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23 April 2024

12th International Congress of Chemical and Process Engineering

CHISA´96

Praha, Czech Republic, 25 – 30 August 1996

Organised by the Czech Society of Chemical Engineering

556th Event of the European Federation of Chemical Engineering

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EVALUATION OF MASS TRANSFER COEFFICIENTS FOR LAMINAR FLOW IN MONOLITHIC REACTORS WITH CATALYTIC WALLS

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Abstract - The local Sherwood (and Nusselt) numbers in a monolithic reactor with an exothermic reaction occurring at the catalytic wall have been evaluated. Fully developed velocity profiles in round channels, with developing concentration (and temperature) profiles have been considered. The influence of Damköhler number, dimensionless activation energy, Lewis number and adiabatic temperature rise has been investigated; a power law kinetics has been assumed, and the effect of the reaction order has been analysed.

Monolithic reactors have a wide application in chemical engineering, both for pollution control and in production processes (Irandoust and Anderson, 1988; Cybulski and Moulijn, 1994). Their greatest advantages are the very limited pressure drop and the large geometric surface/volume ratio, that is interesting in case of fast catalytic reactions. Villermaux and Schweich (1994) have recently pointed out that this type of device is particularly well suited for environmentally benign processes; its greatest advantages are the very limited pressure drop and the large geometric surface/volume ratio.

Monolithic catalysts are constituted of a large number of small straight parallel channels, in which the flow is laminar, obtained in a ceramic or metallic matrix; the wall is coated with a catalyst, and here heterogeneous reaction takes place. Circular, square and triangular cells are commercially available for ceramic monoliths.

The use of a simple one-dimensional model appears very interesting especially for industrial design applications, because it greatly reduces the complexity of the problem and the computation time; this is particularly true for non-axisymmetrical channels. In order to use a lumped parameter model, the fluid to wall heat and mass transfer coefficients must be available; it has been shown that large differences between the predictions of the model can be obtained using different correlations from literature, and average-value correlations cannot be employed, but local ones are required (Barresi *et al.*, 1993).

A few experimental investigations have been carried out on external mass transfer in tubular reactors, in reactive and non reactive conditions, but the results are contradictory; in some cases the correlations proposed predict abnormally small values, even an order of magnitude lower than theoretical predictions (Cybulski and Moulijn, 1994). It has been shown that under reacting conditions, even a small residual contribution of chemical reaction to the overall rate of the process, essentially controlled by mass-transfer resistance, may be sufficient to strongly reduce the apparent Sherwood number (Villermaux and Schweich, 1994); in addition, by experimental investigation, averaged correlations are obtained. Therefore it appears convenient to evaluate the correct Sh and Nu by solving the correspondent two- or three-dimensional problem with the proper boundary conditions.

Many data are available in the literature on Nu values in compact heat exchangers, whose geometry is very similar to that of a monolith. The heat transfer problem in the entrance region of a duct, for a laminar

flowing fluid, is known as the "Graetz problem" and has been widely investigated in the past, considering a variety of channel shapes and boundary conditions (Shah and London, 1978). Recently, contributions for the simplest case of circular ducts have been added also by Nguyen (1992, 1993) and Pagliarini (1991), who analyzed both the developed and developing flow cases and the conjugate problem. A complete analogy with the Graetz-Nusselt problem for heat transfer in a duct with constant wall temperature has been usually assumed in order to evaluate the Sherwood number in mass-transfer controlled conditions; analogy with the constant wall flux case has also been considered, in order to describe the zone of the reactor before the ignition point. But in the actual case of a fluid reacting at the wall the boundary conditions are different and can significantly modify the mass transfer coefficient; this fact has been demonstrated for an isothermal reactor: the largest deviations occur for non-square channels and non-first-order wall-reaction (Tronconi and Forzatti, 1992). Thus for accurate predictions the correlations for mass (and heat) transfer must be properly evaluated, especially if the data of interest are the species emission concentrations, which are much more sensitive than conversion to the value of the Nu and Sh.

Some results are available in the literature for the case of the isothermal reactor: analytical solutions have been proposed for the entrance region of an isothermal reactor, adopting the Lévêque approximation [see Basic and Dudukovic (1991)], while recently Tronconi and Forzatti (1992) evaluated numerically the Sherwood number for an isothermal first order reaction. They considered three different cell shapes, showing that significant variations in the Sherwood number can occur in dependence of the Damköhler number in circular and triangular cells, while the variation is very small in square cells; for Da→0 and Da →∞ the asymptotic Sh approaches the values corresponding to the Graetz-Nusselt problem with boundary conditions H2 (constant axial flux with uniform peripheral wall heat flux) and T (constant temperature), respectively.

Very little work, on the contrary, has been done for the case of heat and mass transfer in a duct with heat generation at the wall due to a surface chemical reaction.

Some modelling works have shown that with exothermic reactions a spike can occur in the Nu and Sh number correlations, in correspondence of the light-off point: this is a consequence of the creation of a second thermal inlet (Heck et al., 1976; Young and Finlayson, 1976); but the dependence on the system parameters was not investigated. Quest and Mewes (1991), on the other side, have carried out a very thoroughly investigation of mass transfer in tubular reactor, considering also the case of exothermic reactions, but only averaged Sherwood numbers, and for nonisothermal cases only averaged mass fluxes, have been reported.

The aim of this work is to evaluate numerically the local Sherwood and Nusselt numbers in the entrance zone of a round channel, with an exothermic reaction occurring at the wall and to show it dependence on the relevant system parameters; orders of reaction both lower and higher than one will be investigated. The analysis will be limited to the case of cylindrical channels, with constant property fluid and hydrodynamically developed flow.

THE MODEL

A Newtonian constant property fluid, with fully developed parabolic velocity profile, is considered; viscous dissipation is neglected. Thermal conduction in the solid and axial diffusion in the fluid are also neglected: in ceramic monoliths and for the range of Re and Pe values generally adopted in monolithic converters these simplifications are valid; a perfectly adiabatic reactor is considered.

The governing equations are:

$$-2\langle v\rangle\left(1-\frac{r^2}{R^2}\right)\frac{\partial T}{\partial z}+\frac{k}{\rho c}\left\{\frac{1}{r}\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial r^2}\right\}=0 \tag{1}$$

$$-2\langle v\rangle\left(1-\frac{r^2}{R^2}\right)\frac{\partial w_A}{\partial z}+\mathcal{D}_A\left\{\frac{1}{r}\frac{\partial w_A}{\partial r}+\frac{\partial^2 w_A}{\partial r^2}\right\}=0 \tag{2}$$

with the boundary conditions

$$T=T_0 \quad ; \qquad w=w_{A0} \qquad\qquad z=0, \qquad 0<r<R \tag{3}$$

$$\rho\mathcal{D}_A\frac{\partial w_A}{\partial r}=k_0\exp(-E/RT)M_A\left(\frac{\rho w_A}{M_A}\right)^n \qquad z\geq 0 \tag{4}$$

$$-k\frac{\partial T}{\partial r}=\left(-\Delta\widetilde{U}_A\right)k_0\exp(-E/RT)\left(\frac{\rho w_A}{M_A}\right)^n \qquad z\geq 0 \tag{5}$$

Uniform temperature and concentration profiles are assumed at the inlet. A general power-law kinetics is considered, where n is the apparent reaction order:

$$r_A''=-k_0 c_A^n\exp\left(-\frac{E}{RT}\right) \tag{6}$$

The energy and material balances must be solved simultaneously, as the reaction rate and the heat generation rate at the wall depends both on the reactant concentration and the temperature at the wall. Introducing the dimensionless variables

$$\Theta=(T-T_0)/\Delta T_{\mathrm{ad}} \ ; \ \Omega=w/w_0 \ ; \ x=z/(D\,\mathrm{Re}\,\mathrm{Sc}) \ ; \ y=(2r/D)^2 \tag{7}$$

the governing equations and the boundary conditions become:

$$\frac{\partial\Omega}{\partial x}=\frac{8}{(1-y)}\left(\frac{\partial\Omega}{\partial y}+y\frac{\partial^2\Omega}{\partial y^2}\right) \tag{8}$$

$$\frac{\partial\Theta}{\partial x}=\frac{8\,\mathrm{Le}}{(1-y)}\left(\frac{\partial\Theta}{\partial y}+y\frac{\partial^2\Theta}{\partial y^2}\right) \tag{9}$$

$$\Omega=1 \ ; \ \Theta=0 \qquad\qquad x=0,\ 0<y<1 \tag{10}$$

$$\left.\frac{\partial\Omega}{\partial y}\right|_{y=1}=-\Omega^n\frac{\mathrm{Da}}{4}\exp\left(\frac{\gamma\delta\Theta}{1+\delta\Theta}\right) \qquad x\geq 0 \tag{11}$$

$$\left.\frac{\partial\Theta}{\partial y}\right|_{y=1}=\Omega^n\frac{\mathrm{Da}}{4\,\mathrm{Le}}\exp\left(\frac{\gamma\delta\Theta}{1+\delta\Theta}\right) \qquad x\geq 0 \tag{12}$$

Axis symmetry is imposed implicitly, by assuming that the solution is a function of y, that is, an even function of r. The solution is dependent on the kinetic law (the order of reaction) and on four additional parameters:

$$\text{the Damköhler number, } \mathrm{Da}=\frac{k_0 c_{A0}^{n-1}\exp\left(-\frac{E}{RT_0}\right)D}{\mathcal{D}_A} \tag{13}$$

the dimensionless adiabatic temperature rise, $\delta=\Delta T_{\mathrm{ad}}/T_0$

the dimensionless activation energy, $\gamma=E/RT_0$

the Lewis number, Le=Sc/Pr.

The local Sherwood number has been calculated according to the following relationships:

$$Sh = \frac{-4\frac{\partial \Omega}{\partial y}\Big|_{y=1}}{\langle \Omega \rangle - \Omega_w} = \frac{\Omega_w^n Da \exp\left(\frac{\gamma \delta \Theta_w}{1+\delta \Theta_w}\right)}{\langle \Omega \rangle - \Omega_w} \tag{9}$$

By applying the orthogonal collocation method (Michelsen and Villadsen, 1978) along the radial direction, the previous set of equations has been transformed into an initial value system of ordinary differential equations, which has been solved by means of the routine lsode of ODEPACK (Hindmarsh, 1983). The calculated Sherwood numbers have always at least 5 significant figures. The precision was verified by comparing a first solution with a more accurate one, obtained by doubling the collocation points and decreasing ten times the bound on the local error of the integrator.

It can be noted that if Le=1, a similarity exists between the energy and mass balance equations, and the respective boundary conditions; this can be evidenced considering the substitution τ=1-Θ. Therefore, limited to the case of equal Schmidt and Prandtl numbers, Sh=Nu; as concerns the concentration and temperature profiles in the channel, one can be obtained from the other immediately considering that Θ = 1 - Ω.

RESULTS AND DISCUSSION

The dependence of the Sherwood (and Nusselt) number on the Damköhler number, activation energy, adiabatic temperature rise, Lewis number and reaction order has been investigated, and will be discussed in the following. The model equations have been solved for the following range of the parameter values: Da = 0.001 ÷ 100; γ = 0 ÷ 30; δ = -0.5 ÷ 1; Le = 0.5 ÷ 100; n = 0.5 ÷ 2.
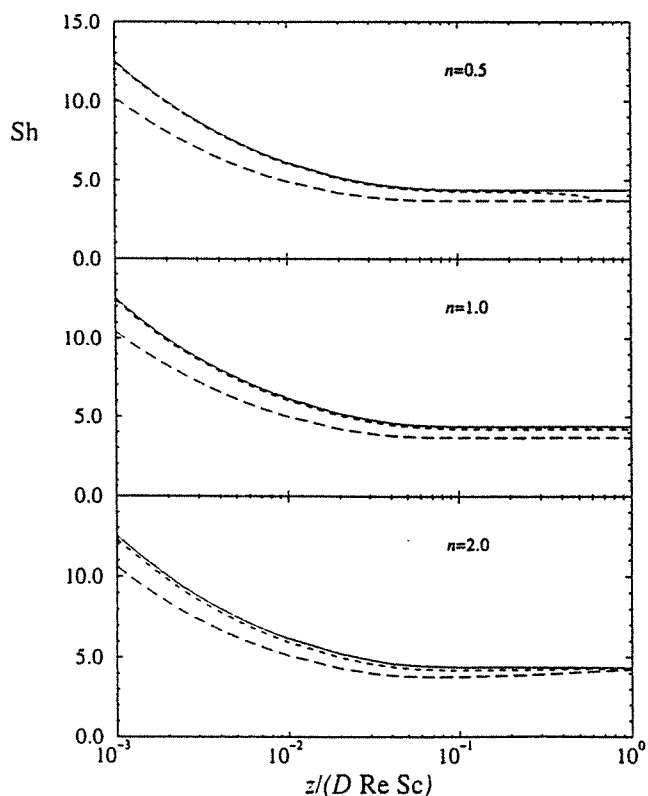

Figure 1. Dependence of local Sh on reaction order n and Damköhler. Athermal reaction (or γ = 0). ——, Da = 0.01; - - - -, Da = 1; − − , Da = 100.
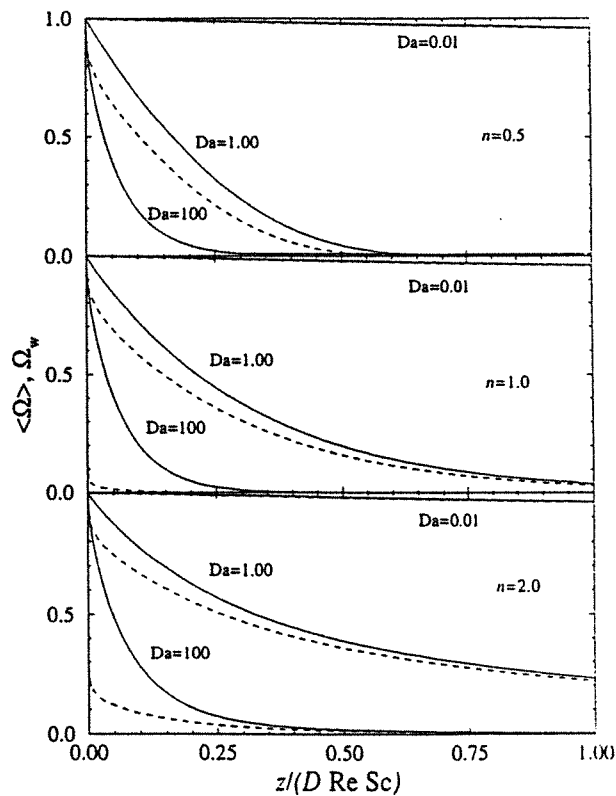
Figure 2. Dependence of concentration profiles on Damköhler and reaction order; conditions as in Fig. 1. ——, average over the cross section; - - -, wall value.

In previous works only first order kinetics has been considered. Here a more general power law equation has been investigated; this is a simplified kinetic law, but still widely used in practical applications. Its use is very convenient to highlight the dependence of the Sherwood number on the kinetic law, as more complex kinetics, included those of the Langmuir-Hinshelwood type, can be approximated by a fractional order kinetics.

In Figure 1 the effect of the reaction order on the behaviour of the Sherwood number is shown in the limit case of an athermal reaction; this is also correspondent to the limit case of reaction with zero activation energy, and therefore independent on the wall temperature (for a constant property fluid). With a first order kinetics, the Sh vs x curves obtained at different Damköhler are parallel, and have different asymptotic values, in the range 4.364 - 3.657 (Da→0 and Da →∞ respectively), as pointed out by Tronconi and Forzatti (1992). A different behaviour is observed for the other orders of reaction, but a dependence on the reaction order can be noted only at high conversion rates (high Da); at very low Damköhler a unique curve is obtained, independent of n.

In Figure 2 the concentration profiles along the

Figure 3. Dependence of local Sh (and Nu) on reaction order n. Exothermic reaction; Le = 1; $\gamma = 20$; $\delta = 1$. Upper graph: Da = 0.1; lower graph: Da = 100.

monolith axis are shown; at high Damköhler values the wall concentration fall to zero quickly, and as a consequence the Sh curve approaches that corresponding to constant concentration; it can be noted that in case of fast reaction the reactant is almost completely consumed when the asymptote in the Sh curve is reached; thus for reactors the asymptotic Sherwood number is of little significance, if the conversion rate is high.

Significant differences can be observed when an exothermic reaction occurs (see Figure 3). At low Da a spike can occur, whose location is slightly affected by the reaction order; at high Da, the Sherwood number becomes independent of n, as shown in the lower graph of Figure 3, where the three curves overlap.

The influence of the Lewis number on the Sherwood and Nusselt number is shown in Figures 4 and 5. A
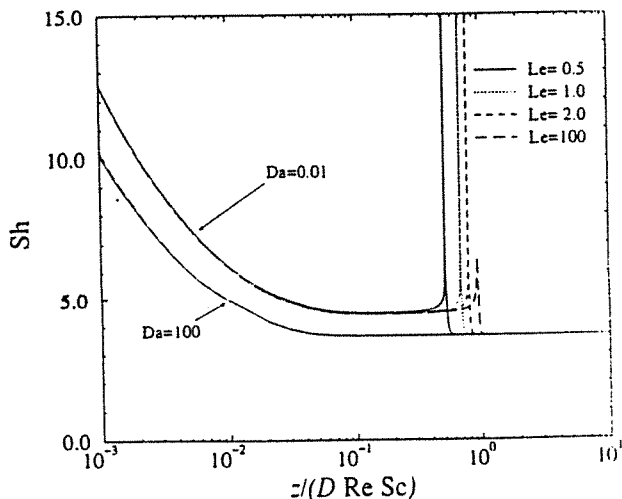

Figure 4. Dependence of local Sh on Lewis number, at low and high Damköhler. $\gamma = 30$; $\delta = 1$; $n = 1$.
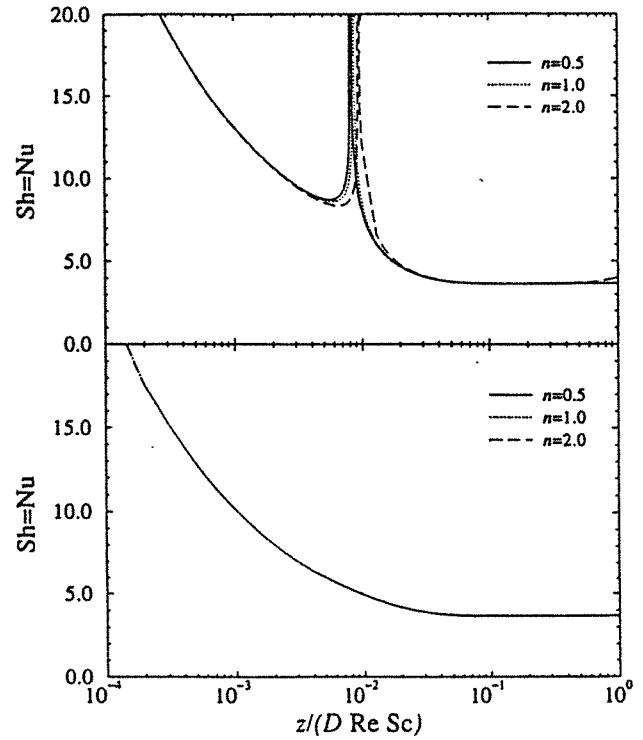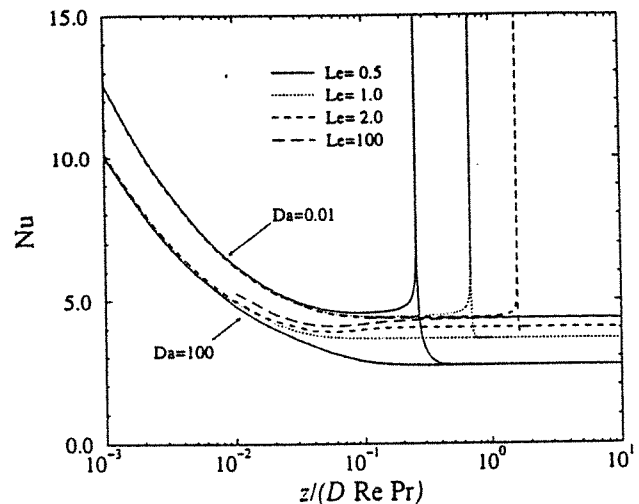
Figure 5. Dependence of local Nu on Lewis number, at low and high Damköhler.; $\gamma = 30$; $\delta = 1$; $n = 1$.

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wide range of Le values, representative of gas and liquid systems, has been considered. The Lewis number takes into account the relative velocity of development of the concentration and temperature profiles; however Nu and Sh are quite sensitive to the Sc/Pr ratio only at low Lewis numbers; in the range of values characteristic of liquid systems, variations have a very small effect.

If Le is different from unit, a different and not symmetrical behaviour occurs for the Nusselt and the Sherwood numbers; it must be noted that in this case the Nu curves are more conveniently plotted using $z/(D\ Re\ Pr)$ as dimensionless coordinate: by this way the curves relative to the entrance zone can be grouped together, similarly to what happens for the Sh curves. In any case, both for the Nu and the Sh number, the location of the spike depends on Le; but while the asymptotic value of the Sherwood number is not affected by the Lewis number, the latter influences the asymptotic Nusselt.

It can be observed that for high values of the dimensionless activation energy the influence of the Lewis number on the asymptotic value is practically independent of Da (see Figure 5), while a small effect of Da is observed for low γ values.

The Damköhler number takes into account the relative rate of reaction at the wall and of species diffusion to the wall; therefore its value strongly affects the behaviour of the Sherwood number, and in particular the ignition in the reactor and thus the location of the eventual spike in the Sh curve; this fact is clearly shown in Figures 3-5. The location of the spike moves toward the inlet when the Damköhler increases; for very high values of Da, the ignition occurs at the very beginning of the channel, and practically all the reactor is in light off conditions. The Da parameter is evaluated at the inlet condition; but the local values of the reaction rate strongly depends on species concentration and temperature; this explain the influence of the kinetic law and of the activation energy and heat effect of the reaction on the position and intensity of the spikes.

Figure 6. Dependence of local Sh (and Nu) on dimensionless activation energy, at low and high Damköhler number. $\delta = 1$; Le $= 1$; $n = 1$.
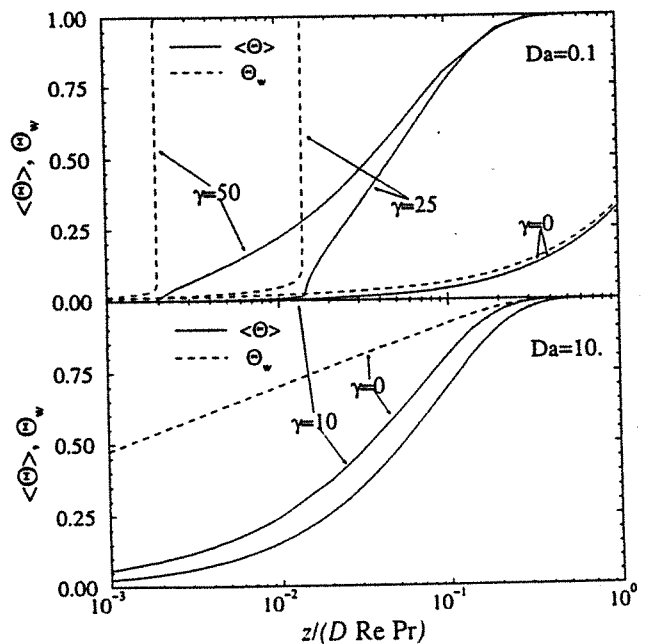
Figure 7. Axial temperature profile for different values of Damköhler and activation energy. $\delta = 1$; Le $= 1$; $n = 1$.

The dimensionless activation energy is a measure of the temperature sensitivity of the reaction, and is the parameter that, with Damköhler, has the strongest effect on the location of the spikes.

Figure 6 shows that an increase of γ ($= E/RT_0$) causes an earlier light off of the reactor, and thus moves the spikes toward the inlet. If ignition occurs at the reactor inlet, Sh becomes very weakly affected by the activation energy value, and a monotonically decreasing curve is obtained in practice. An example of the temperature profile is shown in Figure 7, where the influence of Damköhler and activation energy is evident.
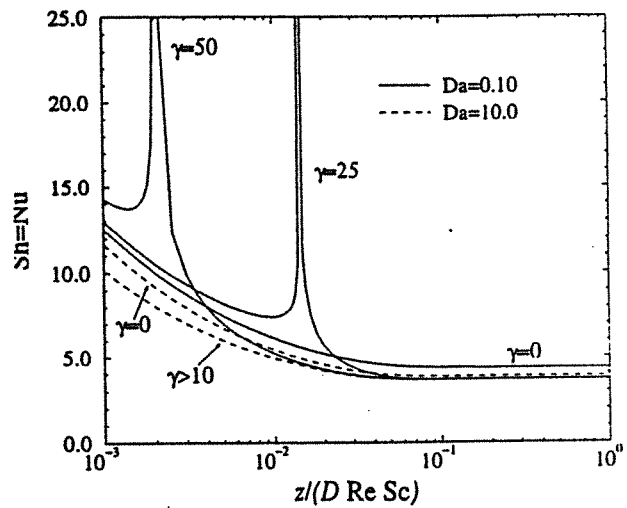
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In the limit of $\gamma \to 0$ (and if the dependence of the physical properties on temperature is neglected), the mass and energy balances become uncoupled, and the Sh curves are equal to those obtained for an isothermal reaction (see Figure 1).

The adiabatic temperature rise accounts for the thermal effect of the reaction; both endothermic and exothermic reactions have been considered. The effect of this parameter is relatively weak; in fact, it must be considered that the values of δ considered are very large for general applications. As expected, δ affects the position of the ignition point, but has small influence on the other regions (Figure 8). Only at intermediate values of the Damköhler some differences are appreciable; in this case the curves corresponding to negative δ values (endothermic reactions), that are generally very close to the limit curve of an athermic reaction, are intermediate between this one and those with positive δ (Figure 9).

The influence of Da, γ and δ on the asymptotic Sherwood and Nusselt number (at Le = 1), is summarised in Fig. 10; the continuous line is the curve corresponding to reactions with no activation energy ($\gamma = 0$), and is also the limit curve for athermic reactions ($\delta \to 0$). The effect of an exothermic reaction is to decrease the asymptotic value: the variation range is comprised, for the circular channel, between 4.364 and 3.657, that is to the same range in which variations occurs for the isothermal case: these limiting values for Da$\to 0$ and Da$\to \infty$ correspond to the solution of the classical Graetz problem with the boundary conditions of constant temperature and constant axial wall heat flux respectively (Shah and London, 1978); in case of non-axisymmetric geometry, the second limit would be that corresponding to constant axial and uniform peripheral wall heat flux, with peripherally varying temperature). For an endothermic reaction the asymptotic values are higher than for the athermal case, but still bounded by the limit value of 4.364. It is evident that the influence of the adiabatic temperature rise is significant only at intermediate values of Da and γ; at high Damköhler, no other parameter is significant.

CONCLUSIONS

The local Sherwood number has been determined in the region of developing concentration profiles in a round channel with a catalytic reaction occurring at
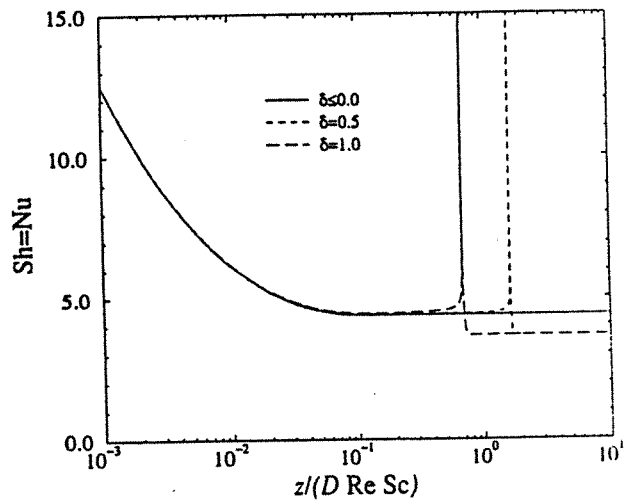

Figure 8. Dependence of local Sh (and Nu) on δ. Da = 0.01; γ = 30; Le = 1; n = 1.
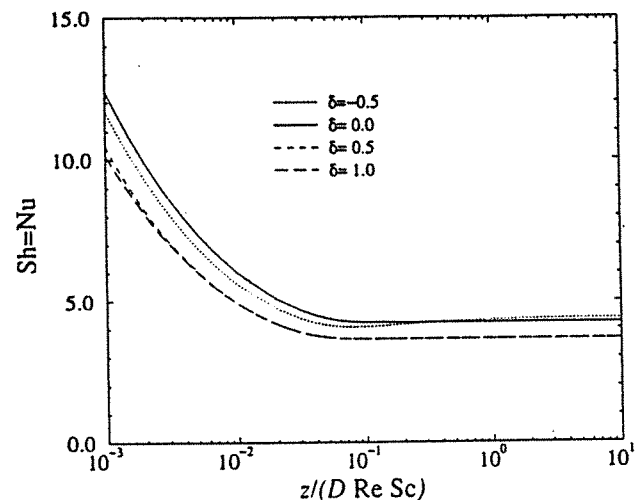

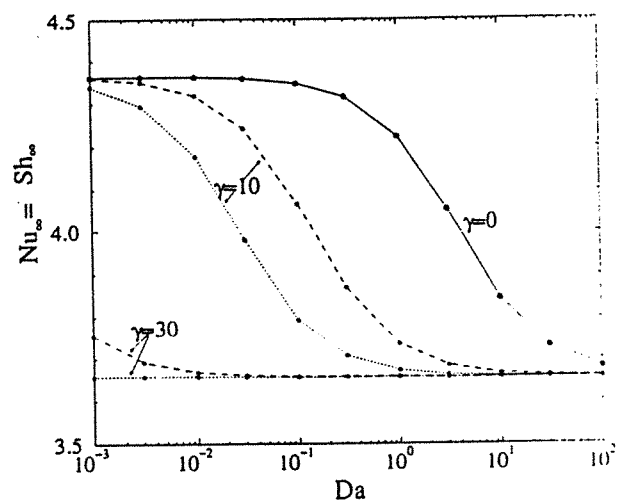Figure 9. Dependence of local Sh (and Nu) on δ. Da = 1. γ = 30; Le = 1; n = 1.

Figure 10. Dependence of asymptotic Nusselt and Sherwood number on Damköhler, dimensionless activation energy (γ) and adiabatic temperature rise (δ), at Le = 1. (———), limit for $\delta \to 0$, or γ=0; (- - - - - -), δ = 0.5; ($\cdots\cdots$), δ = 1.

the wall; both exothermic and endothermic reactions have been considered, and the influence of the kinetic law has also been investigated.

With exothermic reactions the behaviour of the Sherwood number is complex, as ignition can occur in the channel and this causes a spike in the Sh curve, with the formation of a second inlet and a large increase in the transfer coefficient.

The position and intensity of the spikes depend strongly on Damköhler and activation energy, while reaction order, Lewis number and adiabatic temperature rise have a weaker effect; at high Damköhler numbers, ignition occurs at the inlet and a monotonically decreasing curve is obtained in practice.

In isothermal conditions in a round channel at higher Da correspond lower values of the Sherwood number; if light off occur in the reactor, the transition to lower values occur after the spike.

The analogy between heat and mass transfer holds true only at Le = 1; in the other cases the effect of the Lewis number is different for Sh and Nu.

It must be noted that in most chemical engineering applications the use of the asymptotic values would lead to an underestimate of the phenomenon, because large part of the reaction may occur in the zone in which the thermal profile is developing; in some cases no asymptote can be reached, because the reactants are completely consumed before. The accurate evaluation of the heat transfer in reactors in which exothermic reactions are carried out is required in cases in which hot spots can occur and deteriorate severely the characteristics of the catalyst or the performances of the reactor; in this respect it can become important to predict correctly the occurrence of a new thermal inlet corresponding to the light off of the reactor.

Work is currently in progress to extend the current analysis to the case of fluids with temperature variable properties; the influence of the developing velocity profile will be also taken into consideration.

NOMENCLATURE

$\hat{c}$	specific heat
c_A	molar concentration
D	channel diameter
$\mathcal{D}_A$	diffusivity
Da	Damköhler number
E	activation energy
k	thermal conductivity
k_0	kinetic constant
Le	Lewis number (Sc/Pr)
M	molecular weight
n	reaction order
Nu	Nusselt number
R	channel radius
R	gas constant
r	radial coordinate
r_A''	surface reaction rate, def. in (1)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

T	temperature
ΔT_{ad}	adiabatic temperature rise
$\Delta \tilde{U}_A$	internal energy change
v	fluid velocity
w	mass fraction
x	dimensionless axial coordinate, def. in (13)
y	dimensionless radial coordinate, def. in (13)
z	axial coordinate

Greek symbols

γ	dimensionless activation energy, def. in (8)
δ	dimensionless adiabatic temperature rise, def. in (13)
ρ	density
Θ	dimensionless temperature, def. in (7)
Ω	dimensionless concentration, def. in (7)
0	initial conditions
∞	asymptotic value
w	wall conditions
< >	average over the cross section

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