Available online at www.sciencedirect.com

International Journal of Heat and Mass Transfer 51 (2008) 2990–3006

International Journal of HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

The extraordinary effects of energetic reactions on the Nusselt number in a round tube with a uniform heat flux density on the wall

Bo Yu [a], Stuart W. Churchill [b,*]

[a] *Beijing Key Laboratory of Urban Oil and Gas Distribution Technology, China University of Petroleum (Beijing), Beijing 102249, PR China*
[b] *Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 311A Towne Building, 220 South 33rd Street, Philadelphia, PA 19104, USA*

Received 23 February 2007; received in revised form 10 September 2007
Available online 5 November 2007

Abstract

Owing to the exponential dependence of the rate constant for most chemical reactions on temperature, heat transfer through the wall of a tubular chemical reactor is usually necessary to control the rate of reaction. Energetic reactions have been known for some time to affect the Nusselt number critically but prior results are fragmentary. New, coherent and essentially exact numerical results are presented for uniform heating in fully developed laminar and turbulent flow. These results reveal chaotic variations as well as unbounded and negative values. This behavior is explained on both mathematical and physical grounds.

Keywords: Chemical reactions; Forced convection; Chaotic behavior

1. Introduction

The mathematical model formulated by Bernstein [1] for combustion in flow through a ceramic tube (a very complex process stabilized jointly by both wall-to-wall radiation and in-wall conduction, and subject to external heat losses) included an integro-differential energy balance with external exchange represented by a heat transfer coefficient. In order to obtain stable solutions in agreement with experimental measurements, he found it necessary to increase that coefficient by an order of magnitude over the predictions of correlations for non-reactive flow. The association of the current author with that finding led to the investigation whose results are presented herein.

When gas-phase chemical reactions are carried out in steady flow through a tube, heating at the outer surface may be necessary to initiate the reactions. If the reactions are endothermic, heating may also be required to prevent premature self-quenching because of the resulting decrease in temperature. If the reactions are exothermic, cooling may be necessary to prevent a thermal run-away or undesirable side-reactions. In scanning the literature in search of a clue to the aforementioned finding of Bernstein, a number of relevant theoretical analyses and experimental investigations were identified. On the whole, these investigations revealed that energetic reactions may greatly enhance or mildly attenuate the rate of heat exchange as characterized by the Nusselt number. Unfortunately, these prior investigations are fragmentary and incoherent, and have generally gone unmentioned in the literature of both heat transfer and reaction engineering. One objective of the long-term investigation of which the current work is a part is to evaluate such enhancements and attenuations systematically and quantitatively by means of numerical solution of the differential equations of conservation, and, insofar as possible, to explain the results qualitatively and to devise generalized predictive or correlative expressions.

Attention herein is confined to heating or cooling with a uniform heat flux density at the inner surface of the tube. Such a uniform heat flux density has been the thermal

---

[*] Corresponding author. Tel.: +1 215 898 5579; fax: +1 215 573 2093.
E-mail addresses: yubobox@yahoo.com.cn (B. Yu), churchil@seas.upenn.edu (S.W. Churchill).

0017-9310/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.ijheatmasstransfer.2007.09.012

Nomenclature

a	radius of tube
	$a^{+} \equiv a(\rho\tau_{\mathrm{w}})^{1/2}/\mu$
c	specific heat capacity
c_{M}	molar heat capacity
C_{A0}	initial molar concentration of reactant A
D_f	diffusivity of species A
E	molar energy of activation
f	Fanning friction factor $[2\tau_{\mathrm{w}}/\rho u_m^2]$
Gz	Graetz number $[wc/\lambda x]$
j_{w}	heat flux density in y-direction
J	dimensionless uniform heat flux density from wall $[aj_{\mathrm{w}}/\lambda T_0]$
k	reaction rate constant (s^{-1})
K_{0a}	dimensionless rate of reaction $[ak_0/u_m]$
K_{0x}	dimensionless distance from entrance $[xk_0/u_m]$
Nu	Nusselt number $= [2aj_{\mathrm{w}}/\lambda(T_{\mathrm{w}} - T_m)]$
Pr	Prandtl number $= [c\mu/\lambda]$
Pr_t	turbulent Prandtl number
q_{M}	molar heat of reaction (J/mol)
q_{V}	uniform volumetric heat of reaction ($\mathrm{W/m^3}$)
Q	dimensionless ratio of heat of reaction to heat flux from wall $[ak_0C_{A0}(1 - Z_{\mathrm{m}})q_{\mathrm{M}}/2j_{\mathrm{w}}]$
r	radial coordinate
R	r/a
$\widehat{R}$	Rydberg constant (J/K)
Re	Reynolds number $[2au_m\rho/\mu]$
Sc	Schmidt number $[\mu/\rho D_f]$
Sc_{t}	turbulent Schmidt number
T	absolute temperature
u	axial velocity
u'	fluctuating component of axial velocity
$\overline{u'v'}$	time-average of fluctuating components of velocity
$(\overline{u'v'})^{++}$	dimensionless turbulent shear stress $[-(\overline{u'v'})\rho/\tau]$
u^{+}	$u(\rho/\tau_{\mathrm{w}})^{1/2}$
v'	fluctuating component of velocity in y-direction
w	mass rate of flow
x	axial coordinate
X	x/a
y	distance from the wall
y^{+}	$y(\rho\tau_{\mathrm{w}})^{1/2}/\mu$
Z	fractional conversion of reactant A

Greek symbols

α	arbitrary numerical exponent
β	arbitrary coefficient in analogy for reaction and heat transfer
η	arbitrary numerical exponent
λ	thermal conductivity
μ	dynamic viscosity
ξ	dimensionless parameter $[aC_{A0}kq_{\mathrm{M}}/2j_{\mathrm{w}}]$
ρ	specific density
σ	arbitrary numerical coefficient
τ	thermicity $[q_{\mathrm{M}}/c_{\mathrm{M}}T_0]$
τ	shear stress
Φ	dimensionless temperature $[T/T_0]$
χ	arbitrary numerical coefficient

Subscripts

e	equivalent
m	mixed-mean (weighted by the velocity and radially integrated)
M	molar
o	for no reaction
P	predicted
r	at radius r
w	at wall
x	local value at distance x from inlet
0	at entrance
∞	for an infinite temperature

boundary condition of choice in most of the prior theoretical analyses of heat transfer with and without reaction because the mathematical formulation and process of solution are then the simplest. This thermal boundary condition can be closely approximated in practice by countercurrent heat exchange with a fluid in an outer annular passage, for example, by product-to-feed exchange. In the case of heating but not cooling, a uniform heat flux density may be attained in the laboratory by electrical-resistance-heating of the wall. Two limiting cases serve as points of reference herein. One is adiabatic reaction, which may be approximated in practice by means of very good external insulation. The other is isothermal reaction, which corresponds to a negligible heat of reaction and no heat transfer at the wall. They both serve as measures of the effectiveness of heat transfer in compensating for the heat of reaction.

The other common thermal boundary condition, namely a uniform-wall temperature, which can be closely approximated by means of an external condensing fluid (for cooling) or a boiling fluid (for heating) is the subject of a complementary study in progress. A third thermal boundary of practical interest for mildly energetic reactions is that of thermal conduction through imperfect insulation in series with external natural convection and thermal radiation.

Modeling and numerical solution for chemical conversions with or without heat exchange are more difficult than for pure convection because most chemical conversions involve multiple reaction mechanisms, each of which depends exponentially and differently on temperature, and many of which are non-equimolar, thereby perturbing the flow. The general model for reaction consists of a set of partial differential equations for the conservation of species that are nonlinear in temperature and generally in concentration. The partial differential equations for the conservation of species are strongly coupled with those for the conservation of energy as well as with each other. The number of significant chemical-reaction-rate mechanisms, independent chemical species, and numerical parameters associated with the rate mechanisms may exceed 100, 20, and 50, respectively (see for example, Pfefferle and Churchill [2]). This is to be contrasted with pure forced convection, which may be modeled by a single linear partial differential equation, a single dependent variable (the temperature) and three parameters (the Reynolds number, the Prandtl number, and the mode of heat transfer at the wall) insofar as the flow is fully developed and the variation of the physical properties with temperature is neglected. Fully developed convection is a very useful simplifying concept but, in general, the equivalent concept does not exist for chemical conversions or for combined convection and reaction.

Apart from reducing the complexity of the modeling and the process of numerical solution, gross simplifications are essential if the numerical results are to be interpreted and generalized. The first major simplification to be made herein is the postulate of fully developed laminar or turbulent flow. Both entrance effects and transitional effects due to changes in the temperature are thereby excluded from the analysis. The error due to this idealization hinges on the rate of reaction relative to the rate of flow, increasing with that ratio. The second major simplification is the postulate of invariant physical properties other than the rate constant(s) for the reaction(s). Taking the variations with temperature and composition of the density, viscosity, diffusivity, and heat capacity into account would greatly complicate the calculations because the differential momentum balance is then coupled to those for energy and species, and these several partial differential equations must be solved simultaneously. Also, the numerical results would then be specific to a particular reacting fluid. The small errors in Nu_x and Z_{mx} that result from this idealization could perhaps be reduced by using mean values for these physical properties, but this was not done in the current work. The combination of these two postulates excludes radial flow and changes in the longitudinal component of the velocity. The third major simplification is the postulate that the reaction starts at the entrance, which is difficult to achieve experimentally and which has been the subject of considerable theoretical analysis, most of it involving the choice of boundary conditions at the entrance. The fourth and most far-reaching simplification is the postulate of a single, first-order, equimolar, irreversible, homogeneous reaction, thereby minimizing the number of chemical-kinetic parameters. The effects of this postulate can be ameliorated to some extent by the choice of a pseudo-first reaction-rate constant and effective values for the associated parameters.

Because the presentation involves and is influenced by behavior outside the normal scope of convective heat transfer the following overview is perhaps useful. The behavior of tubular chemical reactors in general, the prior work on interactive convection and reaction, and the known relationships between reaction and convection are first each reviewed very briefly. A recently proposed analogy between reaction and convection and its utility in the present context is next described. Finally, new and quite novel numerical results are presented and interpreted in terms of that analogy.

2. A primer on tubular reactors

Heat transfer is only mentioned cursorily in the literature of reaction engineering, and energetic reactions are virtually ignored in the literature of heat transfer. A review by Churchill [3] of the combined process of heat transfer and reaction is a rare exception. Hence, a brief description of the common types of reactors is perhaps appropriate here. As already mentioned, attention is confined to reactions carried out homogeneously. Heterogeneous reactions involving, for example, two fluids, a coating of catalyst on the surface of the reactor, a suspension of catalytic particles, or a fixed bed of catalyst-coated pellets are thus outside the scope of the analysis.

2.1. Adiabatic reactors

In an adiabatic reactor the mixed-mean temperature and the mixed-mean conversion are related exactly through

$$\frac{T_m}{T_0} = 1 + \left(\frac{q_M}{c_M T_0}\right) Z_m = 1 + \tau Z_m \tag{1}$$

Here, $\tau = q_M/c_M T_0$ is the thermicity, that is the maximum rise or fall in temperature in the absence of external heat transfer. If the thermicity is sufficiently small, the rise or fall in temperature may be tolerable, and heating or cooling unnecessary. This is often the case with liquid-phase reactions because of the relatively high heat capacity and density of the reacting fluid, but is rarely so with gas-phase reactions. Adiabatic conditions are considered herein as a limiting case.

To minimize heat exchange with the surroundings by free convection and thermal radiation in parallel and/or to avoid the exposure of personnel to a highly conductive surface at high or low temperature, thermal insulation is usually placed on the outer surface of the reactor or of the heat exchanger if one is present. This practice is not examined herein.

2.2. Heated and cooled reactors

Heat exchange through the surface of a reactor is commonly utilized in order to approach the idealized case of isothermal reaction or to produce some desirable temperature profile with distance through the reactor. In the case of a large thermicity, heating or cooling may be essential to avoid self-quenching, a thermal runaway, or the occurrence of undesirable side-reactions. An explosion is an extreme example of a runaway, the production of NO_x in a flame is an example of an undesirable side-reaction, and self-cooling in the thermally cracking of a light hydrocarbon is an example of quenching.

2.3. Batch reactors

In the absence of heating or cooling, the chemical conversion in a batch reactor follows the same path in time as with axial distance in a tubular reactor for the idealized case of uniformity within the batch reactor and the physically non-existent case of plug flow in the tubular one. This hypothetical commonality, which makes the large body of solutions for batch reactors appear to be adaptable to tubular reactors, has proven to be irresistible to most educators and practitioners. In the event of heating and cooling, batch and tubular reactors are not homologous even within the respective postulates of uniformity and plug flow.

3. Prior work

Tubular reactors are commonly used to carry out homogeneous chemical conversions, usually in conjunction with heat exchange through the surface. Such behavior has therefore been investigated extensively, albeit with some curious constraints. Historically and to this day, most modeling of tubular reactors is based on the postulate of plug flow. This idealization has often been rationalized on the basis that the error in the conversion is negligible. Indeed, for a first-order reaction carried out isothermally in laminar flow the error in the conversion is less 12% and for a second-order reaction and/or for turbulent flow is even less. However, the possible error due to the postulate of plug flow is unbounded for energetic reactions such as those examined herein. In the field of heat transfer solutions for plug flow are recognized as meaningful only in the sense of lower bounding values. Churchill [4] has suggested that the solutions for chemical reactions in plug flow be reinterpreted as those for the physically conceivable, even if unrealistic, case of perfect radial mixing due to an asymptotically large total diffusivity (or an asymptotically small total Schmidt number), and, in the event of an energetic reaction, of an asymptotically large total thermal conductivity (or an asymptotically small total Prandtl number) as well. This interpretation allows the utilization of solutions for the overall conversion in plug flow, which indeed do not differ greatly from those for turbulent flow, without propagating a seriously misleading concept. (The total Prandtl number is ordinarily less than 0.7 and the total Schmidt number less than 0.2 for gaseous mixtures.) However, this interpretation of the solutions for reaction in plug flow is applicable only for adiabatic reactors, not for the heated and cooled ones that are considered herein.

The obvious reason for the persistence of the postulate of plug flow in the modeling of tubular reactors is the great mathematical simplification that results, namely, the elimination of the radial coordinate as a variable, and the reduction of the partial differential equation(s) describing the conservation of species to one or more ordinary differential equations. It may even be possible to integrate the latter in closed form for some conditions. Furthermore, the substitution of time for axial distance divided by the mixed-mean velocity, that is the conversion of the Eulerian formulation to a Lagrangian one, then allows, as already mentioned, the adaptation of the large body of solutions compiled by physical chemists for batch reactors. This reduced formulation comes at the considerable price of the complete neglect of the molecular and turbulent diffusion of momentum, which produces the velocity distribution, as well as that for energy and the individual chemical species. Insofar as plug flow is postulated and the variation of the density with temperature and/or composition may be neglected, the *space–time* ($=x/u_m$) or the *space–velocity* ($=u_m/x$) may be utilized as the independent variable in place of time.

As somewhat of a tradeoff for the errors arising from the postulate of plug flow, reactor engineers and chemical kineticists have developed sophisticated methodologies to take into account kinetic complexities such as multiple and non-equimolar reaction mechanisms. However, in view of the present state of computer technology, the simplifications associated with plug flow, space–time, and space–velocity, as well as those associated with multiple and non-equimolar reaction mechanisms no longer seem to be necessary or appropriate in the classroom or in practice. The only justification for the use of single first-order irreversible, equimolar reaction mechanism in what follows is the objective of illustrating as clearly as possible the effects of interactions between energetic reactions and external heat transfer.

In closely related previous work, Churchill and Yu [5] carried out numerical solutions for the conversion for representative cases of reaction with heat transfer, and had some success in devising algebraic expressions for prediction of the chemical conversion by deriving and utilizing asymptotic solutions as guidelines. Also, Churchill [6] derived an analogy between homogeneous chemical reactions and heat transfer. These two analyses are not reviewed in detail herein but the results are utilized.

Although energetic reactions have been known for over 40 years to enhance or attenuate convection radically, this important aspect of behavior does not seem to have found its way into any of the textbooks and handbooks on heat and mass transfer. The earliest studies of combined reaction and external heat transfer are apparently those of Brian and Reid [7] and Brian [8] who carried out analytical solutions for asymptotic conditions (chemical equilibrium in the bulk of the fluid and a vanishingly small temperature difference) in the turbulent regime of flow and for uniform wall-temperatures. They generalized their results to some extent by expressing their model in terms of partial derivatives of the kinetic expression. The heat transfer coefficient was predicted to be enhanced by as much as a factor of 50.

The subsequent solutions of Rothenberg and Smith [9] for laminar flow and uniform heating predicted lesser but nevertheless significant enhancements. Ooms et al. [10] carried out finite-difference solutions for first-order, irreversible, endothermic reactions in general. They used *penetration* theory (which is of questionable accuracy as a model for turbulent transport in this context) and thereby predicted enhancements of as much as a factor of 7 depending on the values of *Re*, *Pr*, and *Sc*, as well as on three parameters representing the effects of the imposed heat flux density at the wall, the rate of reaction, and the heat of reaction. Experimental work on this subject is quite limited. Brian et al. [11] carried out experimental measurements for a reversible endothermic reaction ($2NO_2 \leftrightarrow 2NO + O_2$) with heat transfer from an isothermal surface, and Edwards and Furgason [12] carried out both experiments and finite-difference computations to determine the effect of the exothermic gas-phase decomposition of ozone on the heat transfer coefficient. The latter investigators found attenuations of up to 27% in the heat transfer coefficient.

All of this early work on the effect of chemical reactions on heat transfer appears to have been ignored in the literature of both reaction engineering and heat transfer. This omission may have occurred because the analyses are ancient and of questionable accuracy and validity, because the experimental data are fragmentary and incoherent, and/or because an explanation for the anomalous behavior has not been established on either physical or mathematical grounds. However, a more likely explanation is that these investigations have simply been overlooked.

4. Structural relationships for combined chemical reaction and convection

Theoretical, speculative, and empirical relationships that help to interpret and correlate the numerically computed values are examined in this section.

4.1. The relationship between the mixed-mean temperature and the mixed-mean conversion

A differential energy balance over a length of the reactor from the entrance up to an axial length designated by x may be expressed as follows:

$$u_m \pi a^2 (T_{mx} - T_0) c\rho = C_{A0} Z_{mx} q_M u_m \pi a^2 + 2\pi a x j_w \tag{2}$$

Eq. (2) may be re-arranged and re-expressed in dimensionless groups of variables as follows:

$$\begin{aligned}\frac{T_{mx}}{T_0} &= 1 + \frac{C_{A0} Z_{mx} q_M}{\rho c u_m T_0} + \frac{2 j_w x}{a u_m \rho c T_0} \\ &= 1 + Z_{mx}\tau + \left(\frac{4x}{Re\,Pr\,a}\right) J = 1 + Z_{mx}\tau + \left(\frac{2\pi}{Gz}\right) J \end{aligned} \tag{3}$$

The second and third terms on the right-hand side of each of the forms of Eq. (3) represent the thermal inputs due to reaction and the heat flux at the wall, respectively. $J \equiv a j_w/\lambda T_0$, which designates the dimensionless heat flux density from the wall, is an obvious analogue of the Nusselt number but is a specified parameter rather than a dependent variable. The symbol $\tau \equiv q_M/c_M T_0$ has already been designated as the thermicity, while, as usual $Re = 2au_m\rho/\mu$, $Pr = c\mu/\lambda$, and $Gz = wc/\lambda x$. Eq. (3), which reduces to Eq. (1) for $J = 0$, provides an exact relationship between T_{mx}/T_0 and Z_{mx} for any value of x/a and of the several specified parameters. It is applicable for positive and negative values of τ corresponding to exothermic and endothermic reactions, respectively, and for positive and negative values of J corresponding to heating and cooling, respectively, at the wall. Ordinarily, τ and J have opposite signs owing to the use of heating or cooling, respectively, to compensate for the reactive cooling or reactive heating. The two dependent variables T_{mx}/T_0 and Z_{mx} are thus related exactly to one another for any value of the independent variable x/a and values of the specified parameters *Re*, *Pr*, τ, and J.

4.2. The relationship between the wall temperature and the mixed-mean temperature

The local temperature of the wall is of practical interest in connection with both heat losses and the safety of personnel. Insofar as the tube wall is thin and/or a good thermal conductor, it may be approximated by the temperature of the fluid at the wall. An expression for this quantity in terms of the local mixed-mean temperature follows from the definition of the Nusselt number:

$$Nu_x \equiv \frac{2 a j_w}{\lambda (T_{wx} - T_{mx})} = \frac{2J}{\frac{T_{wx}}{T_0} - \frac{T_{mx}}{T_0}} \tag{4}$$

Eq. (4) can be rearranged for subsequent convenience as follows:

$$\frac{T_{wx}}{T_0} = \frac{T_{mx}}{T_0} + \frac{2J}{Nu_x} \tag{4a}$$

and can be combined with Eq. (3) to obtain

$$\frac{T_{wx}}{T_0} = 1 + \frac{2J}{Nu_x} + \frac{T_{mx}}{T_0} = 1 + Z_{mx}\tau + 2J\left(\frac{1}{Nu_x} + \frac{\pi}{Gz}\right) \tag{5}$$

Eqs. (4), (4a) and (5) are exact for a uniform heat flux density at the wall. Although T_{wx} is obtained directly from the process of numerical integration of the differential energy and species balances, two dependent variables such as Z_{wx} and T_{mx} are required to evaluate it by means of Eq. (5).

4.3. Relationships between the Nusselt number and the chemical conversion

With the primary objective of providing a functional explanation for the enhancement and attenuation of convection by energetic reactions, and the secondary objective of devising a correlative equation for the calculated values herein, Churchill [6] derived the following exact relationship between the fully developed Nusselt number Nu and the fractional mixed-mean conversion Z_m of the reactant in fully developed laminar flow with an energetic, volumetrically uniform rate of heating due to a reaction, a uniform heat flux density through the wall, radial conduction of heat, but no the radial diffusion of species:

$$Nu = \frac{48}{11 + \frac{3aq_\mathrm{V}}{2j_\mathrm{w}}} = \frac{48/11}{1 + 3Q/11} \tag{6}$$

Here, a is the radius of the tube, q_V is the volumetrically uniform input of energy by reaction, j_w is the uniform heat flux density from the wall, and Q can be identified as the ratio of the input of energy by the reaction to that from the wall. As $Q \to 0$, $Nu \to 48/11$, which is the well-known solution for fully developed laminar convection with uniform heating or cooling and no reaction. For negative values of Q, corresponding to the combination of an endothermic reaction and compensatory heating through the wall or to an exothermic reaction and compensatory cooling through the wall, Nu increases and becomes unbounded and then negative as $-3Q/11$ increases in magnitude, approaches unity, and exceeds unity. For the thermally unbalanced case of a positive value of Q, corresponding to an exothermic reaction and heating from the wall, or the converse of both, Nu is seen from Eq. (6) to decrease slowly as Q increases. Eq. (6), which has exactly the same form as the well-known solution for the effect of viscous dissipation on the heat transfer coefficient, can be interpreted as an analogy between the rates of chemical reaction and of heat transfer, as represented by Q and Nu, respectively, with theoretical coefficient of 3/11.

On purely speculative grounds, Eq. (6) was subsequently generalized by Churchill [6] as follows for the more realistic but much more complex case of developing reaction and developing convection:

$$Nu_x = \frac{Nu_\mathrm{ox}}{1 + \beta Q_x} \tag{7}$$

Here, the subscript o designates a value in the absence of reaction. That is, Nu_{xo} is the local Nusselt number in the absence of reaction, Q_x is the local ratio of the heat of reaction over the cross-section to the heat flux density at the wall per unit differential length of reactor, and β is an arbitrary coefficient.

The enhancement or attenuation of the local Nusselt number is represented by the factor $1/(1 + \beta Q_x)$.

Enhancement and attenuation are characterized by the product βQ_x, not by Q_x and β separately. These variables are identified individually here because Q_x is a dimensionless combination of specified quantities, whereas β is purely empirical. Ordinarily, Q_x is negative, corresponding to the combination of an exothermic reaction and compensatory removal of heat at the wall or to the combination of an endothermic reaction and compensatory heat input at the wall, thereby predicting enhancement of the Nusselt number, but positive values of Q_x are physically possible. Eq. (7) is potentially applicable for fully developed turbulent flow as well as for fully developed laminar flow.

For uniform heating or cooling at the wall, Q_x can expressed as follows:

$$Q_x = \frac{aq_\mathrm{M}kC_{A0}(1 - Z_{mx})}{2j_\mathrm{w}} = \frac{\tau RePrK_{0a}(1 - Z_{mx})}{4J} \tag{8}$$

Combining Eqs. (7) and (8) results in

$$Nu_x = \frac{Nu_\mathrm{ox}}{1 + \frac{\beta aq_\mathrm{M}kC_{A0}(1-Z_{mx})}{2j_\mathrm{w}}} = \frac{Nu_\mathrm{ox}}{1 + \beta\xi(1 - Z_{mx})} \tag{9}$$

Here, $\xi = aC_{A0}kq_\mathrm{M}/2j_\mathrm{w} = \tau RePrK_{0a}/4J$ is a combination of specified variables, namely those that do not vary with the primary independent variable, x. As mentioned previously, j_w and q_M ordinarily have opposite signs resulting in a negative value for ξ as well as for Q_x. Eq. (9) can be interpreted as an analogy between the rate of heat transfer as represented by Nu_x, and the rate of reaction as represented by $kC_{A0}(1 - Z_{mx})$.

The combination of the variation of the temperature in a tubular reactor with radius and axial distance and the temperature-dependence of the reaction-rate constant is usually too great to neglect. The temperature-dependence of a reaction may ordinarily be closely represented by the Arrhenius equation, namely

$$k = k_\infty \mathrm{e}^{\frac{-E}{\widehat{R}\,T}} = k_0\,\mathrm{e}^{\frac{E}{\widehat{R}\,T_0}\left(1-\frac{T_0}{T}\right)} \tag{10}$$

The right–most form of Eq. (10), which was apparently first introduced by Churchill [6], is utilized exclusively herein. The quantity k_0 is the reaction-rate constant at the inlet temperature T_0, as contrasted with the more familiar quantity k_∞, the reaction-rate constant for an infinite temperature. Next, in order to take the variation of the reaction-rate constant as given by Eq. (10) into account in the reactor, Eq. (9) is re-expressed as

$$Nu_x = \frac{Nu_\mathrm{ox}}{1 + \beta(k_{emx}/k_0)\xi(1 - Z_{mx})} \tag{11}$$

Here, k_{emx} is the effective-mean value of the rate constant over the cross-section at x. Finally, the following approximation is proposed for k_{emx}:

$$\frac{k_{emx}}{k_0} \cong \frac{k\{T_{mx}\}}{k\{T_0\}} = \frac{k_\infty\,\mathrm{e}^{-E/\widehat{R}T_{mx}}}{k_\infty\,\mathrm{e}^{-E/\widehat{R}\,T_0}} = \mathrm{e}^{\frac{E}{\widehat{R}\,T_0}\left(1-\frac{T_0}{T_{mx}}\right)} \tag{12}$$

Eqs. (11), (12) and (3) can be combined, and that combination re-expressed as

$$Nu_x = \frac{Nu_\mathrm{ox}}{1 + \beta\xi(1 - Z_{mx})\exp\left\{\frac{E/\widehat{R}\,T_0}{1+(\tau[Z_{mx}+(K_{0x}/\xi)])^{-1}}\right\}} \tag{13}$$

Eq. (13) is the most convenient form of the analogy for most purposes.

4.4. An approximate expression for the mixed-mean conversion

Churchill and Yu [5] proposed and tested several empirical expressions for the prediction of the fractional conversion as a function of K_{0x}, τ, and J for the nearly the same set of conditions as considered herein. The most convenient of these expressions can be expressed as:

$$Z_{mx} = \frac{1 - \mathrm{e}^{-0.963K_{0x}}}{1 - 3.85\tau} + \frac{252JK_{0x}}{Re} \tag{14}$$

Here, $K_{0x} \equiv k_0 x / u_m$ is the primary variable. The coefficient 0.963 is a correction of the exact solution for isothermal plug flow for the effect of diffusion, the term 3.85τ is a correction for the effect of the heat of reaction and the rightmost term a correction for the imposed heat flux at the wall.

4.5. The arbitrary choice of variables

Because of the many dimensional variables and parameters, many choices of dimensionless variables and parameters are possible. The Nusselt number for developing convection in fully developed laminar flow without reaction is a function of Gz only and therefore the latter is usually utilized as the independent variable in developing laminar convection. However, for developing convection in fully developed turbulent flow the Nusselt number is a function of Re, Pr, and x/a separately rather than of their combination in Gz. The ratio x/a was arbitrarily utilized as the independent variable in Eqs. (3), (5) and (13). However, K_{0x} is used exclusively hereafter in keeping with Eq. (14). In any event, these three dimensionless independent variables have the following one-to-one correspondence:

$$K_{0x} = \left(\frac{x}{a}\right) K_{0a} = \frac{\pi Re\, Pr\, K_{0a}}{2Gz} \tag{15}$$

and can readily be substituted for one another.

4.6. The optimal rate of heating or cooling

It follows from Eq. (3) that insofar as the objective is to minimize deviations from the inlet temperature on the mean, that is to compensate for an exothermic heat of reaction by cooling, or for an endothermic heat of reaction by heating, $\tau Re Pr K_{a0}/4J$ should be made equal to $-K_{0x}/Z_{mx}$ by the choice of J. Since Z_{mx}/K_{0x} is not invariant, a fixed numerical value of J cannot completely excise deviations of T_{mx} from T_0. On the other hand, a value of J can be chosen that minimizes the mean deviation of T_{mx} or the deviation of T_{mx} or Z_{mx} from their values for an isothermal reaction for a chosen value of K_{0x} or Z_{mx}. Such a choice may be interpreted as a possible criterion for reactor design. For electrical heating of the tube wall, T_{mx} increases almost linearly with K_{0x} as $Z_{mx} \to 1.0$ because the generation or absorption of heat due to the reaction then becomes negligible whereas the rate of heating from the wall remains constant.

5. Differential models of conservation for reaction and convection

5.1. Laminar flow

For fully developed laminar flow and the indicated simplifications and idealizations, the equation of conservation for species A can be written in dimensionless form as follows:

$$(1 - R^2)\frac{\partial Z}{\partial X} = \frac{1}{K_{0a} Re Sc}\,\frac{1}{R\partial R}\left[R\frac{\partial Z}{\partial R}\right] + \left(\frac{1 - Z}{2}\right)\mathrm{e}^{(E/\widehat{R}T_0)\left(1 - \frac{1}{\Phi}\right)} \tag{16}$$

The corresponding expression for the conservation of energy is

$$(1 - R^2)\frac{\partial \Phi}{\partial X} = \frac{1}{K_{0a} Re\, Pr}\,\frac{1}{R\partial R}\left[R\frac{\partial \Phi}{\partial R}\right] + \tau\left(\frac{1 - Z}{2}\right)\mathrm{e}^{(E/\widehat{R}T_0)\left(1 - \frac{1}{\Phi}\right)} \tag{17}$$

Here, $\Phi = T/T_0$. The boundary conditions for Eq. (16) are $Z = 0$ at $X = 0$, and $\partial Z/\partial R = 0$ at $R = 0$ and $R = 1$. Those for Eq. (17) are $\Phi = 1$ at $X = 0$, $\partial\Phi/\partial R = 0$ at $R = 0$, and $\partial\Phi/\partial R = J$ (for a uniformly heated wall) at $R = 1$.

5.2. Turbulent flow

The time-averaged formulations for turbulent flow corresponding to Eqs. (16) and (17) can be expressed as follows:

$$\frac{u^+}{2u_\mathrm{m}^+}\frac{\partial Z}{\partial X} = \frac{K_{0a}}{Re Sc}\,\frac{\partial}{R\partial R}\left[R\left(1 + \frac{Sc}{Sc_\mathrm{t}}\left[\frac{\overline{(u'v')}^{++}}{1 - \overline{(u'v')}^{++}}\right]\right)\frac{\partial Z}{\partial R}\right] + \left(\frac{1 - Z}{2}\right)\mathrm{e}^{(E/\widehat{R}T_0)\left(1 - \frac{1}{\Phi}\right)} \tag{18}$$

and

$$\frac{u^+}{2u_\mathrm{m}^+}\frac{\partial \Phi}{\partial X} = \frac{K_{0a}}{Re\, Pr}\,\frac{1}{R\partial R}\left[R\left(1 + \frac{Pr}{Pr_\mathrm{t}}\left[\frac{\overline{(u'v')}^{++}}{1 - \overline{(u'v')}^{++}}\right]\right)\frac{\partial \Phi}{\partial R}\right] + \tau\left(\frac{1 - Z}{2}\right)\mathrm{e}^{(E/\widehat{R}T_0)\left(1 - \frac{1}{\Phi}\right)} \tag{19}$$

The boundary conditions are unchanged but supplementary expressions for $(\overline{u'v'})^{++}$, u^+, and u_m^+ are necessary. The expressions used herein are those devised by Churchill [13], namely

$$(\overline{u'v'})^{++} = \left(\left[0.7\left(\frac{y^+}{10}\right)^3\right]^{-8/7} + \left|\exp\left\{\frac{-1}{0.436y^+}\right\} - \frac{1}{0.436a^+}\left(1 + \frac{6.95y^+}{a^+}\right)\right|^{-8/7}\right)^{-7/8} \tag{20}$$

$$\frac{\mathrm{d}u^+}{\mathrm{d}R^2} = \frac{a^+}{2}\left[1 - \left(\overline{u'v'}\right)^{++}\right] \tag{21}$$

and

$$\frac{\mathrm{d}u^+_{\mathrm{m}}}{\mathrm{d}R^4} = \frac{a^+}{4}\left[1 - \left(\overline{u'v'}\right)^{++}\right] \tag{22}$$

The boundary condition for Eq. (21) is $u^+ = 0$ at $R = 1$, and for Eq. (22) is $u^+_{\mathrm{m}} = 0$ at $R = 0$. Eqs. (21) and (22) are independent of Eqs. (18) and (19) and can be solved numerically in advance. Furthermore, the theoretically based correlative equation

$$u^+_{\mathrm{m}} = 3.2 - \frac{227}{a^+} + \left(\frac{50}{a^+}\right)^2 + \frac{1}{0.436}\ln\{a^+\} \tag{23}$$

can be used to predict the computed values of $u^+_{\mathrm{m}} \equiv u(\rho/\tau_{\mathrm{w}})^{1/2}$ almost exactly, thereby precluding the necessity for numerical solution of Eq. (22). *Re* can be evaluated from Eq. (23) for a specified value of $a^+ \equiv a(\rho\tau_{\mathrm{w}})^{1/2}/\mu$ by virtue of $Re = 2u^+_{\mathrm{m}}a^+$. The following expression of Churchill et al. [14] for the turbulent Prandtl number and its analog for the turbulent Schmidt number are arbitrary but, based on prior applications and a fortuitous insensitivity, are presumed not to introduce significant error:

$$Pr_{\mathrm{t}} = 0.85 + \frac{0.015}{Pr} \tag{24}$$

$$Sc_{\mathrm{t}} = 0.85 + \frac{0.015}{Sc} \tag{25}$$

It is difficult to assess the absolute accuracy of Eq. (20) and the ensuing values of $u^+\{y^+, a^+\}$, but a comparison of the predictions of u^+ and u^+_{m} with experimental data by Churchill et al. [15] and an analysis of the sensitivity of those predictions to the arbitrary structure, coefficients, and exponents of Eq. (20) by Churchill et al. [15] indicates that for $a^+ \geqslant 1000$, the error is within the uncertainty of the best experimental data and less than that of any other current models, including large-eddy simulation (LES).

6. Numerical calculations

6.1. Conditions for numerical integration

The illustrative numerical computations were carried out for the following representative parametric conditions: $T_0 = 300$ K, $k = \exp\{20.145 - (5344.5/T)\}$, $Re = 400$ and 37,640, $Pr = 0.7$, $Sc = 0.2$ and $K_{0a} = 0.096$. It follows from the expression for the reaction-rate constant that $k_0 = 10.278\ \mathrm{s}^{-1}$ and $E/\widehat{R}T_0 = 17.815$.

For laminar flow, the computations were carried out for the eight combinations of $\tau = \pm 0.01$ and ± 0.05 with $J = \pm 0.05$ and ± 0.10 that involve opposite signs. For turbulent flow, the computations are examined here only for the eight combinations of $\tau = \pm 0.01$ and ± 0.05 with $J = \pm 0.05$ and ± 0.10 that involve opposite signs although results were obtained for a number of other conditions, mostly involving larger absolute values of *J*. In all cases the computations were recorded for a series of values of K_{0x} up to a value for which Z_{xm} closely approaches unity.

Although the numerical computations produced values of *Z* and T/T_0 as a function of *R* and *X*, only values of Z_{mx}, T_{mx}/T_0, $T_{\mathrm{w}x}/T_0$, and Nu_x were tabulated as functions of K_{0x}. As one exception, values of T/T_0 were tabulated as a function of *R* for a few representative cases. Values of k_{emx}/k_0 per Eq. (12) and values of β per Eq. (13) were calculated from these values. The values of Nu_{ox}, which correspond to $\tau = 0$, are independent of *J*, K_{0a} and *Sc*, and for laminar flow of *Re*, and *Pr* as well. These values were computed as a reference for each condition involving a finite value of τ.

6.2. Tests of the accuracy of the values obtained by numerical integration

The accuracy of the various values obtained by step-wise numerical integration of the partial-differential model was tested in the following ways.

1. Convergence was tested in general by decreasing the step-sizes in radius and axial length.
2. The accuracy of the numerical results for Nu_x for non-reactive laminar flow was tested by comparison with the prior numerical compilations of the Graetz series, as well as with the limiting exact value of 48/11. The accuracy of the numerical results for Nu_x for non-reactive turbulent flow for $Re = 37{,}640$ and $Pr = 0.7$ was tested by comparison with the prior numerical solutions of Yu et al. [16], including the limiting value of 86.10 for $Gz \to \infty$.
3. The accuracy of the numerically computed values of *Nu* for non-reactive turbulent flow and convection was tested by comparison with those predicted by Zajic and Churchill [17].
4. The self-consistency of the computed values of T_{mx}/T_0 and Z_{mx} was tested in terms of Eq. (3).
5. The self-consistency of the numerically computed values of Nu_x, $T_{\mathrm{w}x}/T_0$ and T_{mx}/T_0 was tested in terms of Eq. (4a).

The numerical accuracy in each instance was found to be more than sufficient for all practical purposes.

7. Numerical results for developing reaction and convection in laminar flow

The computed values are too extensive to be presented here in either tabular or graphical form for all of the chosen conditions, so only selective and representative ones are examined.

7.1. Tabulations

Selected characteristic values are listed in Table 1 for an exothermic reaction with a thermicity $\tau = 0.01$ and an

Table 1
Selected characteristics for uniform cooling at the wall in fully developed laminar flow ($Re = 400$, $Pr = 0.7$, $Sc = 0.2$, $k_0a/u_m = 0.096$, $\tau = 0.01$, $J = -0.05$, and $\xi = -1.344$)

k_0x/u_m	Z_{mx}	Nu_{ox}	Nu_x	T_{mx}/T_0	T_{wx}/T_0	k_{emx}/k_0	$-Q_x$	β	Nu_{xP}
0.01	0.009797	22.1346	24.650	1.000024	0.99567	1.00042	1.3314	0.0766	24.85
0.02	0.019425	17.5228	19.971	1.000046	0.99504	1.00082	1.3190	0.0930	20.03
0.05	0.047484	12.8933	15.156	1.000104	0.99351	1.00186	1.2826	0.1164	15.27
0.10	0.091881	10.2678	12.296	1.000175	0.99205	1.00317	1.2244	0.1347	12.47
0.20	0.17335	8.2390	9.9363	1.000245	0.99019	1.00450	1.1160	0.1531	10.16
0.50	0.36213	6.2994	7.4208	1.000001	0.98654	1.00033	0.8441	0.1790	7.63
1.00	0.59693	5.3058	5.9596	0.998528	0.98178	0.97471	0.5280	0.2078	6.07
2.00	0.82408	4.6872	4.9584	0.993432	0.97326	0.88889	0.2102	0.2603	4.99
5.00	0.97558	4.4013	4.44305	0.972730	0.95016	0.60693	0.0199	0.3312	4.57

imposed rate of cooling $J = -0.05$. As can be noted in the table, this rate of cooling comes close to compensating for the heat of reaction, resulting in a nearly constant mixed-mean temperature until the reaction is essentially complete. Accordingly, this condition produced only moderate enhancements of Nu_x; the enhancement rises to a maximum of 20% above that for no reaction at $K_{0x} = 0.20$, and then decreases as $K_{0x} \to \infty$. The quantity Q_x may be observed to decrease in magnitude as K_{0x} increases in accord with Eq. (8). The behavior of the empirical coefficient β and the predicted value of Nu_x, as labelled Nu_{xP}, are discussed subsequently. For the complementary condition of $\tau = -0.01$ and $J = -0.05$ the behavior was similar qualitatively to that in Table 1 and hence the details are not presented herein in tabular form. The slight differences in the values of Z_{mx} and Nu_x are obviously a consequence of the non-linearity of the dependence of the reaction-rate constant on temperature per Eq. (10).

The characteristics for $\tau = -0.05$ and $J = 0.05$, for which the imposed heat flux is dominant over the heat of reaction, are illustrated in Table 2. For this condition, Nu_x is enhanced erratically and attains negative and unbounded values, yet the coefficient β varies monotonically and only moderately with K_{0x}. The following empirical expression was derived to represent computed values of β in Table 2.

$$\beta = 0.23814 + 0.046936\ln\{K_{x0}\} + 0.0026453[\ln\{K_{x0}\}]^2 \tag{26}$$

As can be inferred from the predicted values in Table 2, which are designated as β_P, the coefficients in Eq. (26) were arbitrarily evaluated at $K_{0x} = 0.01$, 0.10, and 1.0. The corresponding predictions of the local Nusselt number, which are designated as Nu_{xP}, are only semi-quantitative, but that is a significant accomplishment considering the chaotic behavior and the simplicity of Eq. (26). The predictions could be made exact at say the peaks in Nu_x or the points of cross-over from positive to negative values at the expense of moderately increased error at other values of K_{0x}.

Table 2
Selected characteristics for uniform cooling at the wall in fully developed laminar flow ($Re = 400$, $Pr = 0.7$, $Sc = 0.2$, $K_{a0} = 0.50$, $\tau = 0.05$, $J = -0.05$, and $\xi = -6.72$)

k_0x/u_m	Z_{mx}	Nu_{ox}	Nu_x	T_{mx}/T_0	T_{wx}/T_0	k_{lmxc}/k_0	$-Q_x$	β	B_p	Nu_{xP}
0.01	0.00986	22.1346	46.444	1.00042	0.99827	1.00748	6.704	0.07808	0.07810	46.445
0.02	0.01965	17.5228	48.585	1.00083	0.99878	1.01496	6.686	0.09562	0.09502	48.020
0.03	0.02940	15.2909	53.233	1.00125	0.99937	1.02244	6.669	0.10689	0.10609	52.201
0.04	0.03910	13.8878	59.590	1.00166	0.99998	1.02993	6.651	0.11532	0.11448	58.031
0.05	0.04875	12.8933	67.709	1.00207	1.00059	1.03743	6.632	0.12208	0.12128	65.580
0.06	0.05836	12.1374	78.089	1.00247	1.00119	1.04494	6.612	0.12773	0.12704	75.296
0.07	0.06793	11.5358	91.593	1.00288	1.00179	1.05245	6.592	0.13259	0.13204	88.007
0.08	0.07745	11.0412	109.70	1.00328	1.00237	1.05997	6.571	0.13686	0.13648	105.153
0.09	0.08694	10.6245	135.07	1.00368	1.00294	1.06750	6.550	0.14066	0.14047	129.361
0.10	0.09635	10.2678	172.83	1.00407	1.00350	1.07501	6.528	0.14409	0.14409	165.780
0.20	0.18821	8.2390	−169.16	1.00793	1.00852	1.15045	6.276	0.16710	0.16945	−146.117
0.30	0.27508	7.2859	−92.184	1.01153	1.01262	1.22521	5.969	0.18079	0.18547	−76.522
0.40	0.35635	6.7024	−94.650	1.01486	1.01591	1.29794	5.614	0.19074	0.19736	−72.370
0.50	0.43155	6.2994	−161.35	1.01788	1.01849	1.36732	5.223	0.19893	0.20688	−99.654
0.60	0.50041	6.0009	−770.59	1.02058	1.02085	1.43217	4.808	0.20636	0.21486	−395.022
0.70	0.56283	5.7695	90.259	1.02296	1.02185	1.49156	4.382	0.21363	0.22174	125.630
0.80	0.61893	5.5842	44.612	1.02502	1.02278	1.54480	3.956	0.22114	0.22780	48.132
0.90	0.66893	5.4324	28.826	1.02678	1.02331	1.59150	3.541	0.22920	0.23323	28.312
1.00	0.71317	5.3058	21.095	1.02825	1.02351	1.63152	3.145	0.23801	0.23814	19.585
2.00	0.93597	4.6872	6.623	1.03199	1.01689	1.73712	0.747	0.39112	0.27194	4.940
5.00	0.99874	4.4013	4.477	1.01292	0.99058	1.25503	0.011	1.59048	0.32053	3.781

Table 3
Numerically computed values of β in fully developed laminar flow ($Re = 400$, $Pr = 0.7$, $Sc = 0.2$, and $K_{0a} = 0.096$)

Predicted	τ	−0.01	−0.01	−0.05	−0.05	0.01	0.01	0.05	0.05	Arithmetic average
	J	0.05	0.10	0.05	0.10	−0.05	−0.10	−0.05	−0.10	
0.07810		0.0820	0.0852	0.0805	0.0835	0.0766	0.0738	0.0781	0.0751	0.0794
0.09502		0.1013	0.1065	0.0985	0.1034	0.0929	0.0884	0.0956	0.0908	0.0972
0.10609		0.1139	0.1208	0.1100	0.1164	0.1031	0.0927	0.1069	0.1006	0.1081
0.11448		0.1235	0.1317	0.1186	0.1262	0.1105	0.1035	0.1153	0.1077	0.1171
0.12128		0.1312	0.1407	0.1254	0.1342	0.1164	0.1083	0.1221	0.1132	0.1239
0.12704		0.1377	0.1484	0.1312	0.1409	0.1212	0.1122	0.1277	0.1178	0.1296
0.13204		0.1433	0.1551	0.1361	0.1468	0.1253	0.1154	0.1326	0.1216	0.1345
0.13648		0.1483	0.1661	0.1405	0.1520	0.1288	0.1181	0.1369	0.1249	0.1377
0.14047		0.1528	0.1665	0.1445	0.1568	0.1320	0.1205	0.1407	0.1278	0.1427
0.14409		0.1569	0.1715	0.1480	0.1611	0.1347	0.1226	0.1441	0.1303	0.1462
0.16945		0.1861	0.2076	0.1738	0.1929	0.1531	0.1352	0.1671	0.1463	0.1703
0.18547		0.2056	0.2322	0.1916	0.2155	0.1640	0.1417	0.1808	0.1548	0.1858
0.19736		0.2212	0.2519	0.2064	0.2343	0.1721	0.1461	0.1907	0.1606	0.1979
0.20688		0.2350	0.2692	0.2195	0.2512	0.1790	0.1495	0.1989	0.1652	0.2084
0.21486		0.2476	0.2850	0.2316	0.2669	0.1853	0.1523	0.2064	0.1694	0.2181
0.22174		0.2596	0.2999	0.2429	0.2816	0.1911	0.1548	0.2136	0.1735	0.2271
0.22780		0.2712	0.3144	0.2537	0.2958	0.1968	0.1571	0.2211	0.1778	0.2360
0.23323		0.2826	0.3285	0.2640	0.3094	0.2023	0.1593	0.2292	0.1823	0.2447
0.23814		0.2938	0.3425	0.2739	0.3225	0.2078	0.1612	0.2380	0.1872	0.2534
0.27194		0.4101	0.5001	0.3572	0.4392	0.2603	0.1727	0.3911	0.2577	0.3486
0.32053		1.1371	3.6114	0.5283	0.9180	0.3312	0.1247	1.5905	0.3851	1.0783

The values of β for the eight conditions chosen for the numerical calculations are listed for a series of values of K_{0x} in Table 3. They reveal a significant variation from case to case and from the prediction of Eq. (26), which, perhaps fortuitosly differs only slightly from their numerical average for each value of K_{0x}. On the other hand, the corresponding predictions of Nu_x, as labelled Nu_{xP}, in Tables 2 and 3, are of acceptable accuracy for all practical purposes for all of the eight conditions of Table 3. This useful result is an obvious consequence of the insensitivity of Nu_x, to β except for conditions that generate extreme behavior. Better predictions could be generated by deriving the equivalent of Eq. (26) for each condition but this would be at the expense of a loss of generality.

7.2. Graphical representations

The computed values of the local mixed-mean conversion and the coefficient β are plotted versus K_{0x} in semi-logarithmic coordinates in Fig. 1a and b, and the local Nusselt number in log-log coordinates in Fig. 1c for the chosen combinations of values of τ and J (with one exception for the Nusselt number). It is apparent that the variations with K_{0x}, τ and J are minor and orderly.

The small perturbations in the mixed-mean conversion from that for an isothermal reaction may be attributed primarily to the deviation of T_{mx}/T_0 and in turn, k_{emx}/k_0 from unity. The mixed-mean conversions for adiabatic flow (not shown) depart further than those for finite values of J because the latter are all compensatory with respect to the heat of reaction.

The plotted values of the coefficient β in Fig. 1b, as determined from Eq. (13) and the essentially exact computed values of Nu_x and Z_{mx}, suggested the form of Eq. (26) and the choice of common values for the coefficients therein as a crude approximation. The variation in β from case to case and with K_{0x} is attributable to the idealizations made in formulating Eqs. (7), (8), (10) and (12), and in particular the neglect of molecular and eddy diffusion of species A. The gross departures from a semi-logarithmic relationship and from one condition to another for K_{0x} greater than unity are associated with extreme numerical sensitivity for conversions approaching unity. These latter departures are of no concern because, for practical as well as intrinsic reasons, interest is focussed on the behavior for K_{0x} significantly less than unity.

The local Nusselt number is seen in Fig. 1c to be enhanced modestly and more or less equally by the energetic reaction for all of the conditions. The one exception, which occurred for $\tau = -0.05$ and $J = -0.05$, is shown separately in Fig. 2. The numerically computed values therein are represented by the symbol ∘ and the predictions of Eq. (13), using numerically predicted values of Nu_{ox}, and values of k_{emx}/k_0 from Eq. (12), Z_{mx} from Eq. (14), and values of β from Eqs. (12), (14) and (26), by the continuous curve. Although the prediction is slightly inaccurate in a quantitative sense, it is invaluable in a qualitative sense and avoids the need for a complete numerical computation for a large series of closely spaced values of K_{0x}. Indeed, the prediction illustrated in Fig. 2 alone justifies the derivation of the analogy. Such behavior could never be explained, let alone predicted without it.

The numerically computed values of T_{mx} and T_{wx} for four conditions are plotted versus K_{0x} in Fig. 3. In Fig. 3a for $\tau = 0$ and $J = 0.05$, for which there is no reaction and hence no enhancement of Nu_x, and in Fig. 3b

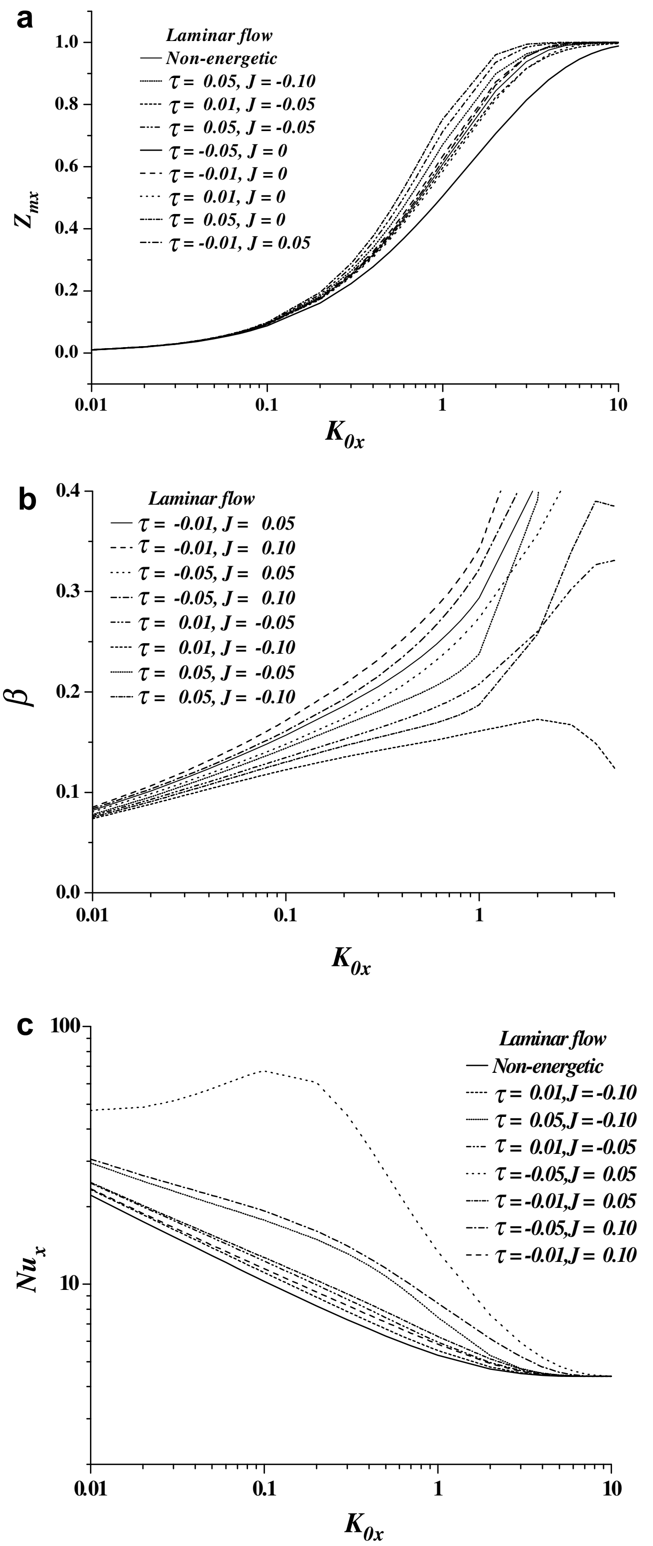

Fig. 1. The axial variation of computed characteristics for an energetic reaction in laminar flow. (a) $Z_{\mathrm{m}x}$, (b) β and (c) Nu_x.

for $\tau = -0.01$ and $J = 0.05$, for which the enhancement is very limited, the curves are widely separated. Their closer approach In Fig. 3c for $\tau = -0.05$ and $J = 0.05$ corresponds to significant but regular enhancement. Their very close approach in Fig. 3d for $\tau = 0.05$ and $J = -0.05$ corresponds to a gross enhancement of Nu_x, and their crossovers to the unbounded values and the change in sign.

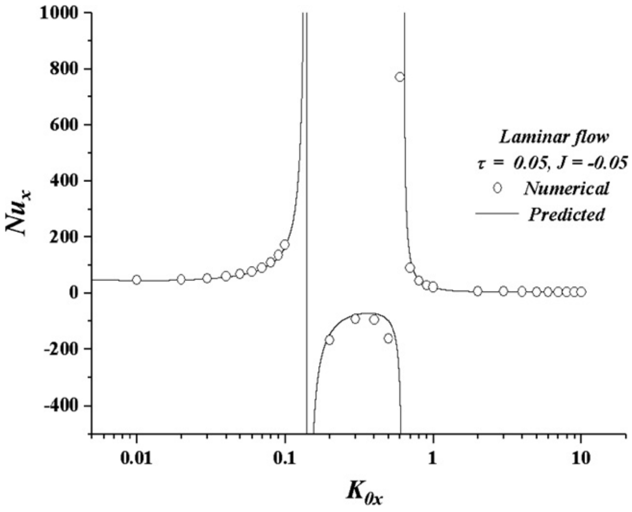

Fig. 2. The axial variation of Nu_x in laminar flow for $\tau = 0.05$ and $J = -0.06$.

The continuous curve in Fig. 2 constitutes a successful mathematical prediction of the erratic behavior of Nu_x but hardly a physical explanation. The criss-crossing of the values of in Fig. 3d provides a rationale for the negative and unbounded values of Nu_x but still not a physical explanation. However, such an explanation may be inferred from the radial temperature distributions in Fig. 3e for three cases: a non-reactive flow ($\tau = 0$); a slightly endothermic reaction with nearly compensatory heating ($\tau = 0.01$ and $J = -0.05$); and strongly exothermic heating with less than compensatory cooling ($\tau = 0.05$ and $J = -0.05$), in each case for $K_{0x} = 1.0$. For the second condition the temperature distribution is seen to depart significantly from that for no reaction, and for the third condition the departure is so great that the mixed-mean temperature falls below the wall temperature even though cooling is taking place at the wall, resulting in a negative value of Nu_x.

The radial temperature distribution may be strongly distorted by a reaction because its rate varies with both radius and axial distance. For example, consider the region near the entrance. For an exothermic reaction with cooling at the wall, the rate of reaction and the rate of release of the heat of reaction are higher near the wall because of the lower axial velocity. Further downstream the effects of the composition and temperature on the rate of reaction may become more important than the velocity distribution.

8. Numerical results for developing reaction and convection in turbulent flow

The behavior of the local Nusselt number for developing convection in fully developed forced convection with a uniform heat flux at the wall and a developing energetic reaction in fully developed turbulent flow might be expected to be similar to that for fully developed laminar

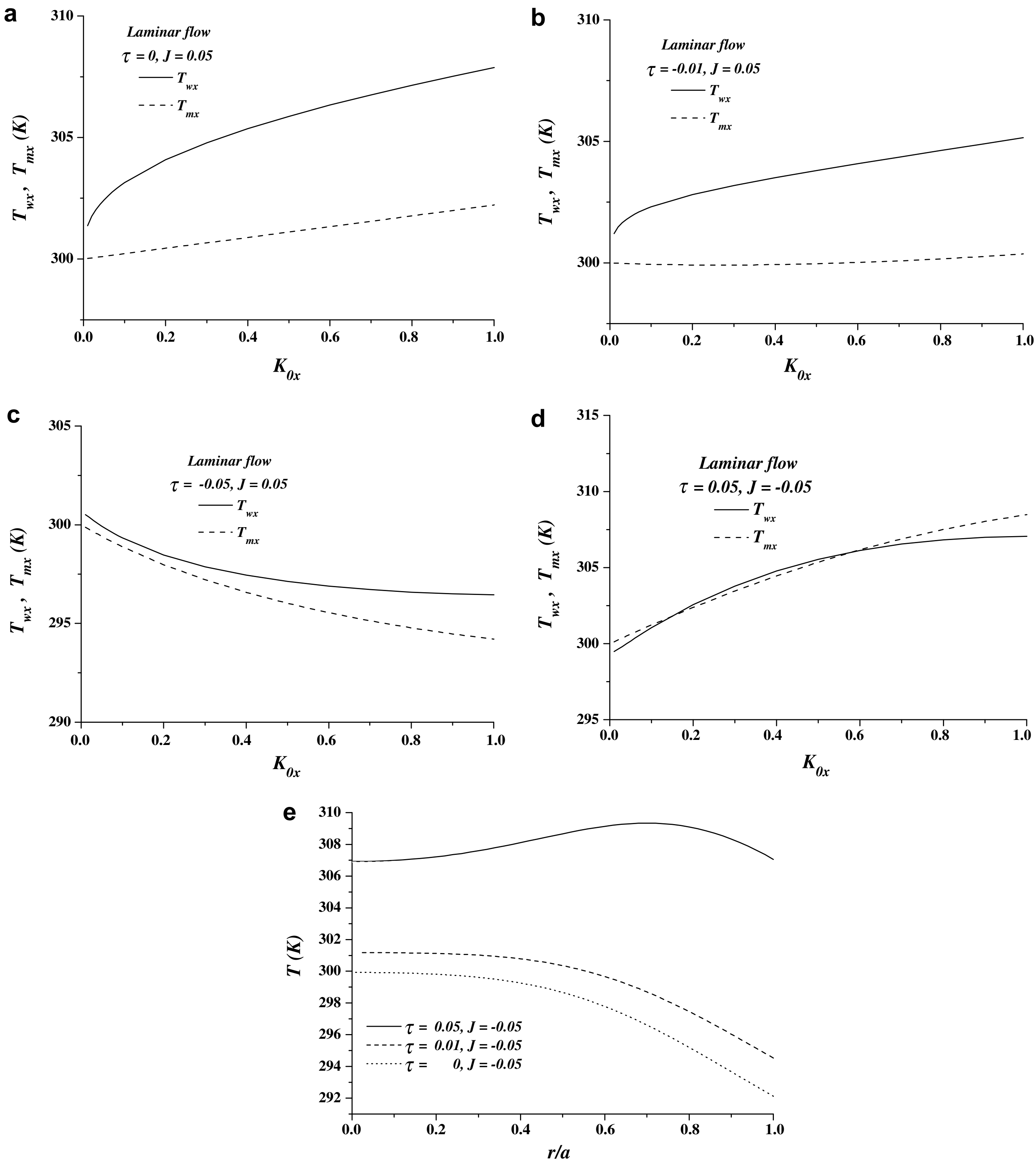

Fig. 3. Temperature distributions in laminar flow.

flow as examined in Section 7. That proves to be the case qualitatively but not quantitatively.

8.1. Tabulations

Two particular conditions were chosen for detailed tabulation of the characteristics for turbulent flow because they represent extremes in the variation of Nu_x. For $\tau = -0.01$ and $J = 0.05$, as illustrated in Table 4, the mixed-mean temperature falls only slightly (less than 1%), but Nu_x attains extreme positive and negative values. For $\tau = -0.01$ and $J = 0.10$ (twice the rate of heating), as illustrated in Table 5, the mixed-mean temperature varies even less, but Nu_x remains positive and bounded although it is enhanced by a factor of over 5. Table 5 includes a lesser number of values of K_{0x} because of the more restrained variations in Nu_x.

Remarkably, the numerically computed values of β in Tables 4 and 5 are almost identical despite the great differences in Nu_x, from which it may be inferred that these latter differences are attributable to the values of Q_x, which are known exactly except for the approximations made for k_{emx}/k_0 and Z_{mx}, namely Eqs. (12) and (14), respectively. Not only are the values of β nearly the same for these two different conditions, but also as illustrated in Table 6, this near-invariance holds for all eight cases. Thus, the applicability of the analogy for turbulent flow, as measured by the invariance of β, is better than for laminar flow, at least within the range of these eight conditions.

The following empirical equation represents the values of β for these eight cases reasonably well:

$$\beta = 0.0229 + 0.00506 \ln\{K_{0x}\} + 0.000349(\ln\{K_{0x}\})^2 \tag{27}$$

The coefficients of Eq. (27) are arbitrarily based on the numerically computed values of β for $\tau = -0.01$ and $J = 0.05$ at $K_{0x} = 0.01$, 0.10, and 1.00.

The predictions of Nu_x by Eq. (13) with β from Eq. (27) are included in Tables 4 and 5 under the heading Nu_{xP}. The semi-quantitative predictions for the chaotic behavior illustrated in Table 4, including the changes in sign and the approach to unbounded values, as well as of the as the monotonic but extreme enhancements in Table 5, over-shadow the minor deviations, which could be reduced individually by tweaking the constants of Eq. (27). Similar representations were attained for the other six cases. Even apart from these semi-quantitative predictions, Eq. (7), and its several extended forms, have proven to be invaluable in explaining such extreme and unexpected behavior.

8.2. Graphical representations

Figs. 4 and 5 are the analogues for turbulent flow of Figs. 1–3 for laminar flow. The mixed-mean conversion is

Table 4
Selected characteristics for uniform heating at wall in fully developed turbulent flow ($Re = 37{,}640$, $Pr = 0.7$, $Sc = 0.2$, $K_{0a} = 0.096$, $\tau = -0.01$, $J = 0.10$, and $\xi = -63.225$)

k_0x/u_m	Z_{mx}	Nu_{ox}	Nu_x	T_{mx}/T_0	T_{wx}/T_0	k_{emx}/k_0	$-Q_x$	B	Nu_{xP}
0.01	0.00993	250.9484	448.0105	0.999903	1.000349	0.99826	62.484	0.0070	446.2
0.02	0.01974	204.3454	436.4400	0.999806	1.000264	0.99654	61.758	0.0086	427.7
0.05	0.04847	160.5389	469.1632	0.999523	0.999949	0.99154	59.647	0.0110	458.9
0.10	0.09413	138.1147	535.7910	0.999075	0.999448	0.98363	56.332	0.0132	533.5
0.20	0.17789	122.2600	583.0863	0.998253	0.998596	0.96932	50.378	0.0174	594.5
0.50	0.38024	107.6940	386.7585	0.996277	0.996794	0.93559	36.658	0.0197	387.9
1.00	0.60521	99.7486	207.8470	0.994106	0.995068	0.89976	22.456	0.0232	205.1
2.00	0.83323	93.8709	124.0324	0.991984	0.993597	0.86592	9.130	0.0266	124.3
5.00	0.98616	89.4916	91.5108	0.990929	0.993115	0.84953	0.7436	0.0297	96.1

Table 5
Selected characteristics for uniform heating at wall in fully developed turbulent flow ($Re = 37{,}640$, $Pr = 0.7$, $Sc = 0.2$, $K_{0a} = 0.096$, $\tau = -0.01$, $J = 0.05$, and $\xi = -126.45$)

k_0x/u_m	Z_{mx}	Nu_{0x}	Nu_x	T_{mx}/T_0	T_{wx}/T_0	k_{emx}/k_0	$-Q_x$	β	Nu_{pP}
0.010	0.00993	250.9484	2032.9591	0.999901	0.999951	0.99824	124.966	0.0070	2010.9
0.020	0.01974	204.3454	−3486.7209	0.999080	0.999776	0.99652	123.513	0.0086	−4602.8
0.030	0.02944	182.6958	−1079.4286	0.999708	0.999615	0.99481	122.082	0.0096	−1176.3
0.040	0.03901	169.5628	−684.7226	0.999612	0.999467	0.99311	120.673	0.0103	−715.8
0.050	0.04847	160.5389	−522.4978	0.999519	0.999328	0.99147	119.285	0.0110	−534.5
0.060	0.05782	153.8626	−434.0729	0.999426	0.999196	0.98983	117.918	0.0115	−437.9
0.070	0.06706	148.6727	−378.4900	0.999335	0.999071	0.98821	116.571	0.0119	−378.1
0.080	0.07619	144.4918	−340.4114	0.999150	0.998951	0.98662	115.244	0.0124	−337.5
0.090	0.08522	141.0317	−312.7896	0.999219	0.998840	0.98617	113.936	0.0127	−308.3
0.10	0.09411	138.1147	−291.9820	0.999067	0.998724	0.98350	112.651	0.0131	−286.5
0.20	0.17785	122.2600	−215.7839	0.998237	0.997774	0.96903	100.734	0.0156	−207.8
0.30	0.25268	115.1160	−207.7963	0.997497	0.997016	0.95628	90.361	0.0172	−199.5
0.40	0.31977	110.7487	−221.3763	0.996833	0.996382	0.94499	81.278	0.0185	−212.8
0.50	0.38009	107.6940	−251.5290	0.996239	0.995841	0.93495	73.283	0.0195	−242.5
0.60	0.43447	105.3895	−302.7334	0.995702	0.995372	0.92600	66.215	0.0204	−293.2
0.70	0.48358	103.5651	−389.8312	0.995220	0.994963	0.91799	59.941	0.0211	−379.7
0.80	0.52804	102.0715	−555.2689	0.994782	0.994603	0.91080	54.352	0.0218	−545.1
0.90	0.56834	100.8188	−996.3524	0.994388	0.994284	0.90434	49.358	0.0224	−961.7
1.00	0.60492	99.7486	−3539.9751	0.994030	0.994002	0.89853	44.885	0.0229	−3759.8
2.00	0.83281	93.8709	180.6121	0.991830	0.992380	0.86451	18.255	0.0270	184.3
5.00	0.98596	89.4916	93.5902	0.990536	0.991604	0.84348	1.497	0.0293	104.3

Table 6
Predicted and numerically computed values of β in fully developed turbulent flow ($Re = 37{,}640$, $Pr = 0.7$, $Sc = 0.2$, and $K_{0a} = 0.096$)

K_{0x}	Predicted	τ	−0.01	−0.01	−0.05	−0.05	0.01	0.01	0.05	0.05	Arithmetic average
		J	0.05	0.10	0.05	0.10	−0.05	−0.10	−0.05	−0.10	
0.01	0.0070		0.0070	0.0070	0.0069	0.0069	0.0070	0.0070	0.0071	0.0071	0.0070
0.10	0.0131		0.0131	0.0132	0.0126	0.0127	0.0132	0.0131	0.0138	0.0137	0.0132
0.20	0.0157		0.0156	0.0157	0.0150	0.0151	0.0156	0.0155	0.0165	0.0164	0.0157
0.30	0.0173		0.0172	0.0174	0.0166	0.0168	0.0172	0.0171	0.0181	0.0179	0.0173
0.40	0.0186		0.0185	0.0186	0.0180	0.0181	0.0184	0.0182	0.0191	0.0190	0.0185
0.50	0.0196		0.0195	0.0197	0.0191	0.0193	0.0193	0.0191	0.0198	0.0196	0.0194
0.60	0.0204		0.0204	0.0206	0.0201	0.0203	0.0201	0.0199	0.0202	0.0200	0.0202
0.70	0.0211		0.0211	0.0213	0.0209	0.0212	0.0207	0.0205	0.0204	0.0202	0.0208
0.80	0.0218		0.0218	0.0220	0.0217	0.0220	0.0213	0.0211	0.0206	0.0204	0.0214
0.90	0.0224		0.0224	0.0226	0.0224	0.0227	0.0217	0.0215	0.0206	0.0204	0.0218
1.00	0.0229		0.0229	0.0232	0.0231	0.0233	0.0222	0.0219	0.0206	0.0204	0.0222

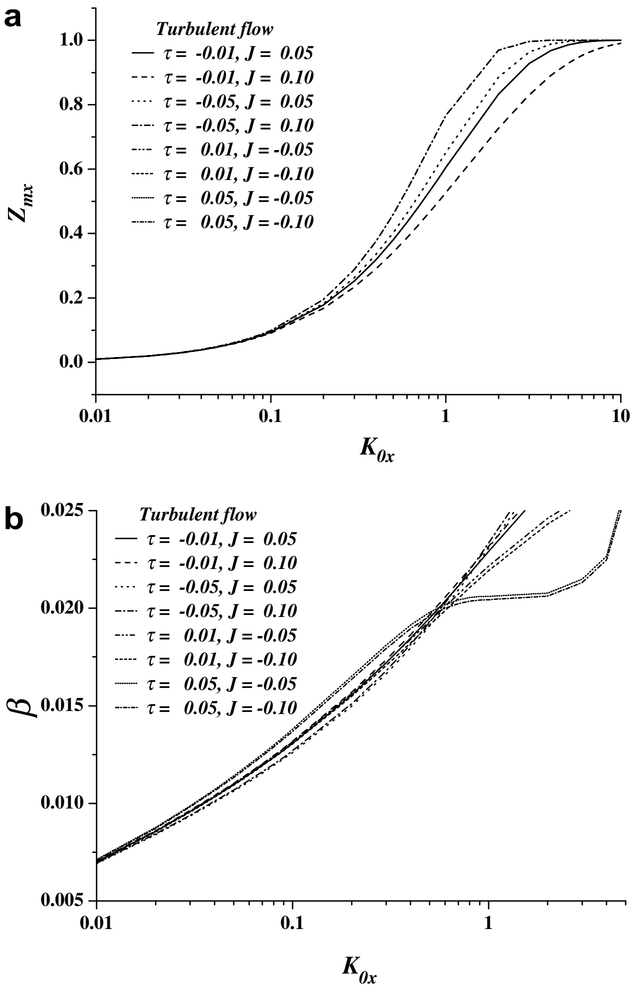

Fig. 4. The axial variation of computed characteristics for an energetic reaction in turbulent flow. (a) Z_{mx} and (b) β.

plotted in Fig. 4a. Only four curves are apparent in addition to the one for isothermal reaction because the conversions for $J = 0.05$ and 0.10 differ negligibly from one another in all cases. However, the five distinct curves may be noted to vary slightly more from condition to condition than they did in laminar flow. Comparison of Fig. 1a and Fig. 4a indicates that the mixed-mean conversion is slightly less in this turbulent flow for endothermic reactions and slightly greater for exothermic reactions than for laminar flow, at least for these conditions.

The values of β plotted in Fig. 4b are much smaller in magnitude than those for laminar flow but also display a semi-logarithmic dependence on K_{0x} and the same near-invariance from one thermal condition to another for K_{0x} less than unity.

The values of Nu_x for the nine chosen cases for turbulent flow are distributed three-each in Fig. 5a–c. The numerically values are represented by the symbols while the predictions of Eq. (27), using numerically predicted values of Nu_{0x}, values of k_{emx}/k_0 from Eq. (12), and values of Z_{mx} from Eq. (14), are represented by the curves. As mentioned previously, the deviations are perhaps tolerable in consideration of the overall qualitative success. The local Nusselt number for turbulent flow may be observed in Fig. 5 to have a wider variation from condition to condition than for laminar flow.

Plots of the longitudinal variation of T_{mx} and T_{wx} and of the radial temperature distribution are similar qualitatively to those for laminar flow and therefore are not shown.

9. Interpretation of the representation of the local Nusselt number in terms of the analogy

The analogy of Churchill [8] between reaction and heat transfer in tubular flow appears, on the basis of the results presented in Sections 7 and 8, to be invaluable for interpretation of the radical variations of the local Nusselt number, very useful in conjunction with Eqs. (12) and (14) for correlation and predictions in turbulent flow and also, but with less accuracy, in laminar flow. However, the specific dependences of Nu_x on Re, Pr, Sc, $K_{0a}\tau$, J, K_{0x}, and Z_{mx}, await definitive confirmation.

10. The role of simulation

An alternative to the use of predictive and/or correlative algebraic expressions such as Eqs. (12), (14), (26) and (27),

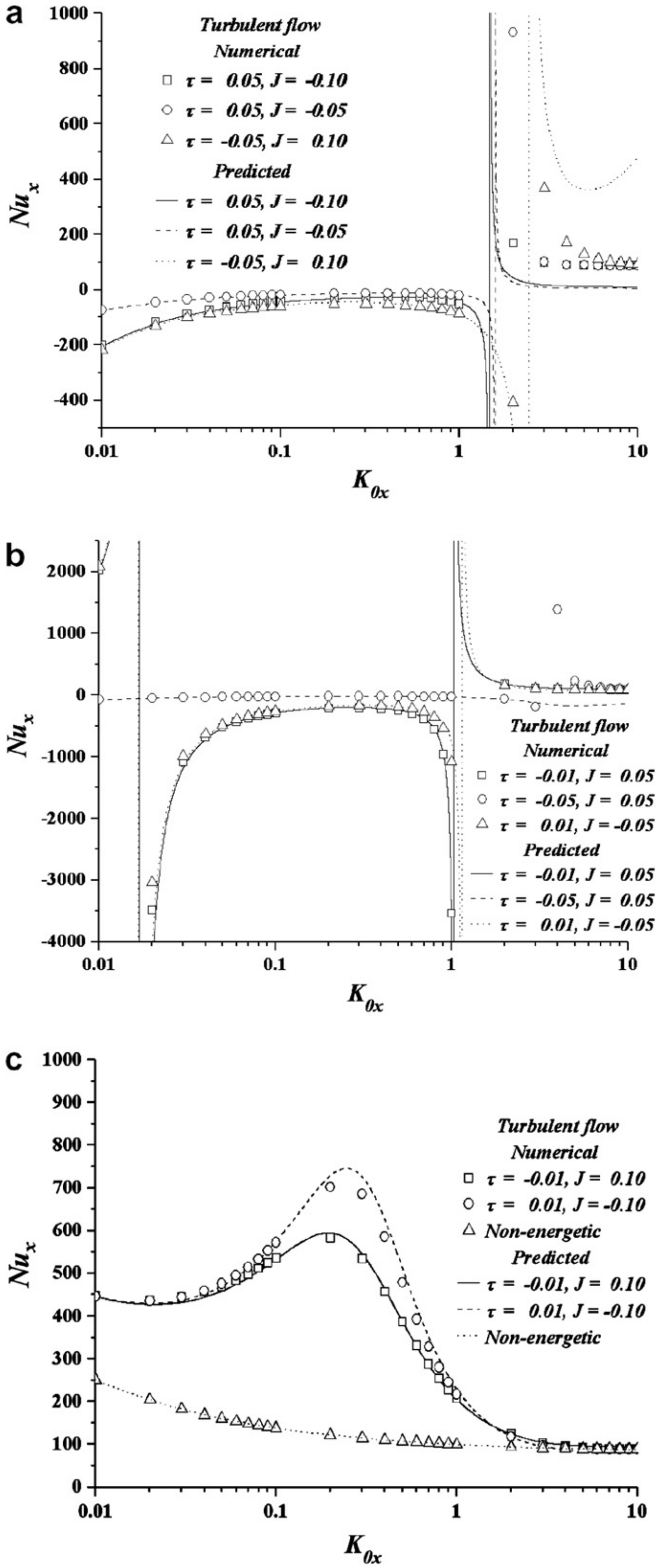

Fig. 5. The axial variation of Nu_x in turbulent flow.

is the numerical solution by finite-difference methods of a mathematical model in the form of the partial differential equations of conservation for momentum, energy, and chemical species for each condition. This was the method used to generate all of the numerical values in Tables 1–6 except those attributed to the predictive algebraic expressions. One consequence of carrying out the computations in this investigation was the recognition that they are within the reach of undergraduate students and practicing engineers.

As an example, consider developing convection without reaction in fully developed flow. For the laminar regime, the execution of a numerical solution requires less programming and less computation for a given degree of accuracy than the classical solutions of Graetz in the form of infinite series. For the turbulent regime, the algebraic analogy of Reichardt as modified by Zajic and Churchill [17] may be of more than sufficient accuracy, but the finite-difference solution does not require significantly more computation, particularly if it is carried out in conjunction with the finite-difference solution for a reacting stream.

The approximations introduced into the analogy by Eqs. (12) and (14) are unnecessary when carrying out a numerical integration, and indeed were not made in the numerical calculations presented herein. It would be possible to take into account the variations in the thermal conductivity, the heat capacity, the heat of reaction, the energy of reaction, and the diffusivity of the reactant with temperature and composition without greatly complicating the numerical integrations, but in the interests of clarity and generality this was not done herein.

On the other hand, taking into the variation of the viscosity and density with temperature and composition, as well as entrance effects, complicates the integration by an order of magnitude, and perhaps places it beyond the reach of both undergraduates and practitioners because the invariant radial velocity distribution is replaced by a partial differential equation intimately coupled with the energy and species balances. Eddy and molecular diffusion of energy and species in the direction of flow could also be taken into account but the resulting complications in modeling and numerical solution are probably not justified by the minute improvement in accuracy.

At the present time, most design packages for homogeneous tubular reactors utilize less accurate models for laminar and turbulent flow than those used herein. Indeed, many of them postulate plug flow, which introduces serious error for both the laminar and turbulent regimes for energetic, gas-phase reactions. These out-dated packages can be expected to be corrected in the next few years, removing the necessity of self-programming in this respect.

In the interests of simplicity, all of the derivations herein been confined to a single, first-order, irreversible, equimolar reaction. Multiple reactions require additional equations for the conservation of species and additional terms for the conservation of energy, thereby complicating but not changing the character of the modeling. Non-equimolar reactions change the density and thereby the velocity field both radially and longitudinally, and pose the same complications as a temperature-dependent viscosity and density.

Numerical simulation has a pervasive and growing role in education and practice in fluid mechanics, heat transfer, and mass transfer, and should be extended to reaction engineering, where education and practice in this respect appear to be frozen in the past. Despite the previously acquired skills of the students in numerical analysis, methodologies and solutions that take into account simultaneous momentum, energy, and mass transfer for chemical conversions in tubular flow are not to be found in the textbooks on reaction engineering or in the packages for computer-aided design. Instead, the solutions and methodologies are based on the concept of "plug flow", which obviates the consideration of momentum, mass, and energy transfer at the price of an error of unknown magnitude.

11. The significance of the local Nusselt number

If two-dimensional simulation is used to model the fields of temperature and composition in a tubular reactor with a specified uniform heat flux density at the wall, neither the heat transfer coefficient nor the Nusselt number necessarily appear in the model or the numerical solution. It is the effect of the heat of reaction on the radial temperature distribution and thereby on the mixed-mean temperature, a lumped parameter introduced in the definition of the heat transfer coefficient, that results in negative and extreme values of the Nusselt number.

Why bother with the Nusselt number? The reason is that lumped-parameter models incorporating the heat transfer coefficient are commonly used for process design and analysis of chemical reactors. Such simplified modeling may no longer be justified in view of the state of the art in computing, but it is consistent with the use of other gross idealizations, in particular plug flow and isothermality, in reaction engineering. In such instances, a quantitative knowledge of the extreme and chaotic variation of the local heat transfer coefficient and Nusselt number is essential. Otherwise the reactor and heat exchanger may be misdesigned to the point of failure.

Lumped-parameter modeling may still today have some justification in case of complex reactive processes that involve several mechanisms of transport as does the aforementioned one modeled by Bernstein [1].

12. Summary and conclusions

From prior numerical calculations and experimental work, although scattered and incoherent it could be inferred that heating or cooling the wall of a tubular reactor might produce irregular and extreme perturbations of the local Nusselt number.

The coherent results obtained in the current work by numerical solution of an ordinary differential model for the conservation of momentum and a partial differential model for the conservation of energy and species confirm that under some conditions a uniform heat flux density on the wall may produce negative, extreme, and even unbounded values of the local Nusselt number as well as a highly irregular variation with axial distance (see Figs. 2 and 5). Accordingly, extreme caution is suggested when designing combined reactors and heat exchangers using lumped-parameter models. Although the mixed-mean conversion is dependent on the local radial and longitudinal variations in temperature, its variation does not echo the drastic excursions in the Nusselt number.

The numerical results presented here are limited to fully developed flow at Reynolds numbers of 400 and 37,640, and, in the interests of simplicity and clarity, to a single first-order irreversible equimolar reaction and to invariant physical properties other than the reaction-rate constant. The modeling for the Reynolds number of 37,640 constitutes an improvement over all prior work in the turbulent regime in that it invokes a nearly exact model for the transport of momentum, energy, and species.

The errors of discretization varied widely from condition to condition and with radius and length. Ad hoc tests indicate that they are completely negligible with respect to the uncertainties associated with the idealizations in the model. The self-consistency of the tabulated values is evidence in that respect.

An exact expression, namely Eq. (3), was derived for the mixed-mean temperature in terms of the thermicity, the specified uniform heat flux density on the wall, the mixed-mean conversion, and the Graetz number. That expression can be used to identify conditions that balance the heat of reaction with the heat flux at the wall and thereby minimize the variation of the mixed-mean temperature on the mean. Another exact expression, namely Eq. (5), was derived for the wall-temperature, but as a function of the local Nusselt number as well as of the several variables that determine the local mixed-mean temperature.

A simple expression in closed-form for the highly idealized case of fully developed laminar convection with volumetrically uniform reactive heating or cooling and uniform heating or cooling on the wall, namely Eq. (6), was derived in previous work, and a generalized form of that expression, namely Eq. (7), was speculated to be applicable for developing reaction and heat transfer. The greatest contribution of Eq. (7) is the identification of the magnitude and sign of the deviation, if any, of the quantity βQ_x from unity as the source of the erratic behavior of the local Nusselt number. Eq. (11), an expanded form of Eq. (7), identifies Q_x as $\xi(k_{emx}/k_0)(1 - Z_{mx})$. The parameter $\xi = \tau RePrK_{0x}/4J$ remains constant and ordinarily negative as the reacting stream flows through tube, whereas $1 - Z_{mx}$ decreases, and k_{emx}/k_0 may increase or decrease.

A lesser but important contribution of Eq. (7) should be mentioned. Empirical expressions such as Eqs. (26) and (27) predict the variation of β with distance down the reactor and together with Eqs. (12) and (14) permit quantitative predictions of Nu_x. Such predictions are illustrated in Figs. 2 and 4.

From Eq. (7) and its amplification as Eq. (13) it may be inferred that the erratic behavior of the local Nusselt number is generated by the varying input or output of thermal energy due to reaction as compared to the uniform heat flux at the wall. However, this is not in itself a physical explanation. The explanation is the varying rate of reaction with radius as well as length, which changes the difference between the mixed-mean and wall temperature even though the heat flux at the wall is unchanged. For example, if an energetic reaction occurs preferentially near the wall the transport to the wall is facilitated and the heat transfer coefficient is increased.

If the coupled partial differential equations of conservation for momentum, species, and energy are simply solved numerically with an appropriate thermal boundary condition, as was done in the course of this work for a homogeneous reaction in fully developed tubular flow with external compensatory heat transfer, the Nusselt number is not directly involved and need not be invoked. Such solutions are within the reach of undergraduate students and practicing engineers. However, the local Nusselt number for this situation has utility in three senses. First, it identifies underlying thermal behavior that might otherwise go recognized. Second, it is an essential input if a reactor/heat exchanger is modeled in one dimension, for example as is done if plug flow is postulated, which is the normal, current procedure in both education and practice. Third, it is a convenient if not essential quantity in modeling behavior in which other mechanisms of transport such as thermal radiation are involved.

Acknowledgements

Y.B. gratefully acknowledges the support from the National Natural Science Foundation of China (No. 50506017), National Research Foundation for the Doctoral Program of Higher Education in PR China (No. 20050425006) and the Key Project of Chinese Ministry of Education (No. 106034).

References

[1] M.H. Bernstein, Pollutant formation and multiple stationary states in radiantly stabilized flames, Ph.D. Thesis, University of Pennsylvania, Philadelphia, PA, 1976.

[2] L.D. Pfefferle, S.W. Churchill, NO_x production from the combustion of ethane doped with ammonia in a thermally stabilized burner, Combust. Sci. Technol. 49 (1986) 235–249.

[3] S.W. Churchill, Compact heat exchangers as chemical reactors, Proceedings of the Fourth International Conference on Compact Heat Exchangers and Enhancement Technology for the Process Industries, ASME, New York, 2003.

[4] S.W. Churchill, Interaction of chemical reactions and transport. 1. An overview, Ind. Eng. Chem. Res. 44 (2005) 5199–5212.

[5] S.W. Churchill, Bu Yu, The effects of transport on reactions in homogeneous tubular flow, Ind. Eng. Chem. Res. 45 (2006) 8583–8595.

[6] S.W. Churchill, Analogy between reaction and heat transfer, AIChE J. 52 (11) (2006) 3645–3657.

[7] P.L.T. Brian, R.C. Reid, Heat transfer with simultaneous chemical reaction: film theory for a finite reaction rate, AIChE J. 8 (1962) 322–329.

[8] P.L.T. Brian, Turbulent flow heat transfer with a simultaneous chemical reaction of finite rate, AIChE J. 9 (1963) 831–840.

[9] R.I. Rothenberg, J.M. Smith, Heat transfer and reaction in laminar flow tube, AIChE J. 12 (1966) 213–220.

[10] G. Ooms, G. Groen, D.P. de Graag, J.F.F. Ballintijn, On turbulent pipe flow with heat transfer and chemical reaction, Proceedings of the Sixth International Heat Transfer Conference, vol. 5, Hemisphere, Washington, DC, 1978.

[11] P.L.T. Brian, R.C. Reid, S.W. Bodman, Heat transfer to decomposing nitrogen dioxide in a turbulent boundary layer, AIChE J. 11 (5) (1965) 809–815.

[12] L.L. Edwards, R.R. Furgason, Heat transfer in thermally decomposing ozone, Ind. Eng. Chem. Fundam. 7 (1968) 441–445.

[13] S.W. Churchill, New simplified models and formulations for turbulent flow and convection, AIChE J. 43 (1997) 1125–1140.

[14] S.W. Churchill, Masahisa Shinoda, Norio Arai, An appraisal of resources and methodologies for prediction of flow and convection in channels, Therm. Sci. Eng. 9 (4) (2001) 9–10.

[15] S.W. Churchill, Bo Yu, Yasuo Kawaguchi, The accuracy and parametric sensitivity of algebraic models for turbulent flow and convection, Int. J. Heat Mass Transfer 48 (2005) 5488–5503.

[16] Bo Yu, Hiroyuki Ozoe, S.W. Churchill, The characteristics of fully developed turbulent convection in a round tube, Chem. Eng. Sci. 56 (2001) 1781–1800.

[17] S.C. Zajic, S.W. Churchill, Prediction of fully developed convection with minimal explicit empiricism, AIChE J. 48 (2002) 927–940.