

SIMULATION OF AN ADIABATIC CONTACT CATALYTIC REACTOR

I. MARSI, P. FEJES† and K. VARGA

Applied Chemistry Department, József Attila University, Rerrich B. tér 1., Szeged H-6720, Hungary

(Received for publication 12 October 1988)

Abstract—The computer simulation of an adiabatic stationary operating contact catalytic reactor for exothermic reactions is investigated, with consideration to the effect of the grain size distribution along the catalyst bed. The optimization of the problem is discussed and several characteristics of such reactors are pointed out.

INTRODUCTION

The temperature profiles developing in contact catalytic reactors fundamentally influence their production, especially if exothermic reactions occur in them. It is therefore necessary to consider the calculation and optimization of these profiles. In the course of the optimization, somewhat contrasting requirements have to be dealt with: increases in the rates of useful reactions, but decreases in the rates of undesired side-reactions and improvement of the equilibrium composition. In some cases the task can be solved by ensuring a constant reaction temperature (for example, the synthesis of methanol and ammonia, or the oxidation of sulphur dioxide). Here the gas streams through several layers of catalyst and it can be cooled between the layers.

Considerable difficulties have to be faced if the optimum temperature profile is not constant or if the small height of the catalyst bed does not allow between-layer cooling. In these cases some novel patented solutions‡ can be of special importance. It is claimed that greater yields can be achieved if the catalyst bed consists of several layers, each characterized by a different mean size of the catalyst grains.

The mathematical description of adiabatic stationary operating contact catalytic reactors is somewhat more difficult if the axial distribution of the grain size has to be considered too. In the present paper several aspects of this problem are surveyed. An attempt is made to clarify how the production, the temperature profiles and the axial distribution of the grain size are correlated.

In the construction of the mathematical model, the following preliminary assumptions were made:

1. The reactor operates in a stationary mode.
2. Radial change of variables can be neglected, i.e.

the conditions at a given z are uniform throughout the entire cross-section of the streaming gas and catalyst bed.

3. The reactions can be described by means of quasi-homogeneous rate equations.

The question of thermal equilibrium between the gas and the catalyst bed will be discussed later (see Discussion), but it must be mentioned in advance that in such reactors it is advisable to consider the heat transfer between the two phases.

With the above assumptions, the mathematical model can be formulated as follows:

$$\frac{dJ_j}{dz} = \sum_{i=1}^m v_{ij} \cdot r_i(c, T_g, T_s, d)$$

$$\text{CH}_3\text{OH}: j = 1, \quad \text{HCHO}: j = 2$$

$$\frac{du \cdot c_p \cdot T_g}{dz} = \alpha \omega(d) [T_s - T_g]$$

$$- \sum_{i=1}^{m_1} r_{i,g}(c, T_g) \cdot \Delta H_i^f$$

$$\lambda(d) \frac{d^2 T_s}{dz^2} = -\alpha \omega(d) [T_g - T_s]$$

$$+ \sum_{i=1}^{m_2} r_{i,s}(c, T_s, d) \cdot \Delta H_i^f \quad (1)$$

Since the general solution of the differential equation system (1) cannot be given in finite form, the treatment will be restricted to a model process, the oxidative dehydrogenation of methanol to formaldehyde over a crystalline silver catalyst. Formaldehyde is formed as an intermediate in a consecutive reaction, and optimum operation requires its maximum yield. The development of this operating mode can be aided via computer simulation, which allows answers to be given to the following questions:

1. What distributions of the concentrations of the

†Author to whom all correspondence should be addressed.

‡F.R.G. Patent Nos 1-231-229, 2-244-586, 3-213-227; Japanese Patent No. 8033-428; Czechoslovakian Patent Nos 182-499, 219-193; Polish Patent No. 117-567; U.S. Patent No. 4-424-397.

individual components and what temperature profiles may develop in the reactor?

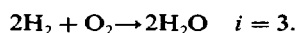
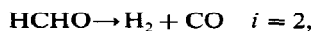
2. (a) how do the same distributions appear under optimum conditions, i.e. when the yield of formaldehyde is at its maximum?
- (b) is there any means of ensuring the optimum operating mode?

To answer question 1, an initial value problem had to be solved. Through the use of Pontriagin's maximum principle, both questions 2(a) and (b) could be answered.

PRELIMINARY TO THE SIMULATION

Rate equations, data bases, initial values

The most important system-variables are the concentrations of CH_3OH , HCHO , H_2 , O_2 , H_2O and CO , these being provided with the indices $j = 1, \dots, 6$, respectively. It is easy to show that the reacting system can be characterized by three independent reactions, which may be selected as follows:



The $\text{CH}_3\text{OH} \rightarrow \text{HCHO}$ conversion is, of course, much more complicated than this simple model might suggest, involving numerous steps, as reported in Madix (1980) and Lefferts *et al.* (1986). Unfortunately, the kinetic parameters for the majority of these steps are not known. Thus, a consideration of the products formed in small amounts is not possible, though this is not required for the purposes of the present calculations. The case of CO_2 is somewhat different. The amount of CO_2 is commensurable with that of CO , and its formation influences both the yield and the exothermicity of the conversion. Thus, a consideration of CO_2 formation could improve the fidelity of the model, but this is hindered by the lack of kinetic parameters. It is to be noted that under near to industrial conditions CO_2 is formed directly from adsorbed methanol through its interaction with non-dissociated oxygen. The proportion of methanol producing CO_2 is primarily influenced by the inlet concentration, but does not vary too much with the temperature of the catalyst bed, the linear gas velocity or the particle size of the silver catalyst in the investigated range of parameters in question (Lefferts *et al.*, 1986). Accordingly, realistic comparisons can be made between catalyst beds characterized by different grain size profiles, on the basis of results obtained via use of the simplified model (1).

Above 420 K, the rate of reaction 1 is determined by the rate of mass transfer of methanol (Gavrilin and Popov, 1975; Robb and Harriott, 1974):

$$r_1 = \frac{D_{\text{ref}}}{\delta} \left(\frac{T_s}{T_{\text{ref}}} \right)^2 c_1.$$

The loss of formaldehyde is primarily caused by its decomposition in the gas phase (Vitvitskii and Averbuh, 1969):

$$r_2 = A_2 \exp(-E_2/RT_g) c_2.$$

It has been stipulated that the H_2 released in reactions 1 and 2 reacts to form water *instantaneously*, and gaseous H_2 is therefore produced only after the consumption of the O_2 originally present:

$$\begin{aligned} r_3 &= r_1 + r_2 \quad (\text{while } \text{O}_2 \text{ is present}), \\ r_3 &= 0 \quad (\text{after the consumption of } \text{O}_2). \end{aligned}$$

As regards differential mass balance equations, two of them are obviously sufficient to describe the reactor: one for CH_3OH and another for HCHO .

Since the catalyst bed and the streaming gas are not in thermal equilibrium, separate enthalpy balances have to be set up for the two. In this a decision had to be taken about the fate of the enthalpy changes caused by the individual reactions: reaction 1 takes place at the interface, reaction 2 in the gas phase, and reaction 3 in both. It is assumed that the rates of reaction 3 do not differ appreciably in the two phases.

In the setting-up of the data bank for the simulation, extensive use was made of literature data. Changes caused in grain sizes influence primarily the values of λ and ω , which can be accounted for through the expressions:

$$\omega(d) = \frac{\omega_{\text{ref}} d_{\text{ref}}}{d} \quad \text{and} \quad \lambda(d) = \text{const}_1 d + \text{const}_2.$$

For the first expression, the geometrical similarity of grains is assumed. The thermal conductivity of the catalyst bed was estimated on the basis of electric conductivities. The conduction is virtually unhindered inside the crystalline silver particles, and hence the conductivity is predominantly affected by the number, area and quality of the contacts between the particles so that it is necessary to consider the contribution of sintering. The dependence of the conductivity on these factors is complicated, but λ increases as the grain size is increased. It would have been unfounded to choose a non-linear dependence of λ on d .

Accordingly, the reactor model involves the differential equation system (1), the solution of which requires a knowledge of the initial values of the dependent variables at $z = 0$. $c_1(0)$, $c_2(0)$, $u(0)$, $T_g(0)$ and $T_s(0)$ can be regarded as known on the basis of the operating mode of existing technologies. The derivative

$$\left. \frac{dT_s}{dz} \right|_{z=+0}$$

has been computed on the supposition that the enthalpy loss by radiation is equal to the enthalpy arriving by conduction:

$$\sigma \epsilon T_s^4 = \lambda \left. \frac{dT_s}{dz} \right|_{z=+0}.$$

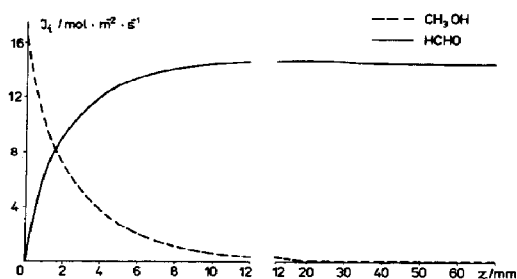


Fig. 1. Component flux profiles developing in the catalyst bed consisting of 2 mm diameter grains.

Radiation is presumed to be the only thermal interaction between the upper surface of the catalyst bed and the gas streaming towards this surface. The re-radiation of gas can be neglected, because of the considerable difference in T_g^4 and T_s^4 . The above equation is therefore approximately correct.

The differential equation system has been integrated by using a modified version of the STIF3 procedure described first by Villadsen and Michelsen (1978).

RESULTS OF THE SIMULATION AND OPTIMIZATION

The first attempt involved the model in which the catalyst bed contained grains with a diameter $d = 2$ mm only. The profiles presented in Figs 1 and 2 show that the silver catalyst exhibits excellent activity, the conversion reaching 50% even at a distance $z = 2$ –3 mm, with full conversion at 1 cm. Qualitatively, the catalyst bed can be regarded as being composed of three zones:

1. "Hot" zone: due to exothermic processes, resulting in heat release, T_g rises sharply; the limit of this zone is characterized by the consumption of O_2 .
2. "Cold" zone: formaldehyde is produced here solely by dehydrogenation; due to the high values of T_g and c_2 , decomposition of the product sets in; T_g remains practically unchanged, as the endothermic reaction, heat transfer and conductivity compensate each other.

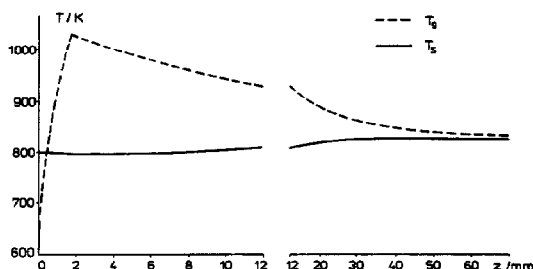


Fig. 2. Temperature profiles developing in the catalyst bed consisting of 2 mm diameter grains.

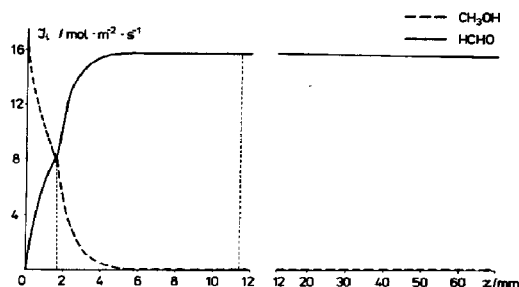


Fig. 3. Component flux profiles developing in the catalyst bed consisting of three layers.

3. "Thermal" zone: the concentration of methanol is very near to zero, and T_g is at a low value, so that chemical reactions do not play a significant role; this zone is dominated by heat transfer and conductivity effects; dT_g/dz remains positive up to nearly the end of this zone, and heat transferred by the gas is therefore conducted backwards into the "cold" zone.

For the reactor to operate in the stationary mode, it is a prerequisite that the enthalpy loss due to the endothermic reactions in the "cold" zone be compensated for by enthalpy gains caused by conduction and heat transfer. Net loss or gain for the whole catalyst bed should be excluded:

$$\left. \frac{dT_s}{dz} \right|_{z=L-0} = 0. \quad (2)$$

This expression is not contained among the boundary conditions, and it can therefore be used to check the computed data. From the value of a non-zero gradient at the end of the catalyst bed, errors in the preliminary suppositions and/or the initial data bank can be deduced. The results obtained in testing the gradient prove the correctness of the supposition that the rates of burning-off of the hydrogen are equal in the interfacial and gaseous phases.

Furthermore, catalyst beds comprising several layers, consisting of different grain sizes, have been simulated. The profiles depicted in Figs 3 and 4 relate

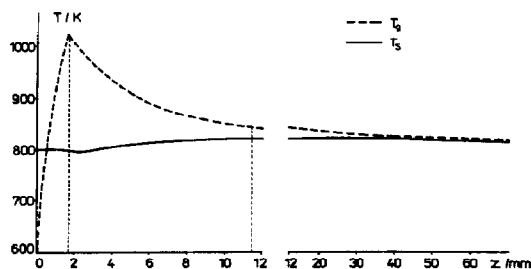


Fig. 4. Temperature profiles developing in the catalyst bed consisting of three layers.

to a catalyst bed comprised of the following zones: a "hot" zone of 2 mm, a "cold" zone of 0.5 mm, and a "thermal" zone of 2 mm diameter grains. As compared with the previous simulation results, it is surprising that the formaldehyde yield is 8.9% higher in this case. It can be conjectured that the higher yield is caused by several beneficial effects: the overheated gas in the "cold" zone loses heat more quickly, and the "back-transfer" of heat by conduction from the "thermal" zone into the "cold" zone is facilitated, in accordance with the requirements of the autothermal stationary operating mode.

It was worthwhile to investigate whether this simple bed arrangement corresponds to the optimum, and if so, to what extent. To answer this question, Pontriagin's principle can be applied (Pontriagin *et al.*, 1961). In this procedure, an extended differential equation system has to be solved, which can be built up as follows:

The "Hamiltonian" of the system can be given as

$$H = \beta \cdot f,$$

where the f_i s are the right-hand-sides of model (1) i.e.

$$\frac{dc_1}{dz} = f_1, \quad \frac{dc_2}{dz} = f_2, \quad \frac{dT_g}{dz} = f_3,$$

$$\frac{dT_s}{dz} = f_4 \quad \text{and} \quad \frac{d^2 T_s}{dz^2} = f_5,$$

and the β_i s are the variables of the following differential equation system:

$$\frac{d\beta_1}{dz} = -\frac{\partial H}{\partial c_1}, \dots, \frac{d\beta_5}{dz} = -\frac{\partial H}{\partial T_s'} \quad (3)$$

(1) and (3) have to be integrated simultaneously. If d is chosen so that H is maximized at any point of the domain $z[0, L]$ the integration results in the optimum concentration, temperature and grain size profiles. The optimization corroborated the previous general picture concerning the advantages of catalyst beds consisting of grains of different mean particle sizes. From this, one point is to be emphasized. If the conditions $0.5 \leq d \leq 2.0$ mm are accepted as lower and upper limits for the mean grain sizes, the catalyst bed operating under the theoretically possible optimum conditions turns out to be essentially that one which is characterized by the profiles of Figs 3–4.

DISCUSSION

Several patents have been published concerning the production of formaldehyde from methanol (see footnote p. 725) in which the catalyst bed is stated to consist of several layers each characterized by a certain mean size of the catalyst grains.

Due to the lack of literature data on this problem, for comparison we had to confine ourselves to such patents, primarily the first two. The grain size distribution claimed in the first two patents and that obtained by computer simulation are to be seen in

Fig. 5. It may be concluded that the results of the optimization are not in contradiction with the claims of the first two patents.

Several particular problems of the simulation will be discussed below.

The concentration, temperature and temperature gradient exhibit different behaviour at the points of contact of two layers of the catalyst bed, e.g. at $z = Z$. As is usual in giving boundary conditions, the functions describing the component and enthalpy transport are required to be continuous even at $z = Z$. For heat conduction in the solid phase, this is true only if the following relation is fulfilled at the point of contact of the layers I and II:

$$\lambda_I \frac{dT_s}{dz} \Big|_{z=Z-0} = \lambda_{II} \frac{dT_s}{dz} \Big|_{z=Z+0}.$$

Since $\lambda_I \neq \lambda_{II}$, grad $T_s(z)$ has a discontinuity point at $z = Z$.

In (quasi-)adiabatic contact catalytic reactors, it can often be observed that the fixed bed and the streaming gas are not in thermal equilibrium. In order to investigate the conditions of deviation from thermal equilibrium, further simulation has been carried out by making use of model (1). The adiabatic operating mode and the validity of equation (2) are required. Through the systematic variation of the parameters, it was investigated which factors the temperature difference between the two phases depends on.

The temperature of the gas phase is determined by the ratios of convection, source and transfer of heat. The quotient of source and convection defines the third Damköhler number:

$$Da_{III} = \frac{\dot{q}_{r,g} L}{c_p u T_0},$$

where $\dot{q}_{r,g}$ is the integral mean value of the expression

$$\sum_{i=1}^{m_g} r_i \Delta H_i^r$$

It is convenient to express the quotient of source and transfer similarly:

$$Fe = \frac{\dot{q}_{r,g}}{\alpha \omega \Delta T} \quad (4)$$

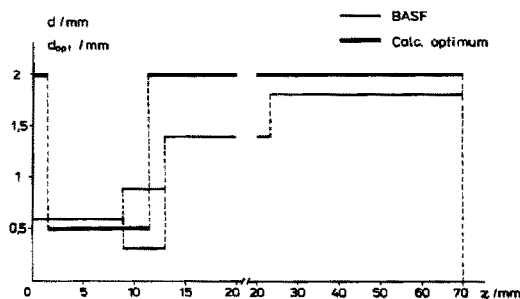


Fig. 5. Axial distribution of grain size, calculated (—) and claimed by F.R.G. Pat. No. 1-231-229 (---).

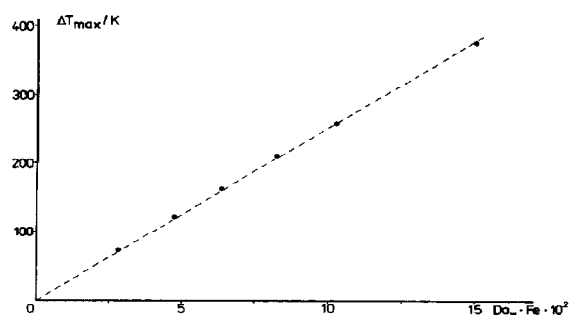


Fig. 6. Correlation of ΔT_{\max} and $Da_{III} \cdot Fe$.

(Dimensionless numbers published in the literature are suitable to express this ratio only after transformation; it is therefore reasonable to consider (4) as a definition.)

Let the deviation from thermal equilibrium be characterized by the maximum of the difference $|T_g(z) - T_s(z)|$, i.e. (ΔT_{\max}) . On the basis of simulation, (ΔT_{\max}) and $Da_{III} \cdot Fe$ can be correlated. The (ΔT_{\max}) vs $Da_{III} \cdot Fe$ plot for $(\Delta T_{\max})(0) = 0$ is shown in Fig. 6.

Figure 6 demonstrates that the two phases are in strict thermal equilibrium only if $Da_{III} \cdot Fe = 0$. This can be achieved most simply if the rates of homogeneous reactions are negligible compared with those of surface reactions. At thermal equilibrium, one enthalpy balance is sufficient, which can often be further simplified. According to the calculations of Beskov (Slinko, 1965), consideration of axial heat conduction offers a marked increase in accuracy only if $Pe < 30$, which occurs rather rarely. Otherwise, model (1) contains only the contributions of convection and chemical source. Reactions in (1) are contact catalytic ones, the rates of which are approximately proportional to ω . This simplified model expresses that in this case the application of numerous layers with different grain sizes can lead to such advantages which can be achieved more easily by ensuring the optimum residence time.

Overall, it can be concluded that model (1) is the simplest one suitable for describing the special features of the reactors in question. The calculations have revealed that, under the conditions presented in the Introduction, novel advantages can be expected from this type of reactor only if homogeneous reactions with non-negligible rates take place in the system.

NOMENCLATURE

- c_j = Concentration of the j th component ($\text{mol} \cdot \text{m}^{-3}$)
- c_p = Heat capacity of the gas mixture at constant pressure ($\text{kJ} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$)
- d = Diameter of catalyst grains (m)
- m = Number of linearly independent chemical reactions
- r_i = Intensive rate of the i th chemical reaction ($\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$)
- u = Linear gas velocity in the catalyst bed ($\text{m} \cdot \text{s}^{-1}$)
- z = Axial distance from bed entrance (m)
- A_i = Pre-exponential coefficient for the i th Arrhenius reaction rate expression
- D = Diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)
- E_i = Activation energy for the i th chemical reaction ($\text{kJ} \cdot \text{mol}^{-1}$)
- ΔH_i^r = Enthalpy change on the i th reaction ($\text{kJ} \cdot \text{mol}^{-1}$)
- J_i = Component flux ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)
- K = Number of components
- L = Length of the catalyst bed (m)
- Pe = Peclet number $Pe = u \cdot c_p \cdot d / \lambda$
- T = Temperature (K)

Greek letters

- α = Heat transfer coefficient ($\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$)
- δ = Thickness of the diffusion boundary layer (m)
- ϵ = Radiation coefficient
- λ = Thermal conductivity of the catalyst bed ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
- ν_{ij} = Element of the stoichiometric matrix for the j th component in the i th reaction
- σ = Stefan-Boltzmann constant ($5.6697 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$)
- ω = Catalyst surface referred to unit volume of the reactor ($\text{m}^2 \cdot \text{m}^{-3}$)

Indices

- g = Gas phase
- s = Solid phase
- ref = Reference value

REFERENCES

- Gavrilin V. N. and B. I. Popov, Oxidation of methanol to formaldehyde on a silver catalyst. *Kinet. Katal.* **6**, 884 (1975).
- Lefferts L., J. G. van Ommen and J. R. H. Ross, The oxidative dehydrogenation of methanol to formaldehyde over silver catalysts in relation to the oxygen-silver interaction. *Appl. Catal.* **23**, 385-402 (1986).
- Madix R. J., *Adv. Catal.* **29**, 38 (1980).
- Pontriagin, Boltianskii, Gamkrelidze and Mishchenko, *Mathematical Theory of Optimal Processes*. GIFML, Moscow (1961). (In Russian).
- Robb D. A. and P. Harriott, The kinetics of methanol oxidation on a supported silver catalyst. *J. Catal.* **35**, 176 (1974).
- Slinko M. G. (Ed.), *Simulation and Optimization of Catalytic Processes*, p. 138. Nauka, Moscow (1965). (In Russian).
- Villadsen J. and M. Michelsen, *Solution of Differential Equation Models by Polynomial Approximation*. Prentice-Hall, Englewood Cliffs, New Jersey (1978).
- Vitvitskii A. I. and A. Ya. Averbuh, Stabilization of the products of the catalytic formaldehyde production. *Zh. prikl. Khim.* **42**, 230 (1969).