Issues in the scaling of exothermic reactions: From micro-scale to macro-scale

K. Sreenath, S. Pushpavanam*

Chemical Engineering Department, IIT Madras, Chennai 600036, Tamil Nadu, India

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ABSTRACT

Micro-reactors are characterized by systems in which at least one dimension is of the order of a few hundred microns. These systems have a high surface area to volume ratio and hence can loose heat effectively to the ambient. This feature renders them as preferable for conducting exothermic reactions which can exhibit runaway behavior. In this work we study the oxidation of 2-octanol using nitric acid as a typical representative system of an exothermic competitive-consecutive reaction system.

A dimensionless analysis of the governing equations is carried out under realistic assumptions and two dimensionless numbers Re and Da are identified which determine the system behavior. We analyze two situations (1) Thermally developing flow and (2) Thermally developed flow. We show that both Re and Da cannot be maintained similar for a micro-system and a macro-system. It is shown that, Da a dimensionless residence time is more important and must be maintained similar between two systems to obtain similar conversions. We also show that when Da is same in two systems whose dimensions are different by three orders of magnitude, the temperature rise in the micro-system is lower than that in the macro-system. Under these conditions the micro-reactor is preferred as it can help us avoid runaway behavior. When the Re is maintained the same in the two systems we see that the micro-reactor shows no significant conversion and there is no appreciable temperature rise in it. When the effect of axial dispersion is included the performance of the micro-system is not affected as compared to that of the macro-system, when Da is matched.

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1. Introduction

Micro-reactor technology allows us the possibility of "scaling-out" or "numbering up" as a means of increasing productivity. This helps us avoid the classical issue of "scaling up" in reactor design which can be challenging as the time scales of both hydrodynamics and reactions cannot be matched at different geometric scales. Micro-reactors find applications in the production of *fine and specialty chemicals*: low volume, high-value products that are selected on the basis of specific molecular properties or functional characteristics. These have applications in industries spanning pharmaceuticals, flavors and essences, agro-chemicals, detergents, vitamins and photographic chemicals [1–3]. These micro-reactors can be connected via a micro-fluidic network for optimal production and efficient separation of species. Scale-up by replication has already proven its value in research and development, and it has proven to be a platform for high-throughput screening of products [4].

Micro-reactors are characterized by systems where at least one of the dimensions is of the order of a few hundred microns. These reactors have a high surface area to volume ratio and hence they are

expected to have better heat transfer characteristics than macro-reactors. Earlier studies suggest that relative to macro-channels, transition to turbulence may occur at a much lower Reynolds number (Re) in micro-channels and the conventional relations for friction factor of macro-channels may not be applicable to micro-reactors [5]. Transition was observed to occur at a critical Reynolds number between 300 and 900, depending on tube material. Based on local velocity measurements using micro-PIV in rectangular silicon micro-channels of hydraulic diameter 50–300 μm, Zeighami et al. [6] concluded that the onset of transition occurs in the Reynolds number range 1200–1600. Lee and Ho [7] concluded that the macro-scale thermo-fluidic relationships are applicable to micro-scale systems under the assumption of developing laminar flows. Qu and Mudawar [8] also analyzed using conventional equations a micro-channel heat sink and concluded that conventional Navier–Stokes equations and the energy equation can adequately predict the fluid flow and heat transfer characteristic of micro-channel heat sinks. Rands et al. [9] used two independent approaches to identify transition from laminar to turbulent flow. Both methods showed transition to occur in the Reynolds number range 2100–2500, consistent with macro-scale tube flow behavior.

Recently investigators have been analyzing performance of reactions in micro-systems. The enhancement of reaction selectivity can be challenging due to the complexity of chemical reactions. Many reaction networks are strongly exothermic and temperature

* Corresponding author. Tel.: +91 044 22574161; fax: +91 044 22570509.
*E-mail address:* spush@iitm.ac.in (S. Pushpavanam).

sensitive. Although exothermic reactions are common in chemical engineering processes, they are hard to treat, especially when the reactions are fast, since the heat liberated can change the temperature of the system instantaneously. Temperature is an important factor to control reactor selectivity [10]. Rosenfeld et al. [11] used micro-mixers to control the molecular weight distribution in continuous two-stage nitroxide-mediated co-polymerization. Micro-reactors can improve the selectivity, as here the temperature is well controlled. The mixing performance in these systems can be intensified by the presence of micro-structures [12]. Ducry and Roberge [13] have studied the nitration of phenol in a micro-reactor system and concluded that micro-reactors show enhanced process safety features combined with improved yields.

A review of developments in micro-reaction technology by Hessel [14], reports that Merck has successfully run a production process involving an organometallic reaction using five miniature mixers for about five years until the life time of the final product ended. The yield was increased by 20% compared with a batch production process. A remarkable aspect of this process is that a former cryogenic process could now be conducted at room temperature without any loss in selectivity. This was possible only because the heat transfer characteristics in the micro-reactor were better than that in macro-reactors.

Scale-up in chemical engineering is done when the ratio of the model system to the actual system is around a factor of five or ten. The scaling factor of a macro-reactor to a micro-reactor is around 1000. With a view to understanding how the behavior of the micro-reactor differs from that of a macro-reactor we theoretically analyze a competitive-consecutive reaction under non-isothermal conditions. In the present study, we compare the behavior of the micro-reactor and the macro-reactor through a dimensional analysis. Our focus is on how the heat transfer characteristic scales, for different conditions of operation and how this influences the progress of the reaction. The paper is organized as follows: in Section 2 we describe the reaction system and justify the basis of the main assumptions. The governing equations are described here. In Section 3 we present the basis of the analysis for various conditions and establish the scaling relationship of the dimensionless heat transfer coefficient with the geometric parameters. We see that total similarity is not possible and analyze different conditions of partial similarity on system behavior. Section 4 describes the results of the simulations of various conditions and we finally summarize our findings in the concluding section.

2. Modeling assumptions and governing equations

We consider a representative reaction system where nitric acid oxidises 2-octanol. In this system the conversion of 2-octanol (A) by nitrosonium ion (B) gives 2-octanone (P) which further decomposes to carboxylic acids (X). The thermodynamic and kinetic parameters for the simulations are obtained from the work of Van Woezik and Westerterp [15], who considered this system under semi-batch conditions. This system can be represented generically as:

$$A + B \xrightarrow{k_1} P + 2B$$

$$P + B \xrightarrow{k_2} X$$
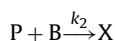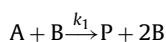
Although, this is a heterogeneous two phase liquid–liquid system we model the system as a pseudo-homogeneous reaction and the reactions are considered to be elementary. We assume plug flow conditions prevail in the reactor. The validity of this assumption stems from the work of Merrill and Hamrin [16]. They have compared the behavior of a plug flow reactor with a laminar reactor for the case of isothermal operation, under constant wall temperature and adiabatic conditions. They conclude that diffusion effects can be safely neglected, i.e., a plug flow reactor is a good approximation of a laminar reactor when $D_{mol} \times t_{ch}/Y^2 < 3 \times 10^{-3}$. Here D_{mol} is the diffusion coefficient, t_{ch} is a characteristic time and Y represents a characteristic length scale. Under these conditions the temperature and the concentration can be considered as constant in the lateral direction. In the present study, the parameters are chosen such that this condition is satisfied. Should this condition be violated axial dispersion effects would have to be included.

The equations governing the system are obtained considering the concentration and temperature changes only in the flow direction (i.e., z-axis). As discussed above we assume that the concentration and temperature is uniform in the lateral direction. Alternately we can view these as describing an ideal PFR. Under these conditions the governing dimensionless steady-state equations described by the component and energy balance along the length of the reactor are:

$$\frac{dC_A}{dz} = -Da_1 e^{(\theta/(1+\varepsilon\theta))} C_A C_B \tag{1a}$$

$$\frac{dC_B}{dz} = Da_1 e^{(\theta/(1+\varepsilon\theta))} C_A C_B - Da_2 e^{(r\theta/(1+\varepsilon\theta))} C_P C_B \tag{1b}$$

$$\frac{dC_P}{dz} = Da_1 e^{(\theta/(1+\varepsilon\theta))} C_A C_B - Da_2 e^{(r\theta/(1+\varepsilon\theta))} C_P C_B \tag{1c}$$

$$\frac{dC_X}{dz} = Da_2 e^{(r\theta/(1+\varepsilon\theta))} C_P C_B \tag{1d}$$

$$\frac{d\theta}{dz} = Da_1 B_1 e^{(\theta/(1+\varepsilon\theta))} C_A C_B + Da_2 B_2 e^{(r\theta/(1+\varepsilon\theta))} C_P C_B - \beta(\theta - \theta_{amb}) \tag{1e}$$

where $r = E_2/E_1$, $\varepsilon = E_1/RT_f$:

$$Da_1 = k_{10}e^{-E_1/RT_f}C_{A_0}\tau; \quad Da_2 = k_{20}e^{-E_2/RT_f}C_{A_0}\tau;$$

$$\tau = \frac{L}{\bar{U}}; \quad \theta = \frac{E_1}{RT_f^2}(T - T_f);$$

$$B_2 = \frac{E_2 C_{A_0}(-\Delta H_2)}{RT_f^2 \rho C_P}; \quad \beta = \frac{\tau}{D}\left(\frac{h_{overall}}{\rho C_P}\right);$$

$$\theta_{amb} = \frac{E_1}{RT_f^2}(T_{amb} - T_f); \quad B_1 = \frac{E_1 C_{A_0}(-\Delta H_1)}{RT_f^2 \rho C_P}$$

In our model we have included the Arrhenius temperature dependency of the reaction and considered the two reactions to have different activation energies and heats of reaction. We assume that the physical properties are constant throughout the process.

3. Theoretical analysis

The key dimensionless parameters which depend on the length scales, time scales and govern the system behavior are:

(i) Reynolds number (Re) which characterizes the hydrodynamics of fluid flow.
(ii) Damkohler number (Da) characterizing reaction time and hydrodynamic residence time.
(iii) Heat loss parameter (β), characterizing the heat transfer to the ambient.

The parameters B_1 and B_2 representing the heats of reaction, are independent of the length scales prevailing in the system. The Reynolds number determines the hydrodynamics of the system. When this number is equal in two systems the flow regimes are identical in them.

It is observed that the heat loss parameter (β) is directly proportional to the over all heat transfer coefficient ($h_{overall}$) and inversely proportional to the diameter (D), i.e.

$$\beta \propto \frac{h_{overall}}{D} \tag{2a}$$

In addition to this it depends on 'τ' as well. The heat flux from the reactor is directly proportional to the temperature difference and the over all heat transfer coefficient. The latter depends upon the individual resistances offered, i.e.

$$\frac{q}{A} = h_{overall}(T - T_{amb}) \tag{2b}$$

and

$$\frac{1}{h_{overall}} = \frac{1}{h_i} + \frac{x}{k} + \frac{1}{h_o} \tag{2c}$$

where $h_i{}^{-1}$ is the resistance offered by convection across the internal film, $h_o{}^{-1}$ is the resistance offered by convection across the external film, x/k is the resistance offered by conduction across the solid wall.

In this study we consider two situations, here:

(1) TUHD: this is the case when the flow is thermally not developed but hydrodynamically developed (TUHD). This is particularly valid in the case of liquid phase reactions as liquids have a high Prandtl number, Pr. The average Nusselt number Nu is given here by [17]:

$$\text{Nu} = \frac{h_{overall}D}{k} = 1.86(\text{Gz})^{1/3} = 1.86\left(\frac{D}{L}(\text{Re})(\text{Pr})\right)^{1/3} \tag{3a}$$

(2) TDHD: here the flow is assumed to be fully developed both thermally as well as hydrodynamically (TDHD). For the case when the surface temperature is a constant we have the average Nu number as [18]:

$$\text{Nu} = \frac{hD}{k} = 3.66 \tag{3b}$$

The dimensionless heat transfer coefficient (β) is inversely proportional to the hydraulic diameter (D_H) when the Da (or τ) and the heat transfer coefficient of the two systems are equal. The parameter β depends on the heat transfer coefficient as well as the residence time or Da. These quantities are determined by the operating conditions.

We now investigate how the parameter 'β' (which depends on Re and Da) scales under different conditions of system operation. The system hence has only two independent parameters Re and Da. In the first case we consider both Re and Da to be the same for both reactors. In the second case we consider only Re to be same and do not impose the condition that Da is to be matched. We then consider the case when Da is matched between the two systems and Re is not matched. For each of these cases which are physically realizable we analyze the system under the two conditions of TUHD and TDHD as discussed above.

3.1. Case 1: matching both Re and Da

Consider a situation where we have the same Reynolds number and Da but one corresponds to a micro-reactor and the other to a macro-reactor. Under the condition $\text{Re}_{mic} = \text{Re}_{mac}$, when the physical properties of the fluids are the same in both systems we have:

$$D_{mic}U_{mic} = D_{mac}U_{mac} \tag{4a}$$

If in addition to this we impose $\text{Da}_{mic} = \text{Da}_{mac}$, the residence times are equal, i.e., $\tau_{mic} = \tau_{mac}$:

$$\frac{L_{mac}}{U_{mac}} = \frac{L_{mic}}{U_{mic}} \tag{4b}$$

From the above equations we have:

$$\frac{D_{mic}}{D_{mac}} = \frac{U_{mac}}{U_{mic}} = \frac{L_{mac}}{L_{mic}} \tag{4c}$$

Since typically we have $L_{mac} \gg L_{mic}$, (4c) implies $D_{mic} \gg D_{mac}$. This is a contradiction as the diameter of the micro-channel must be less than that of the macro-channel. So it is not possible to realistically have the same Re and Da for a micro- and a macro-reactors. This situation where it is not possible to ensure complete similarity by matching all dimensionless groups is discussed extensively [19,20].

3.2. Case 2: matching only Reynolds number for micro- and macro-reactors

Here we analyze the case where Re is equal for both the systems. We study this case by considering the two conditions discussed above:

3.2.1. Condition TUHD: Flow is thermally developing, but hydrodynamically developed

In this case the heat transfer coefficient depends on the flow conditions prevailing in the reactor. The average Nusselt number for developing laminar flow in the reactor is a function of Re and Pr number. The heat transfer coefficient of fluid flowing in the system is now a function of Graetz (Gz) number as discussed earlier and is given by (3a):

Since the Re numbers are maintained equal we have:

$$\frac{h_{mic}}{h_{mac}} = \left(\frac{D_{mac}}{D_{mic}}\right)^{2/3}\left(\frac{L_{mac}}{L_{mic}}\right)^{1/3} \tag{5a}$$

Here we have different Da numbers, i.e., different 'τ'. Using Eq. (4a) we has from the definition of residence time:

$$\frac{\tau_{mac}}{\tau_{mic}} = \left(\frac{D_{mac}}{D_{mic}}\right)\left(\frac{L_{mac}}{L_{mic}}\right) \tag{5b}$$

$$\frac{\beta_{mic}}{\beta_{mac}} = \left(\frac{D_{mac}}{D_{mic}}\right)^{2/3}\left(\frac{L_{mic}}{L_{mac}}\right)^{2/3} \tag{5c}$$

It follows that if the L/D ratio is same for both reactors then the dimensionless heat loss parameter is same for the two systems.

$$\beta_{mic} = \beta_{mac} \tag{5d}$$

We also see that the residence time of the macro-reactor is much higher than that of the corresponding micro-reactor when the Re is matched for the two systems.

3.2.2. Condition TDHD

For this case as discussed earlier for a constant surface temperature we have from (3b):

$$\text{Nu} = \frac{h_{overall}D}{k} = 3.66$$

The relation assumes that the flow is thermally and hydrodynamically developed. The $h_{overall}$ is calculated using the above relation and is higher for a micro-reactor compared to a macro-reactor. Here the Reynolds numbers are same but residence times for the two systems are different $\tau_{mic} \neq \tau_{mac}$. From Eq. (5b), we clearly see that $\tau_{mac} \gg \tau_{mic}$. The residence time in the macro-reactor is significantly more than that prevailing in the micro-reactor as D_{mic} and L_{mic} are much less than L_{mac} and D_{mac}.

Under these conditions the heat transfer coefficient for the micro-reactor is much higher than the macro-reactor as it varies inversely with the hydraulic diameter. The dimensionless heat loss parameter (β) for a micro-reactor and the macro-reactor when they have the same aspect ratio scales as:

$$\frac{h_{mic}}{h_{mac}} = \frac{D_{mac}}{D_{mic}} \qquad (5e)$$

$$\frac{\beta_{mic}}{\beta_{mac}} = \left(\frac{D_{mac}}{D_{mic}}\right)\left(\frac{L_{mic}}{L_{mac}}\right) \qquad (5f)$$

$$\beta_{mic} = \beta_{mac} \qquad (5g)$$

From Eq. (5e) the heat transfer coefficient is more for micro-reactor than a macro-reactor as $D_{mic} \ll D_{mac}$ However the dimensionless heat loss parameter β [Eq. (5g)] is same for both micro- and macro-reactors under the conditions of fully developed flow.

3.3. Case-3: matching only Damkohler (Da) numbers for micro- and macro-reactors

This implies that the residence times are equal for the two systems, i.e., $\tau_{mic} = \tau_{mac}$ as long as we use the same T_f. Here again we analyze the behavior of the system for two conditions.

3.3.1. Condition TUHD
Assuming that the aspect ratio of the two systems are equal we can show as before that:

$$\frac{h_{mic}}{h_{mac}} = \left(\frac{D_{mac}}{D_{mic}}\right)^{1/3} \qquad (6a)$$

Hence we have:

$$\frac{\beta_{mic}}{\beta_{mac}} = \left(\frac{D_{mac}}{D_{mic}}\right)^{4/3} \qquad (6b)$$

From this it is clear that the dimensionless heat loss parameter for the micro-reactor is again much more than that of the macro-reactor as $D_{mac} \gg D_{mic}$.

3.3.2. Condition TDHD
Here the Nu number for a fully developed laminar flow when the surface temperature is constant can be approximated to a constant value of 3.66. For this condition the residence times (τ) are equal for the two systems but they have different Re numbers. We see there that the dimensionless heat transfer coefficient parameter scales as:

$$\frac{\beta_{mic}}{\beta_{mac}} = \left(\frac{D_{mac}}{D_{mic}}\right)^2 \qquad (6c)$$

It is clear that $Re_{mic} \ll Re_{mac}$ as the length scales of the macro-reactor is more than that of the micro-reactor. From Eq. (6c), the dimensionless heat loss parameter (β) for the micro-reactor is inversely proportional to the square of the diameter and is hence significantly higher for the micro-reactor.

4. Results and discussion

We now discuss how the simplified one-dimensional model predicts the behavior of the two reactors: the micro- and the macro-reactors for the various cases and flow conditions. This is obtained by simulations of the dimensionless governing Eqs. (1(a))–(1(e)) in MATLAB 7.4.0. This predicts the dimensionless concentrations and temperatures along the axial direction at steady-state. For all simulations we have used $B_1 = 44$, $B_2 = 149.2$. These values are obtained from the parameters mentioned in Van Woeziek and Westerterp [15].

We first consider the case when the Reynolds numbers are the same for both the micro- and macro-reactors. We first analyze the situation by considering the TUHD case Fig. 1 depicts the variation of dimensionless concentration of species and temperature with axial position when the Reynolds number for the two systems is chosen to be equal to 10. For this case $\beta_{mic} = \beta_{mac}$, even though both the dimensionless heat loss parameters are same, the micro-reactor has a higher heat transfer coefficient [Eq. (3a)] than the macro-reactor. Also we have calculated the thermal entrance length using equation [21]:

$$L_e = 0.05 \times D \times (Re \times Pr) \qquad (7)$$

This thermal entry length for the conditions studied in this work is such that for the micro-reactor it is around 0.05 m, whereas for the macro-reactor it is 2.02 m. For the purposes of the simulation study we have used 0.05 m and 1.25 m as the lengths of the micro- and macro-reactors respectively. This choice helps us to consider both the conditions of TUHD and TDHD for different choices of Pr.

In this case the Da or residence time for the micro-system is lower than that for the macro-system by around three orders of magnitude for the same L/D ratio. Consequently only an insignificant amount of reaction occurs in the micro-reactor (Fig. 1a) as compared to the macro-reactor (Fig. 1b). In these figures the axial position has been made dimensionless with respect to the individual reactor length and hence both go up to unity. Since the conversion is very low there is no increase in the temperature in the micro-reactor. We observe that for the macro-reactor the temperature rises rapidly to a maximum and species 'A' is completely
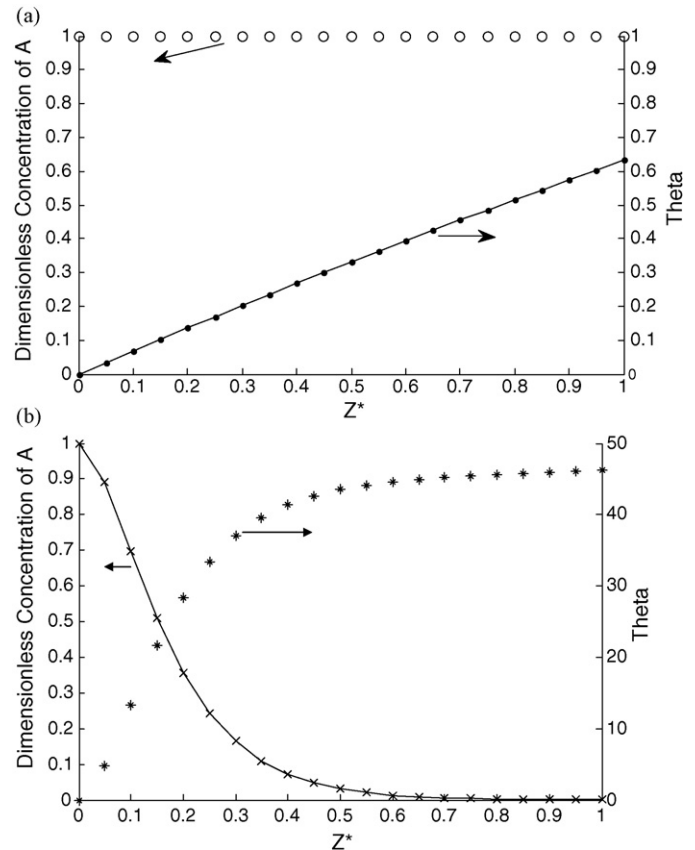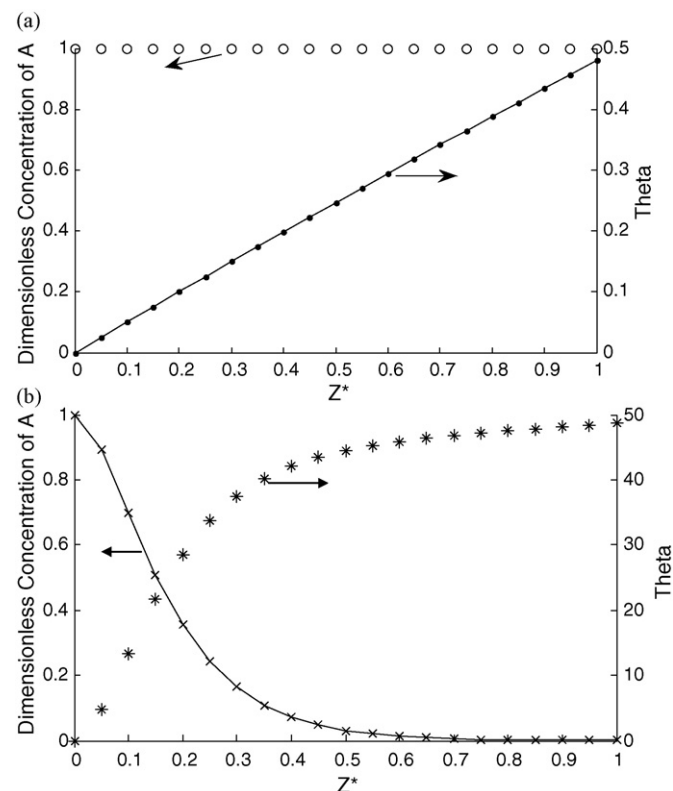

Fig. 1. (a) Micro-reactor and (b) macro-reactor dimensionless concentration and dimensionless temperature (θ) as a function of z^* (dimensionless length) at Re = 10 for thermally developing region. Micro-reactor parameters: $D_{mic} = 5e{-}4$ m; $L_{mic} = 0.05$ m; $\tau_{mic} = 1$ s; $Da_{1mic} = 6.128e{-}4$; $Da_{2mic} = 6.128e{-}6$; $\beta_{mic} = 0.253$; $D_{mol} = 1.45e{-}10$ m^2/s. Macro-reactor parameters: $D_{mac} = 1.25e{-}2$ m; $L_{mac} = 1.25$ m; $\tau_{mac} = 625$ s; $Da_{1mac} = 0.383$; $Da_{2mac} = 3.831e{-}3$; $\beta_{mac} = 0.253$; $D_{mol} = 1.45e{-}10$ m^2/s.
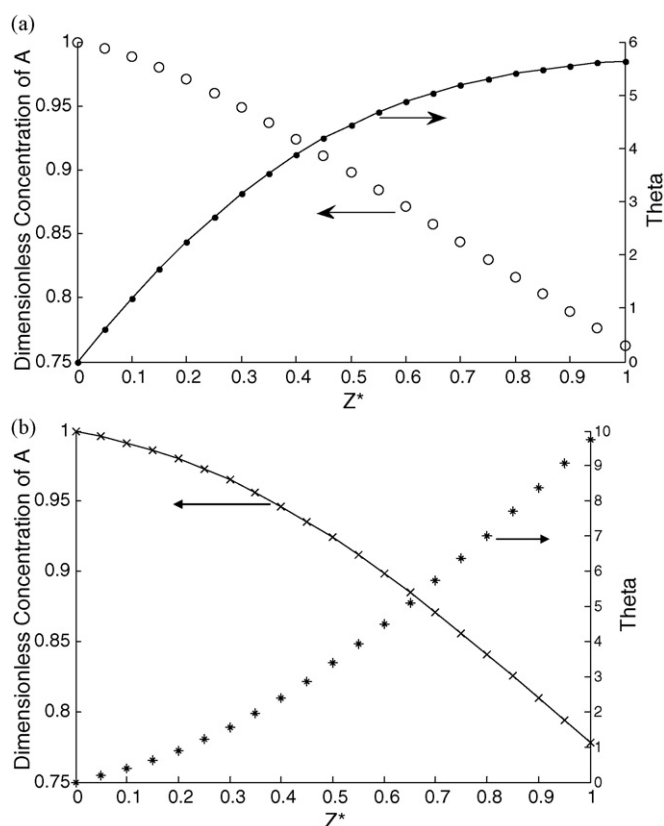
converted at the end of the reactor. In the macro-reactor the Da number and hence the residence time is very high and species 'A' is converted completely and the temperature attained is high. In contrast to this species 'A' hardly gets converted in the micro-reactor as the Da number is very low for the reaction to occur. The parameters used in the simulations are given in the figure caption (Fig. 1).

We next analyze the condition TDHD when the Re are matched for the two systems. Here the dimensionless heat transfer parameter 'β' is again equal for the two reactors. In Fig. 2a, we again see that the temperature rise and the conversion in the micro-reactor are significantly low as in Fig. 1a. Here again as the Da is high the species 'A' reaches complete conversion midway along the macro-reactor (Fig. 2b). We also see that in the micro-reactor the temperature rise is significantly less and we observe that species 'A' hardly gets converted as the reaction is taking place slowly because of low Da number. We conclude that for the case when the Re is matched the residence time of the macro-system is much higher and this contributes to the higher conversion of the macro-reactor and the more severe rise in temperature.

In the next case we study the two systems when Da is matched. The results for the case TUHD are depicted in Fig. 3 where we see that the concentrations evolve along similar patterns. We have appreciable conversion for both systems at the chosen Da or residence time. However the temperature rise of the micro-system is much lower than that of the macro-system. This is because of the better heat transfer coefficient for micro-reactor and also the heat loss parameter, i.e., $\beta_{\mathrm{mic}} \gg \beta_{\mathrm{mac}}$. The residence times now are the same for both the micro- and macro-reactors. As Da is

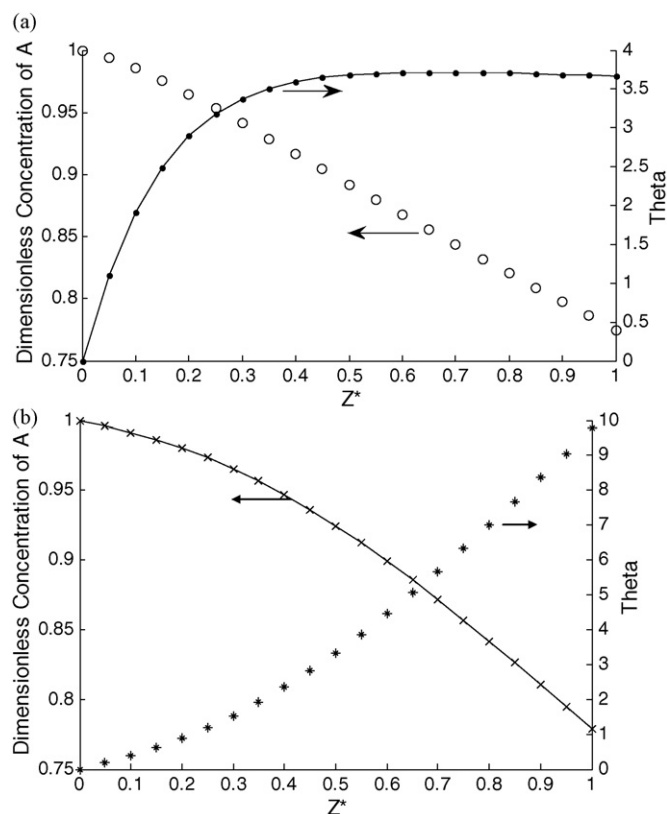**Fig. 3.** (a) Micro-reactor and (b) macro-reactor dimensionless concentration and dimensionless temperature (θ) as a function of z^* (dimensionless length) at same Da for thermally developing region. Micro-reactor parameters: $D_{\mathrm{mic}} = 5\mathrm{e}{-}4$ m; $L_{\mathrm{mic}} = 0.05$ m; $\tau_{\mathrm{mic}} = 50$ s; $\mathrm{Da}_{1\mathrm{mic}} = 0.03064$; $\mathrm{Da}_{2\mathrm{mic}} = 3.064\mathrm{e}{-}4$; $\beta_{\mathrm{mic}} = 3.53$. Macro-reactor parameters: $D_{\mathrm{mac}} = 1.25\mathrm{e}{-}2$ m; $L_{\mathrm{mac}} = 1.25$ m; $\tau_{\mathrm{mac}} = 50$ s; $\mathrm{Da}_{1\mathrm{mac}} = 0.03064$; $\mathrm{Da}_{2\mathrm{mac}} = 3.064\mathrm{e}{-}3$; $\beta_{\mathrm{mac}} = 1.04$.

same in both the reactors the conversion in the macro-reactor is almost same for the chosen τ value as in the micro-reactor even though the macro-reactor sustains a higher temperature. From Eq. (6b), the condition $\beta_{\mathrm{mic}} \gg \beta_{\mathrm{mac}}$ clearly shows that the heat transfer in the micro-reactor is more than that of the macro-reactor. Consistent with this we observe that in the micro-reactor the temperature rise is low and the temperature reaches a constant whereas in the macro-reactor it keep rising along the length of the reactor. Under these conditions it is desirable to conduct the reaction in a micro-system as the temperature rise can be effectively controlled.

Now we discuss the condition TDHD. Fig. 4 shows that the conversion of species 'A' is almost same in both the reactors whereas the temperature rise is more in the macro-reactor than the micro-reactor. Here again we see that the micro-reactor shows better heat transfer properties compared to the macro-reactor at same Da numbers, i.e., at same residence time. This can be understood as $\beta_{\mathrm{mic}} \gg \beta_{\mathrm{mac}}$ see Eqs. (6(b))–(6(c)). The match in the end point conversion that we observe depends on the residence time chosen. For a residence time of 50 s we find that the conversions of both reactors agree reasonably well at the end. For other residence times there may be a mismatch in the end point conversion.

We have also performed simulations by imposing the condition that the desired conversion of reactant 'A' in both the reactors is equal. In this case we have again analyzed the non-isothermal behavior of the reaction systems and determined the residence time required in each reactor to obtain the same conversion. The lengths of the two reactors (micro- and macro-systems) were fixed at 0.05 and 1.25 m respectively. The overall heat transfer coeffi-

Fig. 2. (a) Micro-reactor and (b) macro-reactor dimensionless concentration and dimensionless temperature (θ) as a function of z^* (dimensionless length) at same Re = 10 for fully developed region. Micro-reactor parameters: $D_{\mathrm{mic}} = 5\mathrm{e}{-}4$ m; $L_{\mathrm{mic}} = 0.05$ m; $\tau_{\mathrm{mic}} = 1$ s; $\mathrm{Da}_{1\mathrm{mic}} = 6.128\mathrm{e}{-}4$; $\mathrm{Da}_{2\mathrm{mic}} = 6.128\mathrm{e}{-}6$; $\beta_{\mathrm{mic}} = 0.1764$; $D_{\mathrm{mol}} = 1.45\mathrm{e}{-}10$ m^2/s. Macro-reactor parameters: $D_{\mathrm{mac}} = 1.25\mathrm{e}{-}2$ m; $L_{\mathrm{mac}} = 1.25$ m; $\tau_{\mathrm{mac}} = 625$ s; $\mathrm{Da}_{1\mathrm{mac}} = 0.3814$; $\mathrm{Da}_{2\mathrm{mac}} = 3.814\mathrm{e}{-}3$; $\beta_{\mathrm{mac}} = 0.1764$; $D_{\mathrm{mol}} = 1.45\mathrm{e}{-}10$ m^2/s.
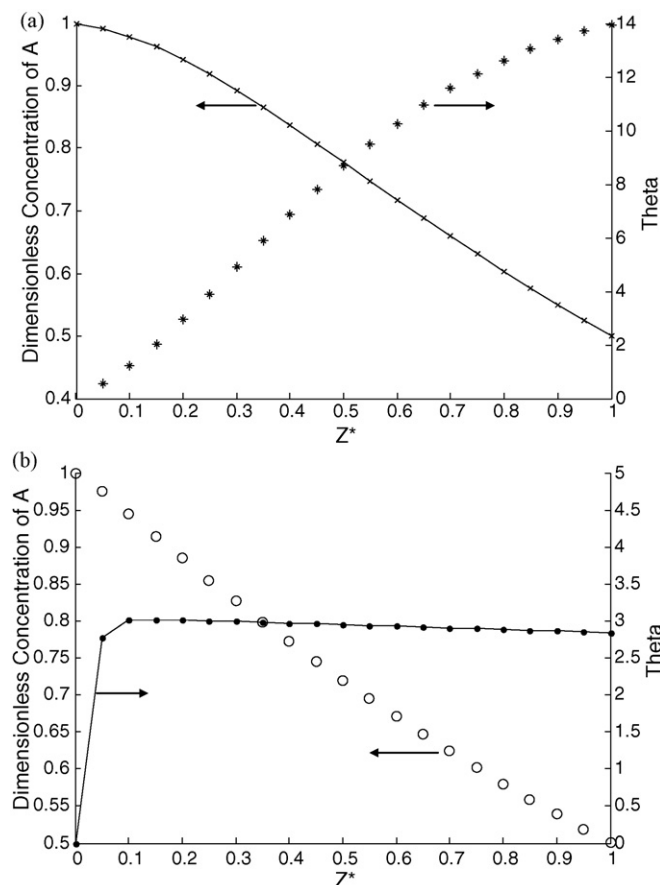
Fig. 4. (a) Micro-reactor and (b) macro-reactor dimensionless concentration and dimensionless temperature (θ) as a function of z^* (dimensionless length) at same Da for fully developed region. Micro-reactor parameters: $D_{mic} = 5e-4$ m; $L_{mic} = 0.05$ m; $\tau_{mic} = 50$ s; $Da_{1mic} = 0.03064$; $Da_{2mic} = 3.064e-4$; $\beta_{mic} = 8.82$. Macro-reactor parameters: $D_{mac} = 1.25e-2$ m; $L_{mac} = 1.25$ m; $\tau_{mac} = 50$ s; $Da_{1mac} = 0.03064$; $Da_{2mac} = 3.064e-3$; $\beta_{mac} = 0.0145$.

Fig. 5. (a) Micro-reactor and (b) macro-reactor dimensionless concentration and dimensionless temperature (θ) as a function of z^*(dimensionless length) for a fixed conversion of 50%. Micro-reactor parameters: $D_{mic} = 5e-4$ m; $L_{mic} = 0.05$ m; $B_1 = 44$; $B_2 = 149$; $\tau_{mic} = 135$ s. Macro-reactor parameters: $D_{mac} = 1.25e-2$ m; $L_{mac} = 1.25$ m; $B_1 = 44$; $B_2 = 149$; $\tau_{mac} = 95$ s.

cient was chosen to be 400 W/m² K. The residence time of the fluid flowing through the reactors to obtain a fixed conversion was determined using an iterative method. For these simulations the values of the other parameters were chosen as $k_{10}e^{-(E_1/RT_f)} = 6.102e-4$ s⁻¹; $k_{10}e^{-(E_2/RT_f)} = 6.102e-6$ s⁻¹; $(h_{overall}/\rho Cp) = 2e-4$ m/s; the results for this are shown in Fig. 5a and b. For 75% conversion the micro-reactor needs a residence time of 252 s and the macro-reactor needs a time of 165 s. Similarly for a 50% conversion in the two reactors the micro-reactor requires a residence time of 133 s while the macro-reactor requires a residence time of 96 s.

The volumetric flow rate required is lower in the micro-reactor than the macro-reactor. The temperature prevailing in the micro-reactor is much lower than that in the macro-reactor because of the better heat transfer in it. We see that the conversion and temperature profiles for the two reactors are similar for the case where the Da numbers are equal. The residence time needed to get a desired conversion of 75% is very high in micro-reactors. We exploit the fact that there is good heat transfer to the environment in a micro-reactor and propose to increase the feed temperature for the micro-reactor to increase the reaction rate and lower the residence time. For this we study the system behavior at different feed temperatures and observe the temperature and concentration profiles along the length of the reactor.

The simulations are performed at fixed parameters, i.e., $D_{mic} = 5.9e-4$ m; $h_{overall} = 449.8$ W/m²; $\beta_{mic} = 17.99$; $L_{mic} = 0.05$ m; $\tau = 10$ s. As we change the feed temperature the dimensionless parameters governing the system change. Fig. 6a and b shows the dimensionless concentrations and temperature profiles along the length of the reactor for different feed temperatures. It shows that as

we increase the feed temperature for a fixed residence time the conversion increases significantly with a low temperature rise in the reactor. The temperature remains constant for a significant portion of the reactor length. At $T_f = 333$ K, we see that we have 50% conversion of A in the reactor. To obtain the maximum conversion by choosing the feed temperature T_f to be 333 K we increased the residence time from 10 to 30 s. The conversion of A becomes almost 100% again with a uniform temperature in the micro-reactor. We see that at $\tau = 30$ s (i.e., at $L_{mic} = 0.15$ m) and $T_f = 333$ K, micro-reactor can achieve maximum conversion with good heat transfer than in the macro-reactor.

The temperature rise in the micro-reactors is of the order of 25 °C while in the macro-reactor it is of the order of 120 °C. These values are estimates of the temperature rise when feed temperature is around 300 K. Durcy and Roberge [13] have reported a temperature rise of around 60 K for the batch-wise nitration of phenol when the initial temperature is around 290 K and a temperature rise of 25 K for the micro-reactor. The results of our simulations for the micro-system reported here are hence is comparable to the results reported [13]. For the macro-system the results are close to the adiabatic temperature rise and have the same order of magnitude as obtained from batch experiments.

We conclude that (i) the micro-system can be operated at higher temperatures since it has better heat transfer characteristics and (ii) it is essential to maintain the same residence time to get similar conversion levels.
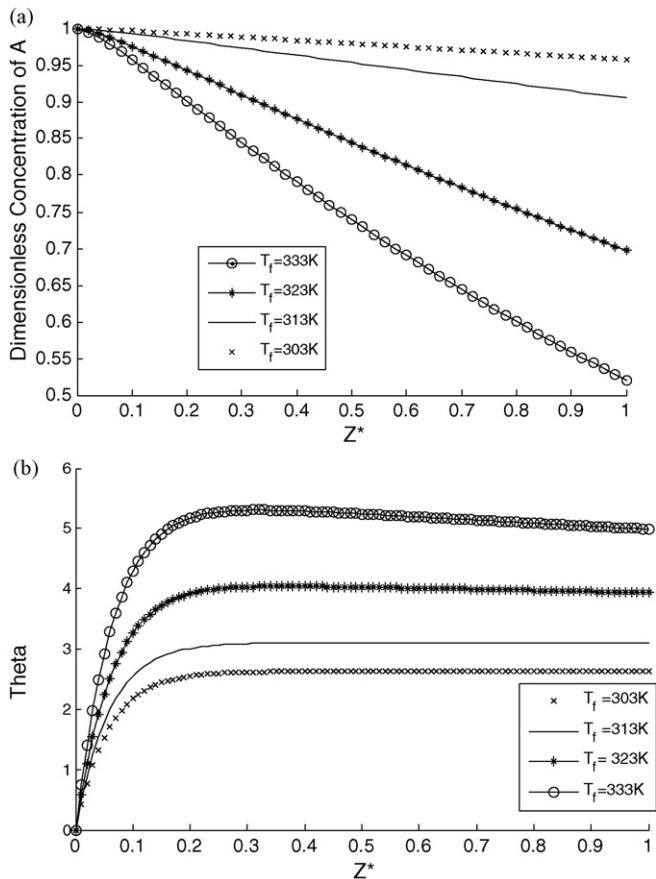
Fig. 6. (a) Dimensionless concentration of 'A' and (b) dimensionless temperature (θ) as a function of z^*(dimensionless length) at different feed temperatures (T_f). Micro-reactor parameters: $D_{mic} = 5e-4\,m$; $L_{mic} = 0.05\,m$; $\tau_{mic} = 10\,s$; $\beta_{mic} = 17.99$.

4.1. Effect of axial dispersion

So far we have analyzed the system assuming that we have plug flow behavior. This is valid as long as $D/uL < 0.001$. To account for the laminar flow in this system we have used an axial dispersion model following Levenspiel [22]. The value of the axial dispersion coefficient is obtained from:

$$\frac{D_{ax}}{ud_t} = \frac{1}{Re \times Sc} + \frac{Re \times Sc}{192} \qquad (8)$$

As we have a non-isothermal model we also include thermal effects and for this we determine the axial thermal dispersion α_D, using the analogy, i.e., replacing Schmidt number (Sc) with Pr number in Eq. (8). While this is strictly valid only for the adiabatic reactor we have employed it for our non-adiabatic system as well. The mass balance equation of species A and the energy balance equation is modified as:
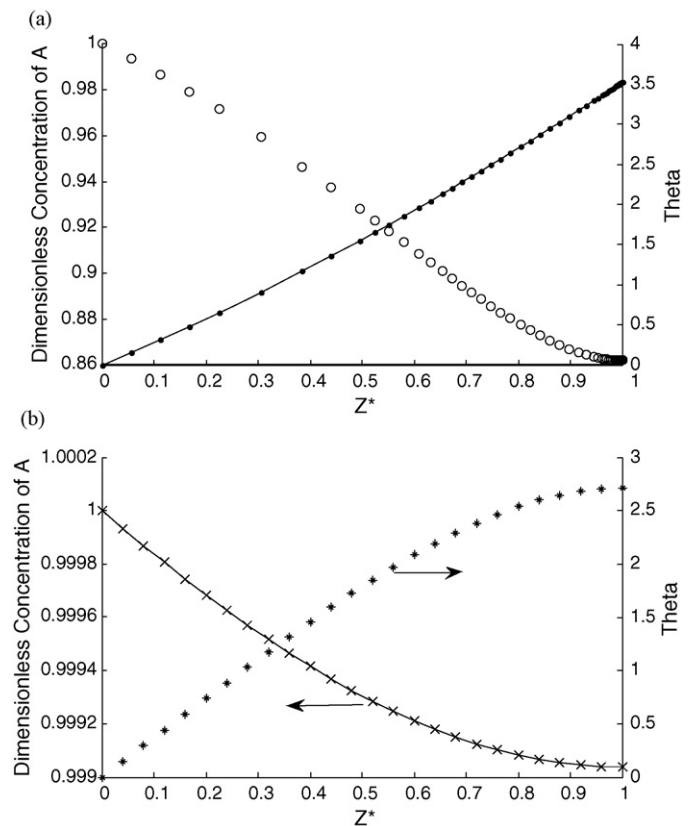
$$\frac{dC_A}{dz} = \frac{1}{Pe_m}\frac{d^2C_A}{dz^2} - Da_1\,e^{(\theta/(1+\varepsilon\theta))}C_A C_B$$

$$\frac{d\theta}{dz} = \frac{1}{Pe_h}\frac{d^2\theta}{dz^2} - Da_1 B_1\,e^{(\theta/(1+\varepsilon\theta))}C_A C_B$$

$$+ Da_2 B_2\,e^{(r\theta/(1+\varepsilon\theta))}C_P C_B - \beta(\theta - \theta_{amb})$$

where

$$Pe_m = \frac{uL}{D_{ax}}; \quad Pe_h = \frac{uL}{\alpha}$$

The mass balance equation for other species is similarly modified. After including this dispersion effect all our equations become

Fig. 7. (a) Micro-reactor and (b) macro-reactor dimensionless concentration and dimensionless temperature (θ) as a function of z^* (dimensionless length) at same Da for thermally developing region with axial dispersion inclusion. Micro-reactor parameters: $D_{mic} = 5e-4\,m$; $L_{mic} = 0.05\,m$; $\tau_{mic} = 50\,s$; $Da_{1mic} = 0.03064$; $Da_{2mic} = 3.064e-4$; $\beta_{mic} = 3.53$; $D_{ax} = 1.03e-5$, $\alpha_{mic} = 1.4e-7$. Macro-reactor parameters: $D_{mac} = 1.25e-2\,m$; $L_{mac} = 1.25\,m$; $\tau_{mac} = 50\,s$; $Da_{1mac} = 0.03064$; $Da_{2mac} = 3.064e-3$; $\beta_{mac} = 1.04$; $D_{ax} = 3.217$, $\alpha_{mac} = 4.14e-2$.

a second order boundary value problem and we solve the equations subject to the additional boundary conditions, i.e.

$$\frac{dC_i}{dz} = 0 \quad at\,z = L; \qquad \frac{d\theta}{dz} = 0 \quad at\,z = L$$

For the sake of concreteness we analyze only the case when Da numbers are equal for the micro- and macro-reactors for the thermally developing and hydrodynamically developed flow. Here the dispersion coefficient $(D_{ax}) = 1.03e-5\,m^2/s$ and thermal dispersion coefficient $(\alpha) = 1.405e-7\,m^2/s$ for the micro-system and the dispersion coefficient $(D_{ax}) = 3.217\,m^2/s$ and thermal dispersion coefficient $(\alpha) = 0.0404\,m^2/s$ for the macro-system. These values are obtained using the correlations (8).

The behavior of the system when the dispersion coefficient is included is shown in Fig. 7. We see that for the micro-system the effect of dispersion is negligible while for the macro-system it is dominant. For the micro-system the behavior of the system with dispersion included is similar to that of the plug flow reactor while for the macro-system the conversion is significantly less as the axial dispersion effects become dominant. This difference we attributed to the differences in the Re of the two systems. We conclude that when the residence times are kept equal the performance of the micro- and macro-systems match only when we have ideal plug flow for both systems. When axial dispersion effects are included the behavior of the two systems change drastically.

5. Summary and conclusions

In the present study, we have discussed how the scaling features of heat transfer and reaction progress compare in the micro- and macro-reactors under different conditions with specific reference to the case of the reaction of nitric acid oxidation of 2-octanol. The reaction is an exothermic reaction between 2-octanol and nitric acid, and is highly temperature sensitive. We find that there are two dimensionless groups which need to be matched Re and Da. However both cannot be matched for similarity and we can at best match only one dimensionless group.

This study shows that it is important to match the Damkohler numbers as opposed to Reynolds number for two systems to get similarity in the performance of reactors We have analyzed the behavior of the micro- and the macro-reactors when the Re is the same for both systems. Here the residence times of the two systems are appreciably different. Consequently the conversion and the temperature rise are significant in the macro-reactor compared to the micro-reactor. However when the Da numbers are maintained identical for the micro- and the macro-reactors we have the same residence time in the two reactors. Here the conversion of species 'A' turns out to be almost same in both the reactors but the temperature rise in the micro-reactor is less than the macro-reactor.

We have also studied the effect of feed temperature on conversion of 'A' in a micro-reactor. In view of the significantly high heat transfer we can increase the feed temperature in a micro-reactor without risking a runaway behavior. This allows us to obtain good conversion with a low residence time. An axial dispersion model was used and we have found that the axial dispersion has a negligible effect for the micro-reactor system while it has a significant effect for the macro-system when the residence times are equal. This difference is attributed to the different Re values prevailing in the two systems. In this work we have analyzed scale-up form a micro-system to a macro-system under different conditions. We have shown conclusively that scale-up from a micro-system to a macro-system is difficult to achieve and it is essential to go for 'numbering up" of micro-plants to increase capacity of production.

Nomenclature

B_1	Heat of reaction term for 1st reaction
B_2	Heat of reaction term for 2nd reaction
C	Concentration (kmol/m^3)
Cp	Heat capacity (J/Kg K)
D_{mol}	Molecular diffusivity (m^2/s)
D_{ax}	Axial dispersion coefficient (m^2/s)
E	Activation energy (J/kmol)
$h_{overall}$	Overall heat transfer coefficient (W/m^2 K)
k	Thermal conductivity (W/m K)
U	Mean fluid velocity (m/s)
T_f	Feed temperature (K)

Greek symbols

α	Thermal dispersion
β	Heat loss parameter
ρ	density (kg/m^3)
τ	Residence time (s)
θ	Dimensionless temperature
ε	E/RT_f

Dimensionless groups

Da$_1$ Damkohelr number for the first reaction = Da$_1$ = $k_1 e^{-E_1/RT_f} C_{A_0} \tau$

Da$_2$ Damkohelr number for the first reaction = Da$_2$ = $k_2 e^{-E_2/RT_f} C_{A_0} \tau$

Pr Prandtl number = Cp $\times \mu/k$

Pe Peclet number = Re $\times$ Pr

Re Reynolds number = DUρ/μ

Sc Schmidt number = $\mu/\rho D_{mol}$

Subscripts

i	Components A, B, P and X
mol	molecule
h	heat
m	mass
mic	micro-reactor
mac	macro-reactor

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