



BEYOND THE LAW OF MASS ACTION IN REACTIVE CLEANING



JAMES HARRIS

Solid catalysts provide active sites on which gaseous or aqueous reactants can react more quickly or with less energy input than if they were to react in solution. Catalysts are very important in many industrial applications, such as the production of ammonia.

W. L. Gore and Associates manufacture catalytic particles for use in *flow-by reactors*. In a flow-by reactor, a thin layer of fluid transports reactants past a bed of catalytic particles, which are embedded within a porous medium saturated in fluid, as shown in Figure 1. The reactants react at the surface of the catalytic particles and the resulting products are carried away in the fluid.

When synthesising a desired chemical product, \mathcal{B} , from a reactant \mathcal{A} , in a flow-by reactor, other reactions may take place that affect how much of this chemical we produce. For example, the desired product may react further, producing an unwanted byproduct, \mathcal{C} . Our goal is to determine the operating regime for the reactor, which we characterise through the flow rate of fluid, that maximises production of \mathcal{B} .

Model

A model for a flow-by reactor must account for the transport, consumption and production of the various chemical species. We consider each of these aspects in turn.

For the transport processes, we assume that the chemical species diffuse in the fluid, as well as being advected by the flow. For simplicity, we assume there is no fluid flow within the underlying porous medium, and that the fluid outside the porous medium flows with a constant rate, U .

If we assume the reactor is much thinner than it is long, then the concentration in the fluid does not change across the thickness of the reactor. The concentration of each species is then a function of position, x , along the length of the reactor, and time, t , and is governed by a reaction–advection–diffusion equation. We now need to specify the rates of reaction.

The rate, r , of a chemical reaction is the rate at which the products are consumed per unit volume, measured in $\text{mol m}^{-3} \text{s}^{-1}$. Chemical reactions are often modelled using the *law of mass action*, which states that the reaction proceeds at a rate proportional to the concentrations of the reactants raised to the power of their stoichiometric coefficients. If we denote the concentration of \mathcal{A} and \mathcal{B} by a and b respectively, then the rates of the reactions



given by the law of mass action are

$$r_1 = k_1 a, \quad r_2 = k_2 b, \quad (2)$$

respectively, where k_1 and k_2 are constants of proportionality. While the law of mass action is applicable to a wide range of reactions, it is not suitable for aqueous and gaseous reactions at the surface of solid catalysts. This is because the reactants need to adsorb to the catalyst before they react. In such cases, it is more appropriate to assume the reactants obey *Langmuir–Hinshelwood kinetics*, for

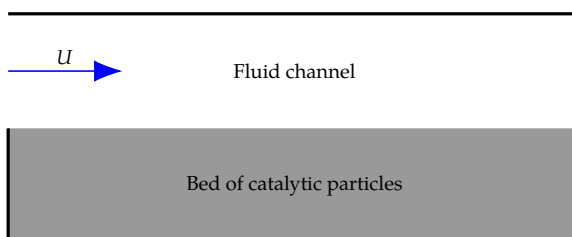


Figure 1 – A flow-by reactor.

which the reaction rates are

$$r_1 = \frac{k_1 K_A a}{(1 + K_A a + K_B b)^2}, \quad r_2 = \frac{k_2 K_B b}{(1 + K_A a + K_B b)^2} \quad (3)$$

where K_A and K_B are termed adsorption constants. When the reactants are in short supply, this reaction rate law behaves like the law of mass action. However, by including the adsorption constants, we can investigate the phenomena whereby one of the reactants can block the active sites of the catalysts when it is in excess.

Results and Discussion

When a flow-by reactor has been operating for a suitably long time at a constant flow rate, the concentration profile along the length of the reactor settles into a steady state. We found that, when the flow rate is sufficiently high, the concentration settles into a steady state similar to that shown in Figure 2, regardless of the initial concentration of \mathcal{A} . In this case, the reactant, \mathcal{A} , supplied at the inlet, does not spend long enough in the reactor to react completely before reaching the outlet. This results in \mathcal{A} blocking the active sites in the catalyst and rendering the rate of the second reaction, which produces C , extremely slow. We call this the *low conversion regime*.

When the flow rate is sufficiently slow, the reactor settles into a steady state like that shown in Figure 3, regardless of the initial conditions. For such flow rates, the reactant, \mathcal{A} , spends sufficiently long in the reactor to be completely consumed, meaning that, close to the outlet, there are unblocked catalysts that produce C . We call this the *high-conversion regime*.

We found that, for a range of flow rates, both regimes are possible. For example, the two concentration profiles plotted in Figures 2 and 3 are steady states for the same flow rate. The steady state that is adopted depends on the initial concentration of \mathcal{A} . If we start with no reactant in the system, then the solution settles into the high-conversion regime, whereas if we start with a suitably high concentration of \mathcal{A} everywhere in the system then the solution adopts the low-conversion steady state. In the latter case, there is a higher outlet concentration of \mathcal{B} . If we were in the former regime, we would have to run the reactor for a short time at a high flow rate and then reduce the flow rate, to transition to the latter regime.

We have gained valuable insight into how the flow speed influences the yield of a reaction exhibiting Langmuir–Hinshelwood kinetics. As this system exhibits multiple steady states, it is important to understand how to manipulate the flow speed to select the regime that maximises the yield of our desired product.

Vasudevan Venkateshwaran, applied mathematician from the modelling and simulation team at W. L. Gore & Associates, commented:

James' work has focused on establishing a chemical reaction modelling approach to estimate the yield and selectivity of a desired product(s) in scenarios where multiple reactions occur within a catalyst composite material producing a mixture of products. James is a very talented mathematician and his work is giving us new insights into the connections and limitations between microscale kinetics and macroscale reactor operation parameters. We plan on using and building upon James' work to understand the effect of different reaction schemes and reactor configurations on yield and selectivity.

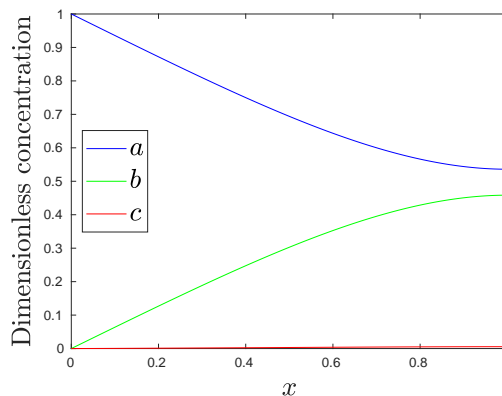


Figure 2 – In this steady state profile, the concentration of \mathcal{A} remains high throughout the reactor, and so hardly any of the unwanted product, C , is produced.

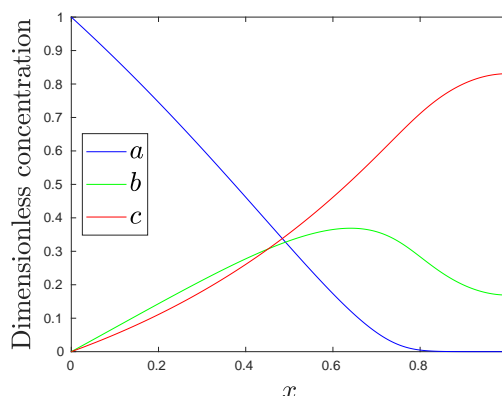


Figure 3 – In this steady state profile, \mathcal{A} is completely used up before it reaches the outlet of the reactor.