Simulation of Chromatographic Reactors

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1. Introduction.

This paper deals with a one dimensional continuous flow reactor in which several gaseous components react with others which are adsorbed onto a solid catalyst. We shall see that the reactor is most efficient if one of the species, B, is introduced via a side flow, rather than at the end of the reactor. It is also necessary to periodically reverse the flow in order to prevent B from leaving the reactor.

In general one would not expect the flow to be uniform in such a reactor since not only are there thermal effects due to the reactions, but the catalyst exerts a drag on the flow which must be overcome by a pressure gradient. The full problem can be solved numerically by using the hierarchical adaptive grid code μ Cobra which is designed to solve the compressible Navier-Stokes' equations and advection diffusion equations for chemical species, but here we will only consider a simpler problem in which the density, velocity and temperature are uniform.

The behaviour of the reactor is largely determined by the fact that the adsorption capacity of the catalyst is much larger than the concentration of species B in the gas phase. If adsorption and desorption are fast compared to the other reactions, then the non-linearity of these processes lead to the formation of steep adsorption fronts which move very slowly relative to the . advection speed. We shall see that it is possible to develop an analytic theory which describes the structure and motion of these fronts and hence makes it possible to estimate the reversal time. This theory can also be used to check the results of numerical calculations.

2. Simplified Equations.

In some cases the concentrations of the reactive species are so small that it is reasonable to neglect the heat released by the reactions and assume that the reactor is isothermal. If we also neglect the drag due to the catalyst, then the velocity and density are also uniform within the reactor.

In the simplest chemical scheme the reactions are

 $A + C \longrightarrow P$ $B \longleftrightarrow C$

where C represents B adsorbed onto the catalyst. For constant gas velocity and density, it is possible to write the equations in the non-dimensional form $\frac{\partial a}{\partial \tau} + \frac{\partial a}{\partial z} = -D_{\lambda}ac$, 2.1a European Symposium on Computer Aided Process Engineering-3

$$\frac{\partial b}{\partial \tau} + \frac{\partial b}{\partial z} = -D_{+}b(1 - c) + D_{-}c + q, \qquad 2.1b$$

$$\alpha \frac{\partial c}{\partial \tau} = D_{+}b(1 - c) - D_{-}c - D_{A}ac, \qquad 2.1c$$

where the variables are

$$a = \frac{A}{A_{0}}, \quad b = \frac{B}{A_{0}}, \quad c = \frac{C}{C_{m}}, \quad z = \frac{x}{L}, \quad \tau = \frac{tv}{L^{0}}, \quad q = \frac{LQ}{\rho_{0}v_{0}A_{0}}.$$

$$D_{A} = \frac{k_{A}\rho_{c}C_{m}L}{v_{0}}, \quad D_{+} = \frac{k_{+}\rho_{c}C_{m}L}{v_{0}}, \quad D_{-} = \frac{k_{-}\rho_{c}C_{m}L}{\rho_{0}A_{0}v_{0}}, \quad \alpha = \frac{\rho_{c}C_{m}}{\rho_{0}A_{0}}.$$
2.2

The parameters are: L length of the reactor; v_0 flow velocity (> 0); A, B number of moles of components A and B per unit mass of gas; A input value of A; C number of moles of component C per unit mass of catalyst; C maximum molar adsorption capacity of catalyst (per unit mass); Q side flow source term (moles per unit length per unit time); ρ_0 gas density; ρ_c effective density of the catalyst; k_{A} molar rate constant for main reaction; k_{A} molar rate constant for adsorption; $k_{\underline{k}}$ molar rate constant for desorption. Here $D_{\underline{k}}$ etc are the Damköhler numbers of the reactions and α (» l) is the relative adsorption capacity of the catalyst.

2.1	Steady Solutions.	If the	solution	is	steady,	the	equations	reduce	to
$\frac{da}{dz} =$	- D _A c,							2.3	a
$\frac{db}{dz} =$	$- D_{+}b(1 - c) + D_{c} +$	· q ,						2.3	њ
n h(1	(-c) - Dc - Dac =	0.						2.3	30

$$D_{b}(1 - c) - D_{c} - D_{a}c = 0$$
. 2.3

For simplicity, let us consider a reactor with zero side flow (q = 0)with both A and B introduced at z = 0. If the reactor is stoichiometric, then the boundary conditions are a = b = 1 at z = 0. Since a and b then satisfy the same equations and boundary conditions, we have a = b. Using this and equation 2.3c in equation 2.3a we get

$$\frac{da}{dz} = -D_{A} \frac{ra^{2}}{[(r+s)a+1]} \quad \text{where } r = \frac{D}{D^{+}}, \quad s = \frac{D}{D^{A}}. \quad 2.4$$

The solution to this that satisfies the boundary conditions is

$$z = \frac{1}{D_{p}} \left[\frac{1}{ra} - \frac{1}{r} - (1 + \frac{s}{r}) \log(a) \right] . \qquad 2.5$$

Clearly a \rightarrow 0 as z \rightarrow ∞ and therefore so do b and c. This conclusion is unaffected by the existence of desorption $(r < \infty)$. The only difficulty is that a decays algebraically at large z and so it is not possible to use very small Damköhler numbers. This clearly places a limitation on the mass flux through the reactor and hence on its efficiency, which can only be overcome by ensuring that c is reasonably close to unity in most of the reactor. It is not possible to arrange this for a steady reactor, but it can be done if b is fed in through a side flow and the main flow is periodically reversed. The behaviour of the reactor is then almost entirely determined by the adsorption

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and desorption processes.

2.2 Fast Absorption and Desorption. In general we expect D_{\downarrow} and D_{\downarrow} to be much larger than D_{A} and if this is true, then it is possible to simplify the equations by assuming that b and c are in equilibrium. In that case equation 2.1b gives

$$c = \frac{rb}{(1 + rb)} \quad 2.6$$

If we neglect the main reaction and the side flow, then the right hand side of 2.1b can be replaced by $-\alpha\partial c/\partial \tau$ to give

$$\frac{\partial}{\partial \tau} \left[b + \frac{\alpha r b}{(1+rb)} \right] + \frac{\partial b}{\partial z} = 0 . \qquad 2.7$$

where we have used 2.6 to eliminate c. This is a non-linear advection equation for the conserved variable

$$u = [b + \frac{\alpha r b}{(1 + r b)}],$$
 2.8

and the effective advection speed is

$$w(b) = \frac{1}{\left[1 + \frac{\alpha r}{(1 + rb)^2}\right]} = \frac{1}{\left[1 + \alpha r (1 - c)^2\right]}.$$
 2.9

2.7 is a nonlinear advection equation in which the advection speed is an increasing function of u or b. The gradient in b therefore decreases with time if $\partial b/\partial z > 0$ and increases if $\partial b/\partial z < 0$. The result is that steep fronts are formed and the timescale for flow reversal is determined by the motion of these fronts.

It is not difficult to show that the speed v_{μ} of such a front is given by

$$v_{f} = \frac{(1 + rb_{L})(1 + rb_{R})}{[\alpha r + (1 + rb_{L})(1 + rb_{R})]} = \frac{1}{[1 + \alpha r(1 - c_{L})(1 - c_{R})]} 2.10$$

where the suffices L,R refer to the states on the left and right of the front. For positive flow velocity, such a front is only possible if $c_L > c_R$ and it can be shown that δ given by

$$\delta = \frac{\alpha v_f (1 - v_f)}{D_c (c_L - c_R)} , \qquad 2.11$$

is a measure of the front thickness. Note that it is determined by the speed of the desorption reaction.

3. Reactor Dynamics.

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It is clear from equation 2.10 that if $\alpha r \gg 1$ and c is not close to unity, then $v_f \sim 1/\alpha r$ and c changes on a timescale of order αr which is much larger than the flow time. The distribution of A is then approximately steady and equation 2.3a tells us that

$$a_1 = a_0 exp(-D_{A_T})$$
, 3.1

where $a_0^{}$, $a_1^{}$ are the input and output values of a and $c_T^{}$ is the total amount of c in the reactor. The reactor is clearly most efficient if $D_1^{}$ is small

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Figure 1. Reversal time as a function of the relative adsorption capacity of the catalyst.



Figure 2. The distribution of A (no markers), B (+ markers) and C (x markers) just before reversal for $\alpha = 100.0$.

since this implies that the reactor is short or the flow rate is large. We should therefore try to make c_T as large as possible, subject to the constraint that no B leaves the reactor. This constraint can be satisfied if we monitor the concentration of B at some point just inside the reactor at the downstream end and reverse the flow once this concentration reaches a threshold value. Since the front is guite steep if adsorption and desorption are fast, this ensures that essentially no B leaves the reactor.

Since c is consumed by the main reaction, it has to be replenished, and it is obvious from equation 2.5 that it is not a good idea to introduce B at the input end of the reactor. It is much better to input it via a side flow at a rate which ensures that almost all the A is consumed. However, the reactor will not be periodic unless the rate at which B is input is less than that required to consume all the A. This is because the concentration of A at the outlet can never be zero and there is also some A lost every time the flow is reversed.

The reversal time is determined by the motion of an adsorption front in which c = 0 ahead and $c = c_f$ (say) behind. For $\alpha r \gg 1$, the speed of this front is approximately $v_f = 1/[\alpha r(1 - c_f)]$. For a given monitoring position and threshold concentration of B, the reversal time is inversely proportional to v_f . It also turns out that c_f is directly proportional to c_T , so the reversal time t_ is approximately given by

$$t_r = K_1 \alpha r (1 + \frac{K}{D_A} 2 \log \frac{a}{a_0})$$
.

Here K_1 and K_2 are positive constants which depend upon the monitoring position and the threshold value of B and we have used equation 3.1 to eliminate c_T . Numerical calculations show that this equation is quite accurately satisfied for a wide range of values of c_T . This can be seen from figure 1 which shows the reversal time as a function of α . Figure 2 shows the distribution of the various components in a typical calculation just before the flow velocity changes from positive to negative.

4. Conclusions.

We have seen that a reactor with periodic flow reversal can be made very efficient if the adsorption capacity of the catalyst is large and the reagent which is adsorbed is introduced via a side flow. Although we have only considered the simplest possible case in which the flow velocity and gas density are uniform, the qualitative behaviour is likely to be the same even if there are substantial thermal and dynamical effects. The only physical process which can make a substantial difference is the presence of a large amount of diffusion since this would increase the thickness of the adsorption fronts and reduce the reversal time.

3.2