

STEADY STATE SIMULATION OF A PACKED BED REACTOR FOR THE PARTIAL OXIDATION OF METHANOL TO FORMALDEHYDE. INFLUENCE OF DIFFUSIONAL PHENOMENA AND CATALYST ACTIVITY DISTRIBUTION WITHIN THE PELLETS

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The scope of this work is to present a real case in which reactor performance predicted theoretically, avoiding the numerical integration within the particle, is compared with experimental findings. The influence of realistic catalytic activity distributions are also studied since minimum extra efforts are needed with the procedure presented in this contribution. The partial oxidation of methanol in a tubular catalytic reactor, studied by Windes *et al.* (1989), giving rise to formaldehyde and carbon monoxide as main reaction products, was used as example for the application of our procedure. Both, inter and intraparticle, diffusional limitations were taken into account. Experimental data and theoretical predictions along the reactor were compared in terms of outlet conversion and temperature profiles showing a fairly good agreement which gives support to the procedure developed in this contribution to predict reactor performance. Furthermore, the effect of different realistic activity distribution function was simulated and its influence on the reactor performance is shown. The obtained results are discussed and some interesting conclusions are withdrawn.

Keywords: Fixed bed reactor; catalytic activity distribution; diffusional limitations

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INTRODUCTION

Fixed bed catalytic reactor design has been the subject of many contributions. Froment and Bischoff (1990), in their well known book, present a thorough analysis of the plug flow pseudo homogeneous model and its limitations are clearly pointed out. It is concluded that, provided the intrinsic kinetic expressions used are realistic and diffusion phenomena – intra and interparticles – are properly taken into account, this model can be safely applied in most circumstances to predict reactor performance. An accurate prediction of effectiveness factor (η) along the reactor length is essential to reduce the heterogeneous system into a pseudo homogeneous one.

Froment and Hofmann (1986) discussed the need of powerful numerical procedures to simultaneously solve the heat and continuity equations in the reactor and within catalyst particles. Diffusion limitations imply the numerical solution of a second order non linear differential equation at each point of the mesh by which reactor length is discretized. According to Feyo de Azevedo *et al.* (1990) the Fickian type model represents a very stiff system of parabolic and eventually elliptic partial differential equations that should be properly handled although is time consuming especially when the dynamic behaviour must be predicted.

When kinetic expressions are linear (pseudo first order) and isothermal conditions within the particle prevail, effectiveness factor can be estimated analytically and the reactor becomes equivalent to the classical plug flow. However for most practical cases Hougen-Watson type kinetic expressions arise when catalytic reactions are to be considered. Under these restraints a numerical scheme must be used to estimate η at each point of the mesh. When Thiele modulus (h) is large special designed procedures, such as spline collocations (Villadsen and Michelsen, 1978) are needed to avoid the instability of the boundary value problem. On the other hand shooting methods like those proposed by Kubicek and Hlavacek (1983) are only stable for moderate values of h depending upon the mathematical nature of the kinetic expression as will be also shown in this contribution.

As a way to optimize the reactor conversion the effect of the catalytic activity distribution within the particles was introduced as external variable. Some contributions have clearly shown that this catalyst distribution function must change along the reactor to optimize outlet conversion. Morbidelli *et al.* (1986) analysis demonstrated that for a single reaction scheme the activity distribution must be chosen in such a way that the average reaction rate must be maximized at each point along the reactor by the properly choose of the activity distribution function ($f(x)$). They

concluded that this goal is achieved by conforming a thin shell of the catalyst within the particle whose position changes along the reactor, at least for the case of a single irreversible n th order reaction. From a practical point of view the industrial production of these type of catalysis particles is not suitable. A more realistic pellet can be produced by controlling the diffusion time of the active species thus obtaining a continuous profile which can be more easily controlled than the shell type. On the other hand in their analysis temperature rise both inside and in the fluid film were not taken into account. Also, as was pointed out more recently by Au *et al.* (1995), most of the theoretical contributions dealing with non uniform catalytic activity pellets are based on linear kinetic expressions since most of the conclusions can be extrapolated, on a qualitative basis, to more complex systems avoiding the numerical integration of the continuity and heat balance equations at the particle level. However when a specific reaction system must be dealt with the above mentioned integration cannot be avoided to predict reactor performance.

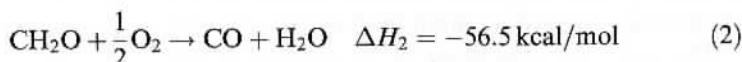
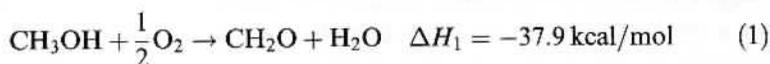
The scope of this work is to present a real case in which reactor performance predicted theoretically, avoiding the numerical integration within the particle, is compared with experimental findings. The influence of realistic catalytic activity distributions are also studied since minimum extra efforts are needed with the procedure presented in this contribution. The partial oxidation of methanol in a tubular catalytic reactor, studied by Windes *et al.* (1989), giving rise to formaldehyde and carbon monoxide as main reaction products, was used as example for the application of our procedure which implies the estimation of η through an approximate technique developed by the authors (Gottifredi *et al.*, 1986 and Gottifredi and Gonzo, 1994). It should be stressed that both, inter an intraparticle, diffusional limitations were taken into account. Experimental data and theoretical predictions along the reactor were compared in terms of outlet conversion and temperature profiles showing a fairly good agreement which gives support to the procedure developed in this contribution to predict reactor performance. Furthermore, the effect of different realistic activity distribution function was simulated and its influence on the reactor performance is shown. The obtained results are discussed and some interesting conclusions are withdrawn.

REACTION SYSTEM

The partial oxidation of methanol, previously studied by Windes *et al.* (1989) in tubular fixed bed catalytic reactor, was chosen in order to compare

experimental conversion data and temperature profiles along the reactor with theoretical predictions obtained with our simplified procedure. The reactor was operated slightly above atmospheric pressure at temperatures ranging between 250 and 380°C. The catalyst was an unsupported Fe₂O₃ and MoO₃ (20 : 80) mixture prepared as irregular shape pellets of 0.00284 m (sphere equivalent diameter with the same volume to external surface ratio). The internal diameter of the reactor was 0.0266 m and its length 0.70 m. Feed composition was a mixture of 5% methanol in air.

According to Windes *et al.* (1989) kinetic behavior of the reacting system can be well described by the following two independent reactions:



They will be referred to as main and side reactions respectively. The intrinsic kinetic expressions obtained experimentally are also given (Windes *et al.*, 1989):

$$r_1 = \frac{A_1 \exp(E_1/RT) p_M^{1/2}}{(1 + A_a \exp(E_a/RT) p_M^{1/2})} \quad [\text{mol of M/s m}^3(\text{cat.})] \quad (3)$$

$$r_2 = \frac{A_2 \exp(E_2/RT) p_F^{1/2}}{(1 + p_F^{1/2})} \quad [\text{mol of F/s m}^3(\text{cat.})] \quad (4)$$

where subindex M and F stand for methanol and formaldehyde respectively. In Table I values of parameters are resumed.

A plug flow pseudo homogeneous unidimensional reactor model was used to predict its performance although the effectiveness factor will take into account both intra and surface concentration and temperature gradients. Accordingly mass and heat balance equations can be written as follows:

$$\frac{dX_M}{dZ} = \Omega \eta_0 r_1 (1 - \varepsilon_b) / F_{M_0} \quad (5)$$

$$\frac{dX_{\text{CO}}}{dZ} = \Omega r_2 (1 - \varepsilon_b) / F_{M_0} \quad (6)$$

TABLE I Parameters

Kinetics	
$A_1 = 6.25 \cdot 10^9 \text{ mol M/s.m}^3 \cdot \text{atm}^{1/2}$	$E_1 = 19 \text{ kcal/mol}$
$A_2 = 5.6 \cdot 10^6 \text{ mol formal./s.m}^3 \cdot \text{atm}^{1/2}$	$E_2 = 16 \text{ kcal/mol}$
$A_a = 27 \text{ atm}_M^{-1/2}$	$E_a = 2 \text{ kcal/mol}$
Catalyst	
$\rho_p = 2000 \text{ kg/m}^3$	$D_{\text{effM}} = 4.9 \cdot 10^{-6} \text{ m}^2/\text{s}$
$\varepsilon_p = 0.57$	$k_{\text{eff}} = 0.1 \text{ cal/m.s.K}$
$D_p = 2.84 \text{ mm}$	
Reactor	
$D_i = 26.6 \text{ mm}$	$L = 0.7 \text{ m}$
$\varepsilon_b = 0.5$	$\rho_b = 1000 \text{ kg/m}^3$
$P_{T_0} = 1.55 \text{ atm (entrance)}$	$P_T = 1.3 \text{ atm (exit)}$
$Y_{M_0} = 0.05$	$F_{M_0} = 0.002404 \text{ mol M/s}$
$C_p = 213.42 \text{ cal/kg.K}$	$G = 2.519 \text{ kg/m}^2.\text{s}$
$T_0 = 523 \text{ K}$	$T_w = 523 \text{ K (uniform)}$
$Re = 300$	$B_{im} = 175$
$U = 53 \text{ cal/m}^2.\text{s.K}$	$B_{re} = 1$

$$\frac{dT}{dZ} = \{ \eta_o r_1 (1 - \varepsilon_b) (-\Delta H_1) + r_2 (1 - \varepsilon_b) (-\Delta H_2) \} / GC_p - \frac{4U}{D_i} (T - T_w) / GC_p \quad (7)$$

where X denotes conversion, Ω the cross section of the reactor tube, η_o overall effectiveness factor for the main reaction, ε_b bed porosity, F_{M_0} methanol flow rate, T temperature, U overall heat transfer coefficient, D_i internal reactor diameter, G flow rate at the entrance and C_p specific heat of the mixture.

It is assumed that pressure decays according to a linear law along the reactor, considering the experimental reactor inlet and outlet pressures.

$$p = p_o - 0.375z \quad (8)$$

and that effectiveness factor for side reaction is always one since this reaction is slow in comparison with main reaction rate.

To estimate η_o it is assumed that the temperature gradient within the particle is negligible (maximum value of $\beta_o \leq 5 \times 10^{-3}$) although heat transfer resistance at the surface of the pellet is taken into account. It should be pointed out that no extra efforts would be needed if non-isothermal pellets had to be dealt with.

The dimensionless continuity equation for the key component (methanol) assuming that effective diffusivities are constant within each pellet is given as

usually:

$$\frac{d}{dx} \left(x^2 \frac{dC}{dx} \right) = h^2 f(x) x^2 R_M(C) \quad (9)$$

where C and $R_M(C) = r_1/r_{1s}$ are the dimensionless concentration and rate of reaction for methanol consumption, related to its surface value at each point in the reactor, $h^2 = (r_{1s} \delta^2 / D_{\text{eff}} C_{M,s})$ being the Thiele modulus and x the dimensionless radial coordinate respectively. (δ being the particle radius).

Equation (9) must be solved in the present case subject to the following boundary conditions:

$$\frac{dC}{dx} = 0 \quad \text{at } x = 0 \quad (10)$$

$$\frac{dC}{dx} = B_{im}(1 - C_s^*)/C_s^* \quad \text{at } x = 1 \quad (11)$$

$$\frac{dT}{dx} = B_{ie}(1 - T_s^*)/T_s^* \quad \text{at } x = 1 \quad (12)$$

where C_s^* and T_s^* are dimensionless surface concentration and temperature with respect to its bulk value at each point of the reactor and B_{im} and B_{ie} denote Biot numbers for mass and energy fluid film transfer.

The activity distribution function ($f(x)$) was also normalized to ensure comparison on fixed amount of catalyst:

$$3 \int_0^1 f(x) x^2 dx = 1 \quad (13)$$

and consequently η is calculated from: and

$$\eta = 3 \int_0^1 R_M(C) f(x) x^2 dx \quad (14)$$

$$\eta_0 = (r_1/r_{10})\eta; \quad h_0^2 = h^2 (r_{10}/r_{1s}) \quad (15)$$

$$C_s^* = \frac{p_{Ms}}{p_{Mo}} = 1 - \frac{h_0^2 \eta_0}{3B_{im}} \quad (16)$$

$$\frac{T_s}{T_0} = T_s^* = 1 + \frac{h_0^2 \eta_0 \beta_0}{3B_{ie}} \quad (17)$$

Usually reactor performance is predicted by a simultaneous numerical solution scheme by which the reactor coordinate (z) is conveniently discretized and at each point Eq. (9) is solved by applying an orthogonal collocation technique (Villadsen and Michelsen, 1978) or a shooting procedure (Kubicek and Hlavacek, 1983). Instead, in this contribution, η_0 is calculated by an approximate procedure which involves a trial and error procedure with algebraic equations (Gottifredi *et al.*, 1986), thus speeding up the numerical integration of the systems (Eqs. 5–8) through a fourth order Runge–Kutta (R–K) routine. Consequently the numerical integration of Eq. (9) is completely avoided.

Nevertheless η_0 approximate values were compared with those obtained by solving Eq. (9) by the shooting method and numerical integration with an R–K routine. In all cases where the numerical scheme remained stable the discrepancy between numerical and approximate η_0 values never exceeded 2%.

Finally reactor conversion and temperature profiles were predicted for five different catalyst activity distribution functions. For the particular case of uniform activity (*i.e.*, $f(x) = 1$) the obtained results can be compared with experimental findings (Schwedock *et al.*, 1989).

It should be stressed that the approximate expression for η_0 allows reactor performance calculation in term of few seconds in a Pentium 100 MH PC while the time increases to few minutes when the numerical integration of Eq. (9) must be performed.

RESULTS AND DISCUSSION

Catalyst Activity Distribution Function ($f(x)$)

Taking into account previous contribution of Li *et al.* (1994) in which realistic $f(x)$ are considered from an experimental basis (Ni on alumina) and also the experimental work of Au *et al.* (1995) the following functions will be analyzed:

a) Uniform (Series 1)

$$f(x) = 1 \quad 0 \leq x \leq 1 \quad (18)$$

b) Parabolic (Series 2)

$$f(x) = (5/3)x^2 \quad 0 \leq x \leq 1 \quad (19)$$

c) Parabolic in a shell (Series 3)

$$f(x) = 4.171(x - 0.3)^2 \quad 0.3 \leq x \leq 1; \quad f(x) = 0 \quad 0 \leq x < 0.3 \quad (20)$$

d) Uniform in a shell (Series 4)

$$f(x) = 1.522 \quad 0.7 \leq x \leq 1; \quad f(x) = 0 \quad 0 \leq x < 0.7 \quad (21)$$

e) Convex profile (Series 5)

$$f(x) = 3 - (5/2)x^2 \quad 0 \leq x \leq 1 \quad (22)$$

Figure 1 is a graphical representation of the catalyst distribution within the pellet showing that while models b, c and d (Eqs. 19–21) concentrate the catalytic activity towards the surface, model e (Eq. 20) produce the opposite effect (*i.e.*, the inner part of the particle is more active than its surface).

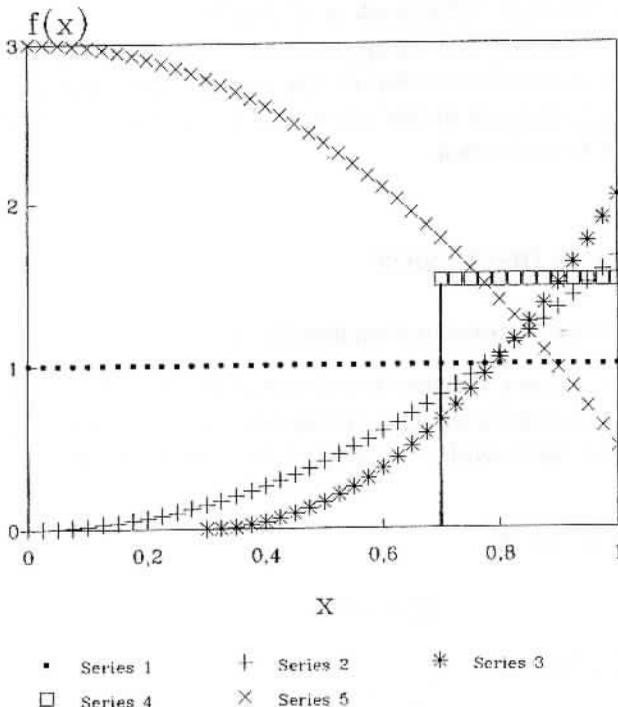


FIGURE 1 Catalyst activity distribution within the pellets according to Eqs. (18)–(22).

Uniform Catalytic Activity

The main scope of the simulation, in this case, was to compare the reactor performance with experimental findings. Schwedok *et al.* (1989) since they were obtained with a fresh catalyst and pellets were prepared from powder of uniform activity.

Figures 2 to 7 show η_o , T_o , $(T_s - T_o)$, $(1 - C_s^*)\%$, methanol conversion and conversion to carbon monoxide as function of the reactor coordinate respectively. In these figures the reactor performance with different activity distribution function (Eqs. 19–22) is also shown.

T_o profile (Fig. 3) is similar to that observed experimentally. The maximum predicted value of T_o is 327°C located at 24 cm from the entrance while the maximum measured value was 335°C located at 30 cm. It should be noticed that the actual reactor is not strictly isothermal in the radial position as was assumed in the model and that the reported temperature was measured at the centerline position of the tube. The main volumetric experimental temperature must be somewhat smaller than the centerline and better agreement would had been observed if predictions had been compared with average temperature. The exit temperature are almost the same (253°C) since no radial gradient are present at this reactor position. Assuming that radial gradients are only important in the region nearby reactor entrance this could also explain the observed discrepancy on T_o maximum position.

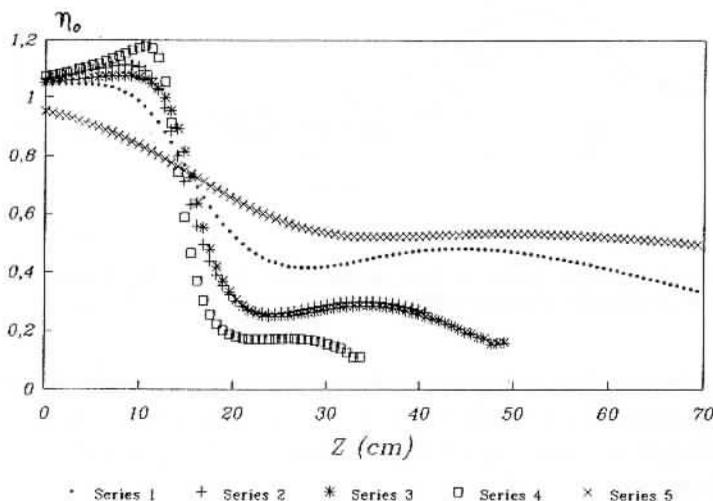


FIGURE 2 Overall effectiveness factor (η_o) as function of reactor coordinate (z) for each activity distribution functions (Eqs. 18–22).

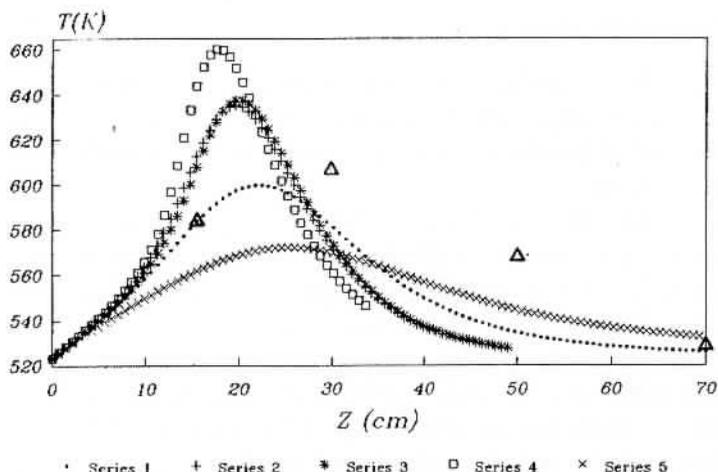


FIGURE 3 Fluid mixture temperature profile (T) along the reactor coordinate (z) for each activity distribution functions (Eqs. 18–22). Centerline experimental values (Δ).

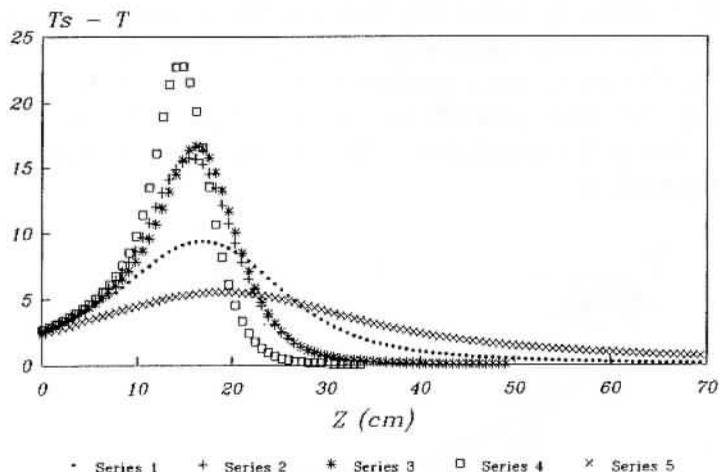


FIGURE 4 Temperature differences, between catalyst pellets (T_s) and fluid mixture (T), along the reactor coordinate (z) for each activity distribution functions (Eqs. 18–22).

Nevertheless conversion profiles (Figs. 6 and 7) are in excellent agreement with experimental observations and exit values are almost the same: 99.7 and 99% for methanol and 4.6 and 4.8% for CO simulated and experimental values respectively.

Transport limitations in this reacting system are clearly seen from Figures 2, 4 and 5. It can be noticed (Fig. 2) that main reaction overall

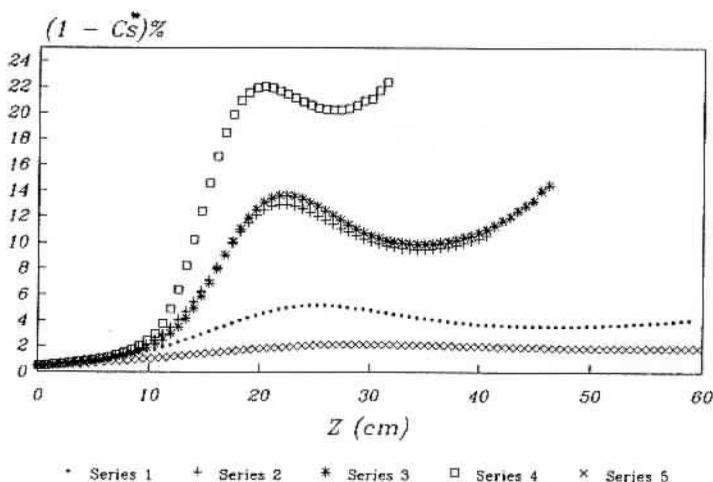


FIGURE 5 Dimensionless concentration percent differences $((1 - C_s^*)\%)$ along the reactor coordinate (z) for each activity distribution functions (Eqs. 18–22).

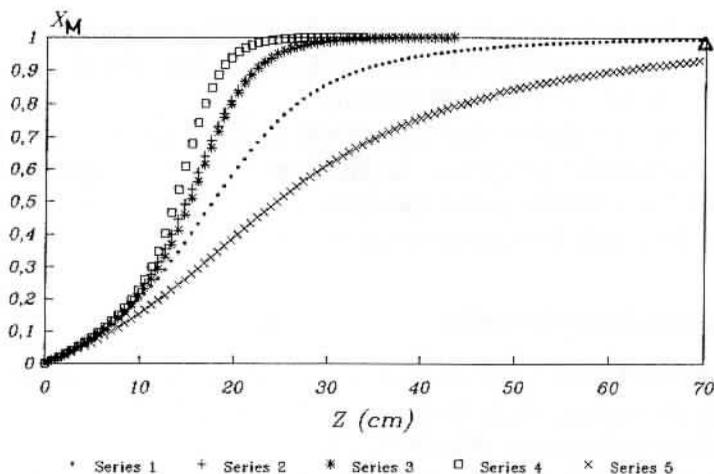


FIGURE 6 Methanol conversion (X_M) along the reactor coordinate (z) for each activity distribution functions (Eqs. 18–22). Outlet experimental value (Δ).

effectiveness varies from 1.042, at reactor entrance where remains almost constant, and then decreases due to heat and mass transport limitations both internal and external (Figs. 4 and 5) to the particle. In this particular case, uniform activity, temperature differences (Fig. 4) are significant, reaching values of 9°C in the region just before the fluid temperature reaches its maximum value (Fig. 3) clearly showing the delay to transfer heat

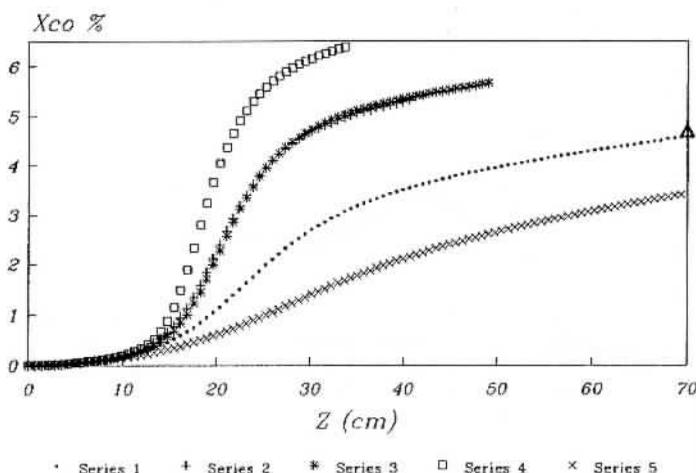


FIGURE 7 Percent conversion to CO ($X_{CO}\%$) along the reactor coordinate (z) for each activity distribution functions (Eqs. 18–22). Outlet experimental value (Δ).

generated by reactions to the fluid caused by the film resistance to heat flow. On the other hand mass transfer external transport limitation (Fig. 5) is not significant in the case of uniform activity.

It can be concluded that the model used to predict the reactor performance for the present case is reasonable and with the approximation introduced to estimate η_0 the numerical effort needed is similar to that required for a truly homogeneous reactor. (see Gonzo and Morales, 1991).

Non Uniform Catalytic Activity

As shown in Figure 1 (Series 2, 3, 4) the catalyst is more concentrated towards the surface while for Series 5 the opposite situation is seen in comparison with the case of uniform activity.

Thus in the first three cases (Series 2, 3, 4) the internal diffusional resistance will be less pronounced than with uniform activity. In Figure 2 it is clearly seen that the overall reaction effectiveness in the region nearby the entrance is always greater than that observed for a uniform activity profile and also the distance from the entrance where η_0 passes through a maximum decreases when compared to the constant catalytic activity. Thus η_0 reaches a value of 1.18 at a distance of only 10.5 cm from the entrance for Series 4 and the corresponding values for Series 2 are $\eta_0 = 1.11$ and $z = 8.4$ cm. On the other hand diffusional internal resistances are more significant for Series 5 where most of the catalyst is distributed in the inner portion of the

particle. It can be seen that the resulting performance is worst than the case of uniform activity and the maximum value of η_o is only 0.95 just at the entrance.

These findings have a direct consequence on conversion. Series 2, 3 and 4 reach 100% methanol conversion at reactor lengths considerably smaller than with a catalyst uniformly distributed. The ratio being 44% for Series 4 and 63% for Series 2. Nevertheless selectivities to formaldehyde are slightly reduced. While for the case of constant activity the selectivity was 95,42% (the experimental value 95,25%) its value decreases to 94,7%, 94,3% and 93,6% for Series 2, 3 and 4 respectively. On the otherhand conversion of methanol for Series 5 is not completed as can be seen in Figure 6. Nevertheless, selectivity is almost unaffected by catalytic activity distribution.

However both T_o and $(T_s - T_o)$ profiles are very much dependent on $f(x)$. When catalytic activity distributions, given by Series 2, 3 and 4, are analyzed fluid temperature reaches considerably higher values than for the case of constant activity. This can certainly be a major drawback since, as pointed out by Windes *et al.* (1989), when temperature difference between the reacting fluid and wall exceeds 170°C the operating conditions are of very difficult control. Maximum T_o values are 599.6 K (33% of reactor length), 635.3 K (30%), 637.2 (31%) and 660.1 K (27%) for uniform and Series 2, 3 and 4 respectively while the corresponding value for Series 5 is 571.8 K (36%).

Moreover, Figure 4 shows that temperature differences between particles and fluid are also strongly affected by $f(x)$. For Series 4 the maximum value can be as large as 22.7°C which can produce hot points that in turn can cause runaway problems in the reactor or considerable loss of products due to cracking side reactions not considered in the model.

The effect of catalytic activity distribution on mass transfer external resistance is shown in Figure 5. As can be seen in all cases where the catalyst is concentrated on the external part of the particle the effect of external mass transport limitation is more significative in the whole section of the reactor. There are two effects. As the entrance methanol concentration is high and the driving force is enough to feed reaction consumption in the pellet. In this region, except for constant activity and Series 5, the overall reaction effectiveness increases and methanol partial decreases in the fluid phase. At a certain point the mass transfer driving force is not sufficient to sustain the reaction and mass transfer limitation is observed. Finally both, reaction effectiveness and external mass driving force decrease maintaining the limitation in the external film. The final increase in film mass limitation

observed in Figure 5 is due to the very low methanol partial pressure in the fluid phase since it has been almost completely consumed.

CONCLUSIONS

The specific case of methanol conversion to formaldehyde with CO formation as side reaction in a tubular non-isothermal reactor was analyzed by simulating the reaction system assuming plug flow pseudohomogeneous model. The internal and external mass and heat transport resistances were taken into account although the model was greatly simplified by using Gottifredi *et al.* (1986) procedure to estimate effectiveness factor of the main reaction which involves the solution of an algebraic equation instead of a second order ordinary boundary value differential equation.

Both uniform and non uniform catalytic activity distribution within the particles were simulated. All the results were presented graphically by plotting η_o , T_o , (T_s, T_o) , $(1 - C_s^*)\%$, X_M and X_{CO} as function of reactor flow coordinate (z).

The model was able to predict reactor performance in close agreement with experimental findings presented by Schwedock *et al.* (1989) in spite of its great simplicity. Temperature profile and exit temperature and conversion predictions show a fair agreement with the experimental reported value as discussed above.

The effect of non-uniform catalytic activity allows an interesting analysis for this particular system. Internal mass transport limitation can be reduced by increasing catalyst concentration towards the surface thus increasing reaction overall effectiveness in regions nearby reactor entrance where an important conversion of methanol is predicted. As net result, this kind of catalysts reduces reactor length needed to achieve full conversion without greatly affecting formaldehyde selectivity.

On the other hand the increase of η_o produces more steep temperature profiles along the reactor since conversion is completed in a reduced length. Moreover temperature differences between particles and fluid stream are considerably larger with these type of catalyst than those with constant activity. These two factors can produced hot reaction points as well as instabilities that can drive the operation near runaway conditions.

Other kind of catalytic pellets with convex activity distribution are not advisable for this particular system. Although they operates reducing both internal and external mass and heat transfer resistences full methanol conversion is not achieved with a reactor of 70 cm.

The method proposed in this contribution can be used to optimize the catalytic distribution function, to study the parametric sensitivity of critical variables and to establish optimal control policies for this particular system. It can be concluded that a number of reactor simulations can take advantage of speeding up computation efforts avoiding the numerical integration of transport equations within the particles, by using the simplified procedure here presented.

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NOMENCLATURE

A_1, A_2	pre-exponential factors
B_{ie}	Biot number for heat transfer
B_{im}	Biot number for mass transfer
C	dimensionless concentration
C_p	specific heat of the mixture
D_{eff}	effective diffusivity
D_t	reactor diameter
E_1, E_2, E_a	activation energies
F	molar flow rate
G	mass flow density
h	Thiele modulus
ΔH	heat of reaction
k_{eff}	effective thermal conductivity
L	reactor length
P	total pressure
r_1, r_2	reaction rate
R_M	dimensionless rate of reaction for methanol
T	temperature
U	overall heat transfer coefficient
x	dimensionless diffusion coordinate
X	conversion
z	dimensional reactor coordinate

Greek Letters

β_0	Prater number
α	particle radius
ε_b	bed porosity
Ω	cross section of the reactor tube
η	effectiveness factor

Subscripts

CO	carbon monoxide
F	formaldehyde
M	methanol
o	global property
w	reactor wall

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