) and George and Grace (1978) who derived a mechanistic model for entrainment based on ejection of particles by bubbles bursting at the bed surface. Integration of equations of motion for ejected particles allows us to estimate particle trajectories and concentrations for any operating conditions and system.

Yates and Rowe (1977) assume isothermal conditions in the freeboard and, for the purpose of estimating particle residence in the freeboard, assume that particles reach a velocity of $U - U_T$ immediately after ejection. This effectively limits their model to particles with $U_T < U$, i.e., those which leave the bed. In the present model, particles with U_T greater or less than U can be treated and thermal gradients are computed. Calculations are based on an industrial-scale catalyst regenerator, a case in which freeboard reaction is known to play an important role (Ford et al. 1977), but the model can be adapted in a straightforward manner for other reactions (heterogeneous or gas-phase solid-catalyzed).

THE REGENERATOR MODEL

Simplified schematic diagrams of the regenerator unit are shown in Figure 1. Bubbles erupt at the surface of the dense fluidized bed, ejecting particles into the freeboard region. Small particles are carried away with the

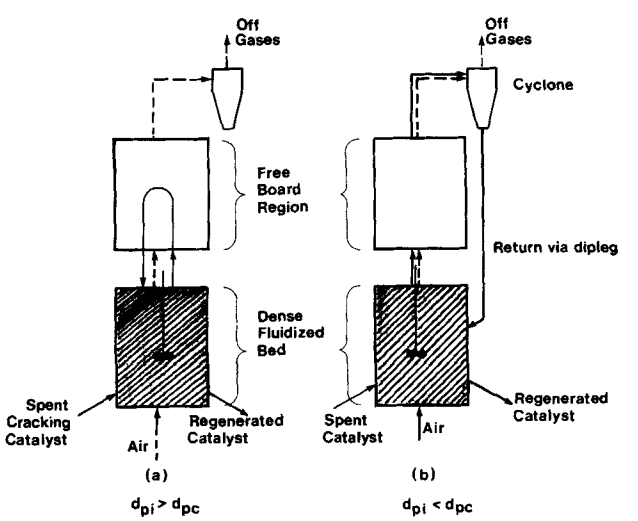

Figure 1. Schematic diagram of the fluidized bed including the freeboard region for (a) particles sufficiently large that they return to the bed surface after ejection into the freeboard, and (b) smaller particles, entrained into cyclones.

gas stream, their terminal velocity being less than the superficial gas velocity. On the other hand, large particles travel upwards and then fall back, since their terminal velocity is larger than the superficial gas velocity. Hence, we consider two kinds of trajectories: (a) particles which return directly to the bed without leaving the freeboard, and (b) particles which return to the bed through the cyclones (Figure 1). Both paths are favorable to the coke transformation since particles in the dilute phase are in good contact with the surrounding gas. Each particle can circulate a number of times through the freeboard during its residence in the regenerator.

To analyze the influence of the freeboard region, a model is developed, based on the following hypotheses: For a dense bed (i.e., bubbling region):

- Gas in excess of that required for minimum fluidization passes through the bed as bubbles. The bubbles are treated as if they are of uniform size and perfectly mixed.
- Reaction in the bubble phase is ignored.
- The dense or emulsion phase behavior is approximated using a CSTR model.
- The CSTR model is also adopted from a thermal point of view, bearing in mind the high degree of particle mixing in vigorously fluidized beds. Temperature gradients between phases are neglected in view of the high heat capacity of the emulsion phase.

For the freeboard region:

- Particle trajectories are computed using the method developed by Do et al. (1972), as modified by George and Grace (1978), to include the dissipation of jets resulting from bubbles erupting at the surface. We neglect particle-particle interactions and clustering.
- We assume piston flow for both gas and solids. Velocity gradients in the radial direction are ignored.
- It is assumed that negligible reaction occurs in the cyclone and in the standpipe returning entrained particles to the dense bed.
- Based on the experimental data and the theoretical predictions of Yousfi and Gau (1974), we assume no choking in the freeboard region. No slug flow is expected for the relatively small cracking catalyst particles and large reactor vessel considered.
- The temperature of the gas entering the freeboard is assumed to equal the dense bed temperature.

In addition to the above we adopt the following general assumptions: Operation is taken as adiabatic and steady state. The kinetic expression for the coke transformation is that presented by Weisz (1966), Weisz and Goodwin (1963, 1966) and Hano et al. (1975) (with diffusional effects neglected). The ratio of carbon dioxide to carbon monoxide is given by a function developed by Arthur (1951). Cyclones are assumed to be located internally within the regenerator unit. With these premises, the basic steady state equation is derived as follows:

Stoichiometry

The coke formula can be represented as CH_n, where n normally lies between 0.5 to 2. In this work, we take $n = 2$. The reactions are then

$$\left.\begin{aligned} CH_2 + O_2 &\rightarrow CO + H_2O \qquad r = k_1 C_c y \\ CH_2 + 1.5\,O_2 &\rightarrow CO_2 + H_2O \qquad r = k_2 C_c y \end{aligned}\right\} \quad (1)$$

Oxygen Balances

Bubble phase:

$$-\frac{dy}{dt} = \frac{q}{V_b}(y - y_e) \qquad 0 \leq t \leq t_R \quad (2)$$

Emulsion phase:

$$N_{mf}(y_0 - y_e) + \frac{N_b q \rho_A}{t_R M_A}\int_0^{t_R}(y - y_e)\,dt = k' y_e C_c W \quad (3)$$

Freeboard region:

$$-N_0 N_T \frac{dy}{dz} = k'\left\{\sum_1^n (1-\epsilon)_i^{\uparrow} C_{ci}^{\uparrow} + \sum_1^n (1-\epsilon)_i^{\downarrow} C_{ci}^{\downarrow}\right\} y A \rho_s \quad (4)$$

Coke Balances

Dense bed:

$$(F_s C_c^0 + F_{se}^{\uparrow} C_{ce}^{\uparrow} + F_{sH}^{\downarrow} C_{cH}^{\downarrow}) - (F_s C_c + F_{sH}^{\uparrow} C_c) = k y_e C_c W \quad (5)$$

Freeboard region:

$$-F_{si}^{\uparrow}\frac{dC_{ci}^{\uparrow}}{dz} = r_i^{\uparrow} A (1-\epsilon)_i^{\uparrow} \rho_s \quad \text{for} \quad d_p = d_{pi}^{\uparrow} \quad (6)$$

$$F_{si}^{\downarrow}\frac{dC_{ci}^{\downarrow}}{dz} = r_i^{\downarrow} A (1-\epsilon)_i^{\downarrow} \rho_s \quad \text{for} \quad d_p = d_{pi}^{\downarrow} \quad (7)$$

Thermal Balances

Overall:

$$F_s c_{ps} T^0 + F c_{pg} T^0 - F_s c_{ps} T - F c_{pg} T_e = \frac{\Delta H_{RT} F_s C_c^0 X_c}{M_c} \quad (8)$$

Freeboard region:

$$-\frac{d}{dz}\left[c_{ps}\left(\sum_1^n F_{si}^{\uparrow} T_i^{\uparrow} - \sum_1^n F_{si}^{\downarrow} T_i^{\downarrow}\right) + F c_{pg} T_g\right] = \frac{\Delta H_{RT} A \rho_s}{M_c}\left[\sum_1^n r_i^{\uparrow}(1-\epsilon)_i^{\uparrow} + \sum_1^n r_i^{\downarrow}(1-\epsilon)_i^{\downarrow}\right] \quad (9)$$

Integration of Equations (2) to (9), when a distribution of particle diameters is considered, is cumbersome. To simplify matters, the integration has been performed for different monodisperse particle size distributions. With this procedure, the influence of each particular diameter can be analyzed.

Equations (2) and (3) can be integrated analytically to give

$$y = y_e + (y_0 - y_e)\exp\left(-\frac{q}{V_b}t\right) \quad (10)$$

$$B(y_0 - y_e) = k' y_e C_c \rho_s (1-\epsilon) V_e \quad (11)$$

The influence of gas bypassing the bed appears via the factor B,

$$B = N_{mf} + N_{T_2}\left[1 - \exp\left(-\frac{q}{V_b}t_R\right)\right] \quad (12)$$

Equations (5) and (11) can then be used to derive a second order equation whose solution is

$$C_c = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a} \quad (13)$$

where

$$a = k' W (F_s + F_{sH}^{\uparrow}) \quad (14)$$

$$b = (F_s + F_{sH}^{\uparrow})B + y_0BkW - k'WC_c^0(F_s + F_{se}^{\uparrow}\alpha + F_{sH}^{\downarrow}\beta) \quad (15)$$

$$c = -(F_s + F_{se}^{\uparrow}\alpha + F_{sH}^{\downarrow}\beta)C_c^0B \quad (16)$$

$$\alpha = C_{ce}^{\uparrow}/C_c^0 \quad \text{and} \quad \beta = C_{cH}^{\downarrow}/C_c^0 \quad (17)$$

Only the positive root of Equation (13) has physical meaning. Equation (13) may be simplified in the case of a single particle diameter. When $U_T < U$, $F_{sH}^{\downarrow} \to 0$ and $F_{sH}^{\uparrow} = F_{se}^{\uparrow}$. On the other hand, when $U_T > U$, $F_{se}^{\uparrow} \to 0$ and $F_{sH}^{\uparrow} = F_{sH}^{\downarrow}$. Equations (13) and (8) are solved numerically, to yield the temperature and the coke concentration in the fluidized bed. It is evident from Figure 1 that α and $T_e^{\uparrow}$ or β and $T_H^{\downarrow}$ depend on the coke transformation in the freeboard region. An iterative method has been employed to find T and C_c. Values of α, $T_e^{\uparrow}$ or β, and $T_H^{\downarrow}$ are first assumed. Equations (8) and (13) are then solved numerically. With the resulting values of C_c and T, Equations (4), (9), (6) and/or (7) can be used to obtain the corresponding $C_c^{\uparrow}$ and $T^{\uparrow}$ (or $C_c^{\downarrow}$ and $T^{\downarrow}$) profiles. New estimates of α and $T_e^{\uparrow}$ or β and $T_H^{\downarrow}$ can then be obtained. Iterations continue until C_c and T reach constant values. The final T and C_c are the steady state values with the freeboard region included. It is straightforward, to show that there is only one steady state solution for the cases considered.

PREDICTIONS OF THE MODEL AND DISCUSSION

The model has been tested for conditions typical of those employed in an industrial-scale regenerator of Destileria La Plata, YPF, Argentina. Bed diameter is 14 m and the total height of the unit, 10 m. The air flow rate, 68.4 to 79.4 m³/s (at 474°C and 1 atm) corresponds to an inlet superficial velocity range of 0.44 to 0.51 m/s. Solids enter at 474°C with a flow rate of 412 to 601 kg/s. In specifying the oxygen content and temperature of the fluidizing air, allowance is made for combustion of fuel oil. Bubble diameters are estimated using the correlation of Basov et al. (1969) with a grid hole diameter of 19.05 mm. Interphase mass transfer coefficients are calculated from the equations derived by Davidson and Harrison (1963) and derived by Kunii and Levenspiel (1969). The kinetic constants we use were suggested by Weisz and Goodwin (1966) for particles of 90 μm and coke concentrations less than 6%.

Trajectories of particles in the freeboard are calculated first, with an approximate and constant value of temperature. It would be straightforward to go through a further iteration in which the temperature progression along the freeboard is used to improve the trajectory calculations, but the accuracy of the model does not warrant such refinement at this stage. For most of the calculations, the performance of the dense bed is analyzed based on a single phase perfectly mixed (CSTR) reactor. As shown by Errazu et al. (1979), high mass transfer rates in the grid region cause the Behie and Kehoe (1973) grid model to approach a single phase CSTR. Other bubbling bed models are considered further below.

Coke conversions are plotted against the total height of the dense bed in Figure 2, for different particle sizes, with and without, the freeboard region included. The

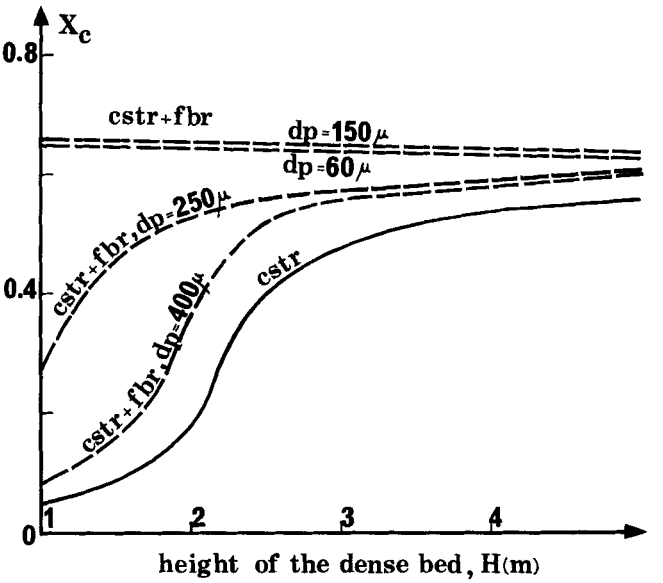

Figure 2. Influence of particle size and depth of dense bed on overall coke conversion with, and without, the freeboard region (FBR) included. Inlet coke concentration: 0.0075 kg/kg catalyst, $(H + H_F) = 10$ m, $Q = 73.9$ m³/s, $T^0 = 474$°C, $F_s = 506$ kg/s.

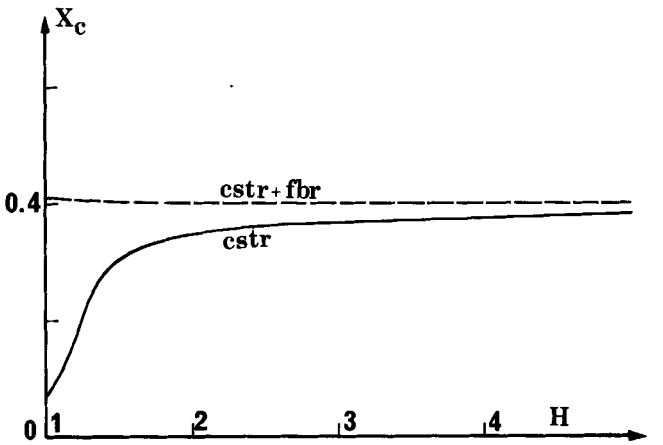

Figure 3. Effect of including the freeboard region (FBR) for an inlet coke concentration of 0.012 kg/kg catalyst and 60 μm particles: $(H + H_F) = 10$ m, $Q = 73.9$ m³/s, $T^0 = 474$°C, $F_s = 506$ kg/s.

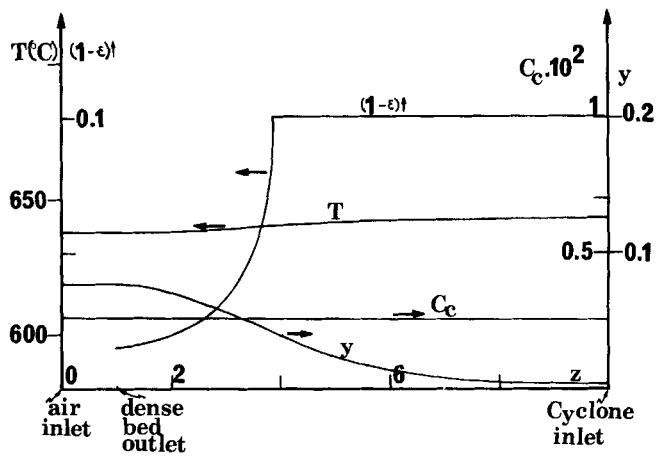

Figure 4. Temperature, coke concentration, oxygen concentration and particle concentration profiles within the unit for $H = 1$ m, $C_c^0 = 0.0075$ kg/kg catalyst, $d_p = 60$ μm, $Q = 73.9$ m³/s, $T^0 = 474$°C and $F_s = 506$ kg/s.

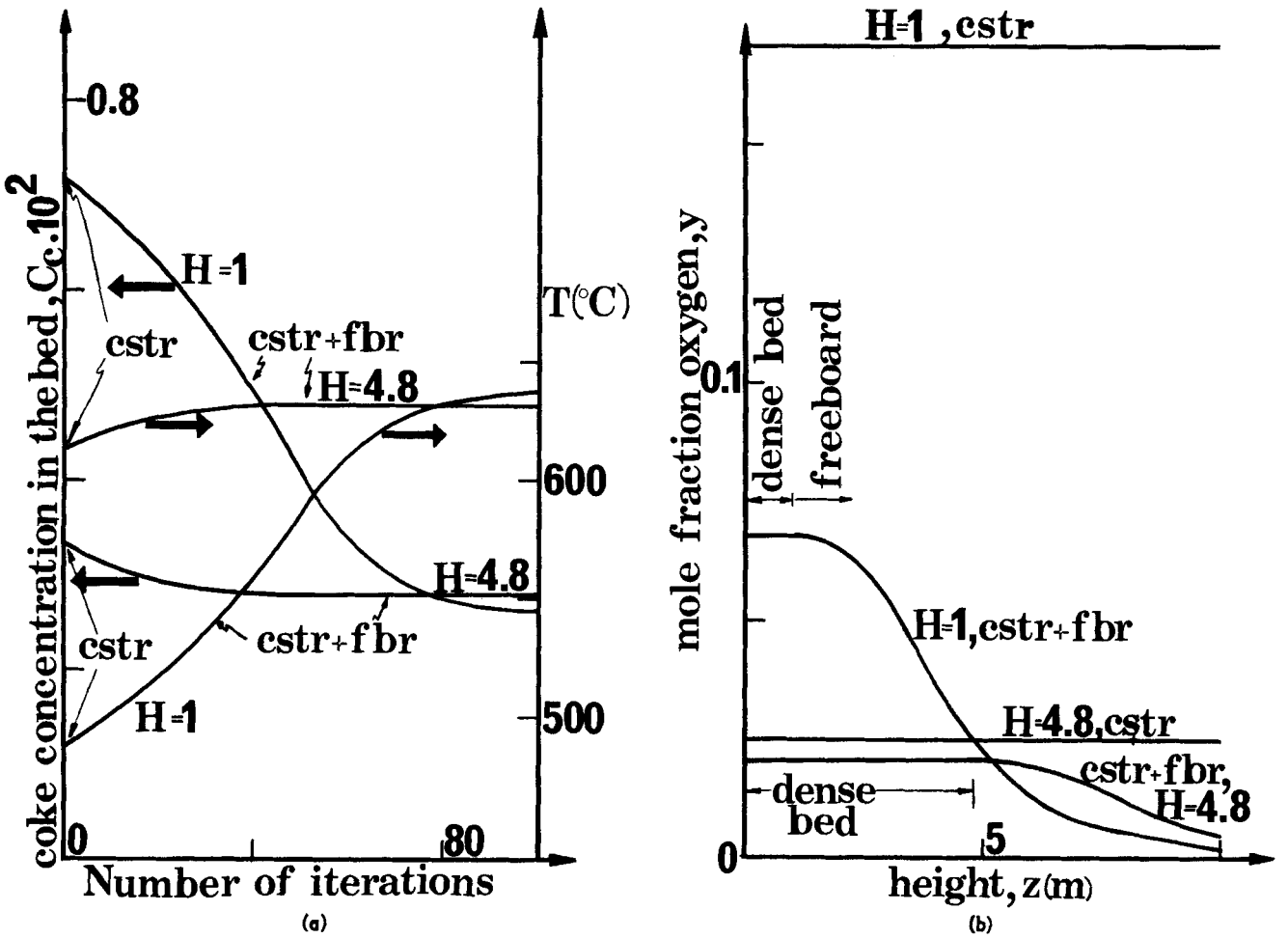

Figure 5. (a) Variation of bed coke concentration and temperature with number of iterations after addition of freeboard region (FBR) to a bed (modelled as a CSTR) in which the freeboard region had been neglected. (b) Variation of oxygen concentration with height for the final steady states before and after addition of the freeboard region (FBR). ($H + H_F$) = 10 m, Q = 73.9 m³/s, C_c^0 = 0.0075 kg coke/kg catalyst, d_p = 60 μm, F_s = 506 kg/s.

effect of the freeboard can be quite significant, especially for shallow beds and for cases where the particle diameter approaches d_{pc}, the particle diameter at which $U_T = U$. Similar curves are shown in Figure 3, for a higher initial coke concentration. Comparing Figures 2 and 3, we see that the effect of the freeboard is somewhat less significant as C_c^0 increases.

Profiles of temperature, voidage, and concentration within the unit appear in Figure 4 for a given set of conditions. The predicted increase in temperature is similar to measured increases in the industrial unit. Relatively small changes of T and C_c with height in the freeboard suggest that the overall effect of the freeboard results primarily from the cumulative effect of particle recirculation to the bed via the cyclones.

In order to understand the influence of the freeboard region, it is helpful to rewrite Equation (5) in the form:

$$X_c = \left[\frac{ky_\infty \dfrac{W}{F_s} + R}{1 + ky_\infty \dfrac{W}{F_s} + R} \right] \tag{18}$$

where

$$R = \frac{F_{sH}^{\uparrow}}{F_s} \left\{ 1 - \gamma \frac{F_{se}^{\uparrow}}{F_{sH}^{\uparrow}} - \delta \frac{F_{sH}^{\downarrow}}{F_{sH}^{\uparrow}} \right\} \tag{19}$$

with

$$\gamma = \frac{C_{ce}^{\uparrow}}{C_c} \quad \text{and} \quad \delta = \frac{C_{cH}^{\downarrow}}{C_c} \tag{20}$$

When $F_{sH}^{\uparrow} \to 0$ or $\gamma = \delta = 1$, no reaction occurs in the freeboard. Then $R \to 0$ and Equation (18) reduces to

$$X_c = \left[\frac{k^* y_\infty^* \dfrac{W}{F_s}}{1 + k^* y_\infty^* \dfrac{W}{F_s}} \right] \tag{21}$$

Considering the $R \to 0$ condition as a reference situation, Equation (18) can be rewritten as:

$$X_c = \left[\frac{k^* y_\infty^* \dfrac{W}{F_s} + \Delta(ky_\infty) \dfrac{W}{F_s} + R}{1 + k^* y_\infty^* \dfrac{W}{F_s} + \Delta(ky_\infty) \dfrac{W}{F_s} + R} \right] \tag{22}$$

where $\Delta(ky_\infty) = ky_\infty - k^* y_\infty^*$. The influence of the freeboard depends on both the R and the $\Delta(ky_\infty)W/F_s$ values. R accounts for reaction occurring in the freeboard and is a function of solid flow rates, particle residence times, oxygen concentrations, and temperatures in the freeboard. $\Delta(ky_\infty)$ arises from the variation of (ky_∞) with temperature and oxygen concentration in the dense bed due to recycling of solids from the freeboard. Figure 5 shows the interrelationship between these two factors.

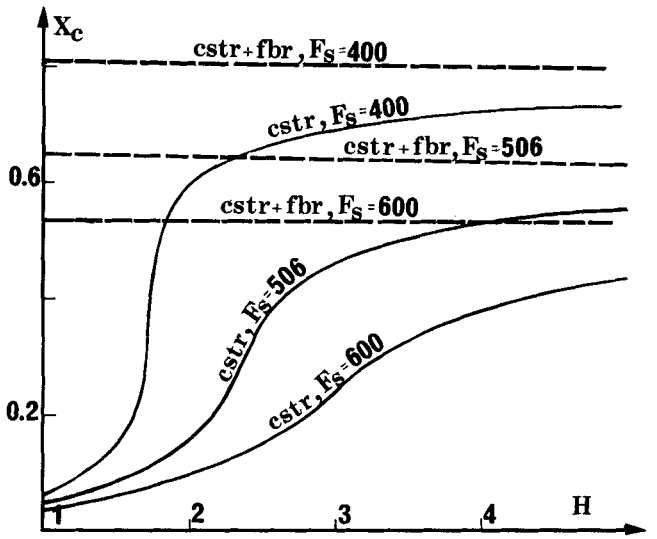

Figure 6. Influence of changing the solids feed rate on the overall coke conversion for an inlet coke concentration of 0.0075 kg/kg catalyst and 60 μm particles: $(H + H_F) = 10$ m, $Q = 73.9$ m^3/s, $T^0 = 474$°C.

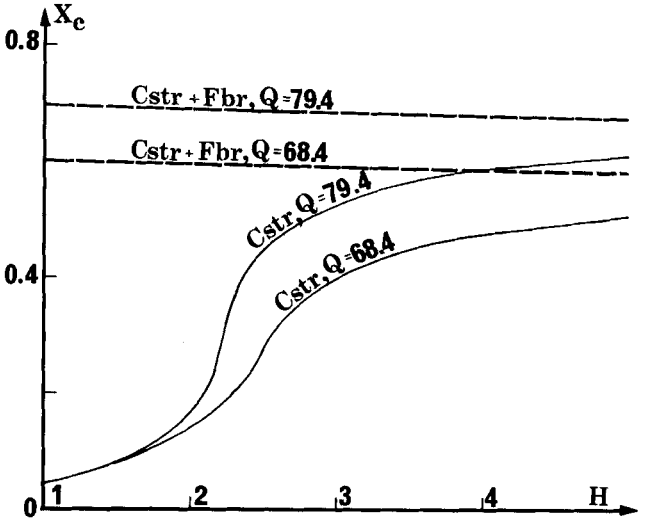

Figure 7. Influence of the superficial gas velocity on the overall coke conversion for an inlet coke concentration of 0.0075 kg/kg catalyst and 60 μm particles: $(H + H_F) = 10$ m, $F_s = 506$ kg/s, $T^0 = 474$°C.

When the freeboard region is added to a bubbling bed in which freeboard effects are ignored (represented by a CSTR), the coke concentration in the bed decreases and the bed temperature increases. Convergence to the new steady state is relatively slow, as indicated in Figure 5(a). For a bed depth of 1.0 m, reaction ignition occurs, and the final (steady state) coke concentration and temperature are far from the initial values. As shown in Figure 5(b), both $\Delta(ky_\infty)$ and R are significant. The oxygen concentration in the dense bed drops from 0.171 down to 0.068 [due to the $\Delta(ky_\infty)$ term] and there is a significant further drop (from 0.068 to 0.002) due to the R term. For a deeper bed, $H = 4.8$ m, the overall changes in conversion and temperature due to addition of the freeboard are much less than for the shallower bed, as shown in Figure 5(a).

Figure 2 indicates that an optimal particle diameter exists, giving a maximum value of X_c in the regenerator. For $d_{pi} < d_{pc}$ the ejected particles are entrained by the gas and return to the fluidized bed through the cyclones. If d_{pi} is increased, the particle residence time and particle concentration in the freeboard increase, leading to more conversion there, so X_c is increased. This behavior continues until $d_{pi} = d_{pc}$. Increases in d_{pi} beyond d_{pc} change substantially the particle trajectories, with solids returning directly to the fluidized bed without passing through the cyclones. Further increases in d_{pi} cause a reduction in solids residence time and concentrations in the freeboard, so that X_c is diminished. In the limit $d_{pi} >> d_{pc}$, the effect of the freeboard is small. This behavior can be observed in Figure 2, where an optimal particle diameter exists between 150 and 250 μm. Particle diameters larger than 400 μm approach the curve for a CSTR without freeboard effects.

As C_c^0 changes from 0.0075 to 0.012 (Figures 2 and 3), the effect of the freeboard region on overall conversion becomes less important. This arises because, as Errazu et al. (1979) show, when higher C_c^0 values are considered, the reactor operation is essentially controlled by the oxygen supply. Since little oxygen remains in the freeboard, there is little reaction there, and X_c approaches the value for the dense bed without the freeboard region included. However, for shallow beds ($H < 1.0$ m), the oxygen concentration in the freeboard is still significant. The freeboard then plays an important role in determining the overall conversion.

The effect of varying the solid flow rate, F_s, is shown in Figure 6, for 60 μm particles. When F_s varies, there is not only a definite shift of the curves for the dense bed itself (labeled CSTR), but also in those where the freeboard region is included (labeled CSTR + FBR). From Equation (22), X_c depends on R and $ky_\infty W/F_s$, both functions of F_s.

Figure 7 shows the influence of the gas flow rate. The separation of CSTR curves as H increases can be understood, bearing in mind the results of Errazu et al. (1979). In a fluidized regenerator, there are two characteristic operating conditions: conditions controlled by the initial coke concentration and conditions controlled by oxygen supply. Since oxygen-control becomes more significant as the bed depth is increased, increasing Q has more influence for deeper beds. When we include the freeboard region in the model, there is a large increase in coke conversion. A higher Q not only increases the supply of oxygen, but also causes additional particle entrainment.

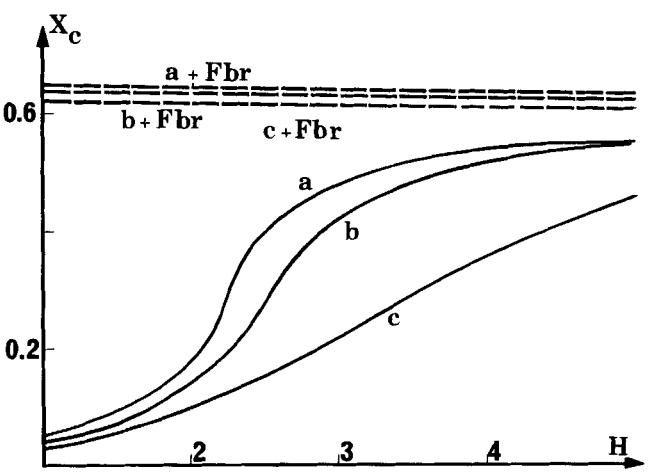

Figure 8. Influence of the model chosen to represent the dense bed part of the fluidized bed with and without the freeboard region considered. a: CSTR model; b: Davidson and Harrison model; c: as in b only with lower interphase mass transfer given by Kunii and Levenspiel: $(H + H_F) = 10$ m, $Q = 73.9$ m^3/s, $F_s = 506$ kg/s, $T^0 = 474$°C.

When Q changes from 68.4 to 79.4 m³/s, the F_{sH}/F_s ratio changes from 12.0 to 14.0. This affects both R and X_c. Particle concentration in the freeboard however, remains nearly constant for the 60 μm particles considered. The large variation in conversion for low H arises because particles make more circuits through the freeboard as Q increases. For $H > 3$ m the sensitivity of X_c to gas flow decreases, and the additional conversion due to the freeboard is nearly constant for the conditions studied.

Finally, in Figure 8 it is shown that freeboard effects are not highly dependent on the model used to represent the dense fluidized bed. Solid lines show results for three models in which the freeboard is not considered: (a) a simple CSTR, as considered in Figures 2 to 7, (b) the two-phase model in which perfect mixing of gas in the dense bed is assumed, described by Davidson and Harrison (1963), and (c) the same model as in (b), only with interphase mass transfer coefficients derived from Kunii and Levenspiel (1969).

Broken lines show the corresponding conversions when the freeboard is added. In each case, the variations in conversion result from the $(\Delta(ky_*)W/F_s + R)$ term in Equation (22). The new curves are closer together than the three curves for the bubbling bed alone. As a consequence, the conversion is less sensitive to the model adopted for the dense bed when the freeboard region is included. Note that the variation in conversion due to inclusion of the freeboard region can be more important than the discrepancy between competing bubbling bed reactor models.

The results of the work reported here show the importance of considering the freeboard in modeling fluidized bed reactors. Results also show the need for more extensive knowledge of particle trajectories and flow patterns in the freeboard region, especially for $d_p \simeq d_{pc}$ and high gas velocities, where particle interactions become important. Previous work (Behie and Kehoe 1973, Errazu et al. 1979) demonstrates that the grid region, like the freeboard, can also play an important role. The freeboard region cannot simply be analyzed as a heterogeneous reactor in series with the dense bed. This is the case because recycle of particles has an important influence on X_c, especially for heterogeneous reactions (like the catalyst regenerator) with high heats of reactions. While the placement of cyclones is not considered explicitly, it is clear that internal cyclones, as assumed in the calculations, will give higher conversions than external cyclones. In the case of external cyclones, some heat would be lost by the recirculated solids resulting in a temperature drop in the unit and a reduction in the overall conversion.

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NOTATION

A = cross-sectional area of the column (m²)
B = factor defined by Equation (12) (Kmol/s)
C_c = coke concentration of the cracking catalyst (kg coke/kg catalyst)
c_{pg} = gaseous mixture heat capacity (Kcal/kg°C)
c_{ps} = cracking catalyst specific heat (Kcal/kg°C)
d_{pi} = particle diameter (μm)
d_{pc} = critical particle diameter when $U_T = U$ (μm)
f = group defined as ρ_A/M_A (Kmol gas/cm³)
F = mass flow rate of air (kg/s)
F_s = mass flow rate of particles fed to unit (kg/s)
H = height of dense phase fluidized bed (m)
H_F = freeboard height (m)
k = kinetic constant (Kmol gas/Kmol O_2 · s)
k' = $(k_1 + 1.5\,k_2)/M_c$
k^* = k value when $R \to 0$
k_1 = $k/(1+\sigma)$ = kinetic constant for the transformation reaction of coke to CO (Kmol gas/Kmol coke · s)
k_2 = $k\sigma/(1+\sigma)$ = kinetic constant for the transformation reaction of coke to CO_2 (Kmol gas/Kmol coke·s)
M_A = molecular weight of air (kg/Kmol)
M_c = molecular weight of coke (kg/Kmol)
N_b = number of bubbles in the bed at any instant
N_0 = number of holes in the grid
N_T = gas molar flow fed to each grid hole (Kmol/s)
N_{mf} = gas molar flow rate required to maintain the bed at minimum fluidization (Kmol/s)
N_{T_2} = $N_T N_0 - N_{mf}$ (Kmol/s)
Q = gas volumetric flow at 1 atm and 474°C (m³/s)
q = volumetric flow rate from a bubble to the emulsion phase (m³/s)
r = coke reaction rate per unit catalyst weight (kg coke/kg catalyst · s)
R = dimensionless group defined by Equation (19)
t = time
t_R = bubble residence time
T = temperature (°K)
U = superficial gas velocity (m/s)
U_T = particle terminal velocity (m/s)
V_b = bubble volume (m³)
V_e = volume of dense phase = $H_{mf}A$ (m³)
W = total catalyst weight in the regenerator (kg)
X_c = coke conversion = $1 - (C_c/C_c^0)$
y = oxygen molar fraction
z = axial coordinate (m)

Greek Letters

α = $C_{ce}^{\uparrow}/C_c^0$
∞ = $C_{cH}^{\downarrow}/C_c^0$
γ = $C_{ce}^{\uparrow}/C_c$
δ = $C_{cH}^{\downarrow}/C_c$
σ = CO/CO_2 molar ratio
ΔH_{R1} = heat of formation of CO (Kcal/Kmol)
ΔH_{R2} = heat of formation of CO_2 (Kcal/Kmol)
$\Delta H_{RT} = \Delta H_{R1} + \dfrac{\sigma}{1+\sigma}\Delta H_{R2}$ (Kcal/Kmol)
ρ = density (kg/m³)
ϵ = void fraction

Subscripts and Superscripts

$\uparrow$ = particles moving upwards in the freeboard
$\downarrow$ = particles moving downwards in the freeboard
$*$ = value when freeboard region is not included
0 = entry
A = air
e = exit from the unit
g = gas
H = at the bed surface
i = discrete particle size range
s = solid

∞ = emulsion phase
mf = minimum fluidization

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Computation of Phase and Chemical Equilibrium:

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Part I. Local and Constrained Minima in Gibbs Free Energy

Several methods are reviewed for determining compositions in multiphase, reacting mixtures at equilibrium. Wolfe's quadratic programming algorithm is applied and results compared with the Rand method (Dluzniewski and Adler 1972), NASA method (Gordon and McBride 1971) and the George et al. (1976) implementation of Powell's method. For poor guesses in compositions, local and constrained minima in Gibbs free energy may arise, giving incorrect phase distributions.

SCOPE

The objective of this research has been to devise new methods for calculating compositions in phase and chemical equilibrium that are applicable for use in simulators. The methods should provide the proper blend of generality, reliability, and speed.

Today's simulators permit calculation of phase equilibrium for, at most, three phases (vapor-liquid-liquid), involving no solids, and no chemical reaction.

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