

THE EXTRAORDINARY EFFECTS OF AN ENERGETIC, HOMOGENEOUS CHEMICAL REACTION ON INTERNAL CONVECTIVE HEAT TRANSFER IN TUBULAR FLOW

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Abstract

Although it was first noted over 40 years that the combination of an energetic reaction and heat transfer at the wall may result in a great enhancement or a modest attenuation of the convective heat transfer coefficient, this behavior appears to have gone unmentioned in textbooks and handbooks on either reaction engineering or heat transfer

New detailed and coherent and numerical solutions that take radial diffusion of momentum, energy, and species into account confirm the validity of the enhancements and attenuations and in addition reveal that the enhancement may vary chaotically along the length of the reactor. This seemingly anomalous behavior is explained by means of a semi-theoretical model, by examination of the longitudinal wall-temperature profile, and by examination of the radial profile of the temperature within the fluid..

Introduction

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 reaction. 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 required to prevent a thermal run-away or undesirable side-reactions. A number of theoretical analyses and experimental investigations have 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 of combined reaction and convection are fragmentary and incoherent, and have generally been overlooked in the literature of both heat transfer and reaction engineering.

The objective of the long-term investigation, of which the current work is a part, is to evaluate the validity of the several idealizations such as plug flow that are so prevalent in reaction engineering. The limited objective herein is to evaluate the validity and scope of the afore-mentioned 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.

Attention herein is confined to heating or cooling by means of a uniform heat flux density on the wall of the tube. This has been the thermal boundary condition of choice in most of the prior theoretical analyses of convection because the mathematical formulation and the process of solution are then the simplest. Uniform heating at the wall 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 of cooling a uniform heat flux density may be attained in the laboratory by electrical resistance heating of the wall. Adiabatic reaction, the limiting case of a uniform heat flux density approaching

zero may be approximated in practice by means of very good external insulation. An isothermal reaction corresponding to a negligible heat of reaction and no heat transfer at the wall serves as a reference condition for 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 boiling fluid (for heating) is the subject of a complementary study in progress by Yu and Churchill¹. A third thermal boundary of practical interest is that of imperfect external insulation in series with natural convection and thermal radiation.

Modeling and numerical solution for chemical conversions with or without heat exchange are more difficult than the for pure convection because most chemical conversions involve multiple reaction mechanisms of various orders, most of which are reversible, each of which depends exponentially and differently on temperature, and many of which are non-equimolar, thereby perturbing the flow. The general model for combined reaction and heat transfer consists of a set of partial differential equations for the conservation of species that are nonlinear in temperature and generally in concentration. These 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 rate mechanisms, independent chemical species, and the numerical parameters associated with the rate mechanisms may exceed 100, 20, and 50, respectively. This is to be contrasted with pure 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 variation of the physical properties with temperature may be 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.

Even apart from reduction of 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. Four major simplifications are made for those reasons. The first of these 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 this ratio. The second simplification is the postulate of invariant physical properties other than the rate constant(s) for the reaction(s). Taking the variations in density, viscosity, diffusivity, and heat capacity with temperature and composition into account would greatly complicate the calculations because the differential momentum balance is then coupled to those for energy and species, and these several differential equations must be solved simultaneously. Also, the numerical results would then be specific to a particular reacting fluid. The small errors in Nu and Z_m that result from the idealization of invariant physical properties could perhaps be reduced by using mean values, but this was not done herein. The third simplification is the postulate that the reaction starts at the entrance, which is difficult to achieve experimentally. 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 combination of these four simplifications excludes changes in the radial and longitudinal velocity. The effect of temperature on the reaction-rate constant(s) is taken into account, although somewhat approximately.

In previous related work, Churchill and Yu² 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, Churchill³ derived an analogy between homogeneous chemical reactions and heat transfer. The results of these two analyses are utilized herein.

Prior work on enhancement and attenuation of convection due to reaction

The earliest studies of combined reaction and external heat transfer are apparently those of Brian and Reid⁴ and Brian⁵ 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. Subsequent solutions of Rothenberg and Smith⁶ for laminar flow and uniform heating predicted lesser but nevertheless significant enhancements. Ooms et al.⁷ carried out finite-difference solutions for first-order, irreversible, endothermic reactions in general, using *penetration* theory (which is of questionable accuracy as a model for turbulent transport) 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.⁸ carried out experimental measurements for a reversible reaction ($2NO_2 \leftrightarrow 2NO + O_2$) with heat transfer, and Edwards and Furgason⁹ 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 because an explanation for the anomalous behavior has not been established on either physical or mathematical grounds, but a more likely explanation is that these investigations have simply been overlooked.

A speculative relationship between reaction and convection

Before presenting the new numerical solutions, it is expeditious to examine the aforementioned new analogy between chemical reaction and convective heat transfer derived by Churchill³ because it provides guidance for the choice of variables for the numerical modeling and for graphical display of the numerical results. . . The analogy is based on the following exact solution derived by Churchill¹⁰ for a volumetrically uniform rate of reaction in fully developed laminar flow in a round tube with a uniform heat flux density at the wall, radial conduction, but no molecular diffusion:

$$Nu = \frac{48/11}{1 + \frac{3}{11}Q} \quad (1)$$

Here $Nu = 2a j_w / \lambda (T_w - T_m)$ and $Q = a q_v / 2j_w$ is the ratio of the heat of reaction to the heat flux from the wall. The value of 48/11 may be recognized as the exact solution for fully developed convection without a reaction. It was thereupon speculated that Eq. (1) could be

generalized to encompass developing convection and reaction and both laminar and turbulent flow. The resulting expression is

$$\frac{Nu_x}{Nu_{x0}} = \frac{1}{1 + \beta Q_x} \quad (2)$$

Here $Nu_x \equiv 2a j_w / \lambda (T_{wx} - T_{mx})$ is the local Nusselt number at axial distance x from the inlet, Nu_{x0} is its value for no reaction, Q_x is the local ratio of the heat of reaction to the heat flux density at the wall per unit differential length of reactor, and β is the arbitrary coefficient in place of 3/11. For the laminar regime, Nu_{x0} is given by the well-known series solution of Graetz¹¹, but is perhaps more readily evaluated for laminar as well as turbulent flow by means of the numerical algorithm used herein to evaluate Nu_x . For a uniform heat flux density at the wall

$$Q_x = (k_{emx}/k_0)\xi(1-Z_{mx}) \quad (3)$$

Here, Z_{mx} is the mixed-mean conversion, k_{emx}/k_0 is the ratio of the effective-mean value of the reaction-rate constant with respect to both length and radius to its value at the inlet temperature T_0 , and $\xi \equiv \tau Re Pr K_{0a} / 4J$ is a combination of the specified parameters, namely the thermicity $\tau = Q_M / c_M T_0$, the dimensionless heat flux density $J = a j_w / \lambda T_0$, the Reynolds number $Re = 2au_m \rho / \mu$, the Prandtl number $Pr = c\mu / \lambda$, and the dimensionless rate of reaction at the inlet $K_{0a} = k_0 a / u_m$.

Approximation of the effective-mean value of the reaction-rate by its value at the mixed-mean temperature leads to

$$\frac{k_{emx}}{k_0} \cong \frac{k\{T_{mx}\}}{k\{T_0\}} = \frac{k_\infty e^{-E/RT_{mx}}}{k_\infty e^{-E/RT_0}} = e^{\frac{E}{RT_0} \left(1 - \frac{T_0}{T_{mx}}\right)} \quad (4)$$

An energy balance over the reacting fluid from the inlet to any length x can be expressed as

$$\frac{T_{mx}}{T_0} = 1 + \frac{C_{A0} Z_{mx} q_M x}{\rho c u_m T_0} + \frac{2j_w x}{a u_m \rho c T_0} = 1 + Z_{mx} \tau + \left(\frac{4K_{0x}}{Re Pr K_{0a}} \right) J \quad (5)$$

Here, $K_{0x} = k_0 x / u_m$ is the dimensionless axial distance through the reactor. The second and third terms on the right-hand side of both forms of Eq. (11) represent the contributions of reaction and heat exchange, respectively, to the mixed-mean temperature.

Equations (2) – (5) can be combined to eliminate Q_x , k_{emx}/k_0 , and T_{mx} , thereby obtaining

$$\frac{Nu_x}{Nu_{x0}} = \frac{1}{1 + \beta \xi (1 - Z_{mx}) \exp \left\{ \frac{E/RT_0}{1 + (\tau [Z_{mx} + (K_{0x}/\xi)])^{-1}} \right\}} \quad (6)$$

Eq. (6) is uncertain functionally by virtue of the speculative adaptation of Eq. (1) for developing reaction and heat transfer and numerically by virtue of the approximation of k_{emx}/k_0 by Eq. (4).

Eq. (6) constitutes an expression for heat transfer, as represented Nu_x , and reaction, as represented by Z_{mx} , and thereby can be interpreted as an analogy. In order to implement Eq.

(6) a value or expression for Z_{mx} is required. Churchill and Yu² 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 is:

$$Z_{mx} = \frac{1 - e^{-\alpha K_{0x}}}{1 - \chi \tau} + \alpha J K_{0x} \quad (7)$$

Their recommended values for the coefficients α , χ , and σ are listed in Table 1. Eq. (7) is of limited accuracy but the consequent error is reduced in the prediction of Nu_x .

Table 1. Recommended Empirical Coefficients for Eq. (7)

Condition	α	χ	σ
$Re = 400, Pr = 0.70, Sc = 0.2$	0.937	3.96	0.710
$Re = 37640, Pr = 0.70, Sc = 0.2$	0.988	3.73	0.00585
Approximation for all $Re, Pr = 0.70, Sc = 0.2$	0.963	3.85	$252/Re$

Eq. (7) could be used to eliminate Z_{mx} from Eq. (1), resulting in an expression for Nu_x as a function only of K_{0x} , but at the price of the inclusion of the uncertainty associated with Eq. (7) and of a loss in clarity.

Expectations based upon the analogy

Insofar as Eq. (2) is valid, enhancement and attenuation of Nu_x are characterized by the product βQ_x , not by Q_x and β , separately. They are identified individually here because Q_x is a dimensionless combination of specified quantities, whereas β is merely an empirical coefficient. Enhancement occurs only when β and Q_x have opposite signs, and extreme enhancement occurs only when their negative product approaches unity. 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, but positive values of Q_x are physically possible. According to Eq. (3), Q_x would be expected to decrease and approach zero with axial length owing to the increase in Z_m , but this increase may be counterbalanced to some degree if T_{mx} and thereby k_{emx} increase, or abetted if T_{mx} and thereby k_{emx} decrease.

Ideally, β would be invariant with respect to ξ and to K_{0x} , but that is hardly to be expected owing to the conjectural extension of Eq. (1) to Eq. (2). Churchill³ found the variance with ξ to be relatively constrained but different in the laminar and turbulent regimes, and the variance with K_{x0} to be relatively constrained in both regimes. Accordingly, Eqs. (2) and (6) are very useful in a qualitative sense, that is in terms of understanding, and as a structure for correlation, but of limited value for *a priori* predictions.

Insight as to the enhancement and attenuations also follows from the definition of Nu_x in that for a fixed heat flux density at the wall, the value of Nu_x varies inversely with the numerical difference between T_{mx} and T_{wx} , and a precipitous enhancement implies a rapid and close approach of these latter two values as x varies. Values of T_{mx} are readily predicted by means of Eq. (5) but an equivalent expression does not exist for T_{wx} . However, it can be related to Nu_x , T_{mx} , and J through the definition of Nu_x rearranged as

$$Nu_x \equiv \frac{2aj_w}{\lambda(T_{wx} - T_{mx})} = \frac{2J}{\frac{T_{wx}}{T_0} - \frac{T_{mx}}{T_0}} \quad (8)$$

Eq. (8) can in turn be rearranged for convenience as:

$$\frac{T_{wx}}{T_0} = \frac{T_{mx}}{T_0} + \frac{Nu_x}{2J} \quad (8A)$$

Eq. (8A) is exact for a uniform heat flux density.

Numerical calculations

Methodology

The partial differential expressions for the conservation of energy and of species A were integrated numerically by means of finite-differences to determine T and Z as functions of r/a and K_{0x} . The quantities T_{mx}/T_0 , T_{wx}/T_0 , Nu_x , Z_{mx} and k_{emx}/k_0 were in turn computed as functions of K_{x0} alone. The illustrative numerical calculations were carried out for the following representative parametric conditions: $T_0 = 300\text{K}$, $k = \exp\{20.145 - (5344.5/T)\}$, $Re = 400$ and 37640 , $Pr = 0.7$, $Sc = 0.2$, and $K_{0a} = 0.096$. It follows from the first two of these numerical values that $k_0 = 10.278\text{s}^{-1}$. The model of Churchill and Zajic¹², which incorporates semi-empirical expressions for $-\rho u'v'/\tau$ and Pr_t , was utilized for radial transport of momentum, energy, and species by the turbulent fluctuations. The following empirical expression was utilized for the turbulent Prandtl number, which is a parameter in that model:

$$Pr_t = 0.85 + \frac{0.015}{Pr} \quad (9)$$

Eq. (8) with Sc substituted for Pr was utilized for Sc_t . Complete calculations were carried out for a number of combinations of τ , J , and Re , as described next.

Conditions for numerical integrations

The differential mathematical model was solved numerically for the previously indicated fluid-mechanical, thermal, and chemical conditions. For laminar flow ($Re = 400$), calculations were carried for all combinations of $\tau = -0.01$ and -0.05 with $J = 0.05$ and 0.10 , as well as for all combinations of $\tau = 0.01$ and 0.05 with $J = -0.05$ and -0.10 . For turbulent flow at $a^+ = 1,000$ ($Re = 37,460$), calculations were carried out for all cases of $\tau = \pm 0.01$ and ± 0.05 with $J = \pm 0.15$, ± 0.20 , ± 5.0 , and ± 10 that involve opposite signs. The results were tabulated for the following values of K_{0x} : 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, and 10

The local Nusselt number for pure convection without reaction, Nu_{x0} , serves as a quantitative basis for evaluation of the enhancement or attenuation of heat transfer by an energetic reaction. Calculating a sufficient number of *eigenvalues* and *eigenfunctions* in the aforementioned solution of Graetz¹¹ and then summing the series is very tedious. On the other hand, the same scheme of numerical integration as devised in the current work for combined reaction and convection in both laminar and turbulent flow requires considerably

less computation and predicts not only the Nusselt number but the entire two-dimensional field of temperature and composition with more than sufficient accuracy.

Computed values of the local Nusselt number for no reaction

Representative values of Nu_{xo} as so-computed for both laminar and turbulent flow with no reaction are listed in Table 2 as a function of K_{0x} . The customary independent variable for pure laminar convection is $Gz = wc/\lambda x = \pi K_{0a} Re Pr / 2 K_{0x} = \pi a Re Pr / 2x$. A third possible independent variable is $x/a = K_{0x}/K_{0a}$. For specified values of Re , Pr , and K_{0a} , the three independent variables K_{0x} , Gz , and x/a bear a one-to-one correspondence. K_{0x} was chosen as the primary independent variable herein because of its common use in chemical reactor engineering and its commonality for both laminar and turbulent flow.

Table 2. Local Nusselt Numbers in Developing Convection with Uniform Heating

K_{0x}	Nu_{lam}	Nu_{turb}	K_{0x}	Nu_{lam}	Nu_{turb}	K_{0x}	Nu_{lam}	Nu_{turb}
0.01	22.14	250.9	0.09	10.62	141.0	0.80	5.584	102.1
0.02	17.53	204.3	0.10	10.27	138.1	0.90	5.432	100.8
0.03	15.29	182.7	0.20	8.239	122.3	1.00	5.306	99.75
0.04	13.89	169.6	0.30	7.286	115.1	2.00	4.687	93.87
0.05	12.89	160.5	0.40	6.702	110.7	5.00	4.401	89.49
0.06	12.14	153.9	0.50	6.299	107.7	10.00	4.3854	88.68
0.07	11.54	148.7	0.60	6.001	105.4	20.00	4.3852	88.63
0.08	11.04	144.5	0.70	5.769	103.6	∞	4.3636	86.10

Tests of the accuracy of the values of Nu_x obtained by numerical integration

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

- 1) Convergence was tested in general by decreasing the step-sizes in radius and axial length.
- 2) The accuracy of the results for Nu_{xo} in Table 2 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.
- 3) The accuracy of the numerical results for $Nu\{K_{xo}\}$ for non-reactive turbulent flow for $Re = 37640$ and $Pr = 0.7$ was tested by comparison with the prior numerical solutions of Yu et al.¹³, including the limiting value of 86.10 for $Gz \rightarrow \infty$
- 4) The accuracy of the numerically computed values of Nu for non-reactive turbulent flow and convection was tested by comparison with those of Churchill and Zajic¹².
- 5) The compatibility of the computed values of T_{mx}/T_0 and Z_m was tested in terms of Eq. (5).
- 6) The compatibility of the numerically computed values of Nu_x , T_{wx}/T_0 and T_{mx}/T_0 was tested in terms of Eq. (8A).

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

Numerical results for developing reaction and convection in laminar flow

The computed values are too extensive to be presented here in full numerical detail for all conditions. Furthermore representative values have been presented by Churchill³. Instead, because of the functional insight provided thereby, the results are presented primarily in graphical form or by reference to Eq. (6).

Tabular representations

The aforementioned tabulations of numerically computed values by Churchill³ reveal that in the laminar regime the values β vary only moderately with τ and J for a given value of K_{0x} , and only moderately with K_{0x} for a fixed value of τ and of J . These variations, which were to be expected because of the speculative origin of Eq. (3) and the several approximations made in its implementation as Eq. (6), suggest that the analogy is useful in a qualitative but not a quantitative sense. That is, it provides insight but not numerically accurate predictions. Similar results were obtained for the turbulent regime but the values of β differed significantly from those for the laminar regime, indicating that the functional dependence on Re per ξ is not exact.

Graphical representations

The mixed-mean conversion for several combinations of values of τ and J is plotted versus K_{0x} in log-log coordinates in Fig. 1, and the local Nusselt number for several conditions in Fig. 2, in all cases for $K_{0a} = 0.096$, $Re = 400$, $Pr = 0.7$, and $Sc = 0.2$. Curves for a non-energetic reaction ($\tau = 0$) are included as a condition of reference. The effects of the thermicity and of the heat transfer at the wall on the conversion are only second-order for the chosen conditions. By contrast, the local Nusselt number for some of the same and some different conditions is seen to be enhanced for all values of K_{0x} for all of the chosen thermicities, and grossly and chaotically for $\tau = -J = 0.05$. It may be noted that the inverse condition, that is $\tau = -0.05$ and $J = 0.05$, as well as $\tau = 0.05$ and $J = -0.10$, produce a single strong maximum in Nu_x , but that none of the other chosen combinations other than $\tau = -J = 0.05$ produced any vestige of chaotic behavior.

Numerical results for developing reaction and convection in turbulent flow

The conversion in turbulent flow is even less dependent on the thermicity and heat flux density at the wall than in laminar wall and therefore is not illustrated here. Since Eqs. (2) – (8) remain directly applicable, similar behavior to that for laminar flow might be expected for the effect of an energetic reaction on convection in turbulent flow. That proves to be the case qualitatively but not quantitatively. Fig. 3, which displays results for $a^+ = 1000$ ($Re = 37,640$) reveals strong chaotic attenuation as well as enhancement of the local Nusselt number. Since ξ is negative, that is τ and J have opposite signs for all of these conditions, attenuation implies a negative value of β .

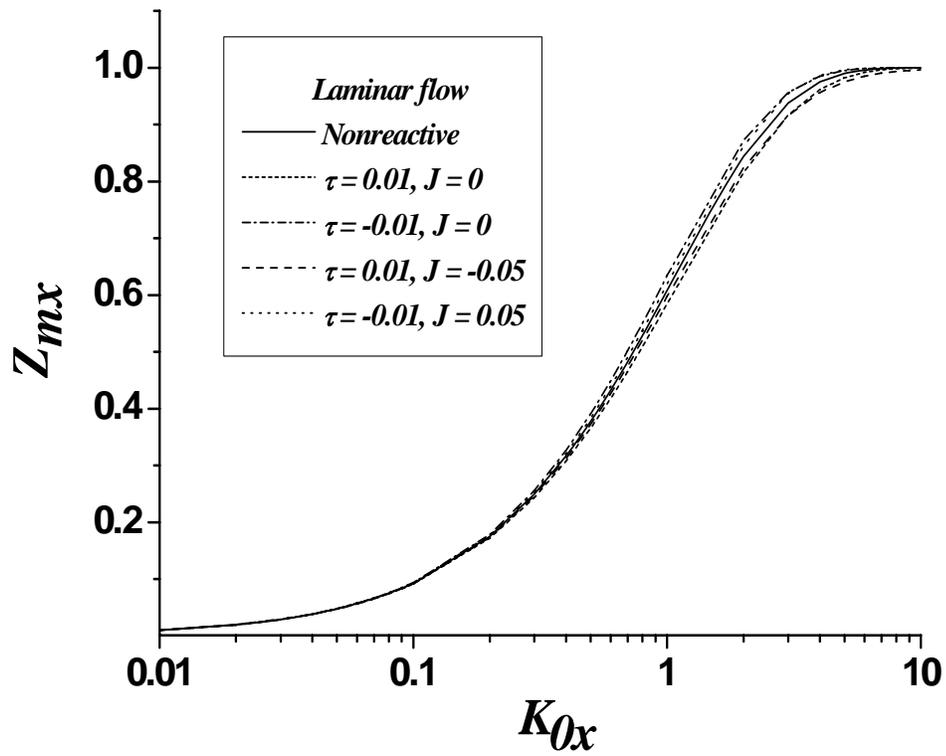


Figure 1. Mixed-mean Conversions in Laminar Flow

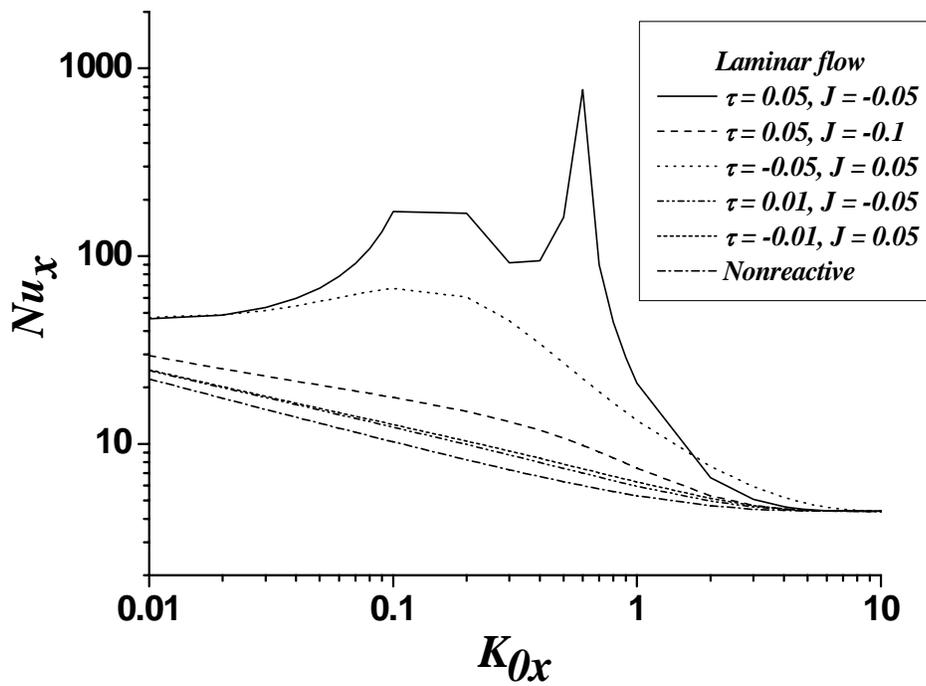


Figure 2. Local Nusselt Number for Laminar Flow with an Energetic Reaction

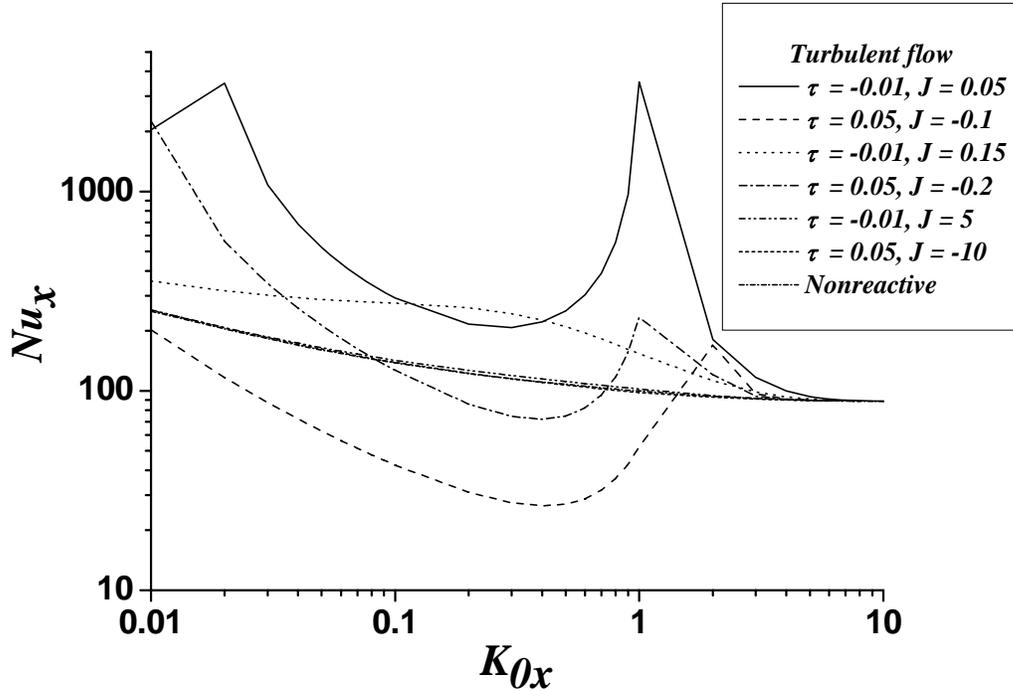


Figure 3. Local Nusselt Number for Turbulent Flow with an Energetic Reaction

Explanations for the Enhancement of the Nusselt Number by an Energetic Reaction

The explicit objective of this investigation was to confirm and improve on the accuracy of the previous predictions and observations of enhancement and attenuation of the Nusselt number by an energetic reaction. This can be said to have been accomplished by the computed values, some of which are illustrated in Figs. 2 and 3. A second implicit objective was to explain this seemingly anomalous behavior. Three approaches follow.

An Explanation in Terms of the Analogy

Eq. (2) provides a mathematical explanation for enhancement by virtue of a negative value of the product βQ_x , for extreme enhancement by virtue of the product βQ_x approaching -1 , and for attenuation by virtue of a positive value of βQ_x . Furthermore, Eq. (3) provides an explanation for multiple peaks in Nu_x in that Q_x , by virtue of its proportionality to $1-Z_{mz}$, decreases with K_{0x} , but this decrease may be counterbalanced by an increase in k_{emx}/k_0 . These possibly competing effects open the door to multiple peaks in Nu_x even if β were invariant with respect to K_{0x} . Indeed, Churchill³ demonstrated that an empirical linear correlation of β with K_{0x} can closely reproduce the variation of Nu_x with K_{0x} even for $\tau = -J = 0.05$, the condition that generated the extreme curve in Fig. 2. The representation of the enhancement by Eq. (2) is not, however, a physical explanation in that this expression has a conjectural origin.

An Explanation in Terms of the Mixed-mean and Wall Temperatures

An alternative source of explanation is the definition of Nu_x , namely Eq. (8), from which it follows that

$$\frac{Nu_x}{Nu_{x0}} = \frac{(T_{wx} - T_{mx})_o}{T_{wx} - T_{mx}} \quad (10)$$

and that

$$(T_{wx} - T_{mx})_o = \frac{J}{Nu_{x0}} \quad (11)$$

The quantity $(T_{wx} - T_{mx})_o$ can thus be computed from the specified value of J and the independently computed value of Nu_{x0} . As previously mentioned, there is no expression for the prediction of the wall temperature. Although T_{wx} is computed in the process of solving the differential energy balance numerically and is required to calculate Nu_x , there is no expression for its prediction. Thus, T_{wx} in Eq. (10) is analogous to β in Eq. (3) in that it must be calculated from Eq. (8) and computed values of Nu_x .

Numerically calculated values of T_{wx} and T_{mx} for laminar flow are plotted versus K_{0x} in Fig. 4 for four representative cases. The upper-left plot is for non-reactive flow and corresponds to Nu_{x0} and the Graetz solution. The upper-right plot corresponds to nearly isothermal flow, that is to nearly perfect compensation for the heat of reaction by the imposed heat flux,. The lower-left plot is for the condition that produced the strong chaotic enhancement in Fig. 2. The strong enhancement for this condition is associated with the nearness of the curves for T_{wx} and T_{mx} , and the two peaks in Fig. 5 to the two near-intersections of T_{wx} and T_{mx} . The short range of values of T_{mx} below T_{wx} is apparently due to

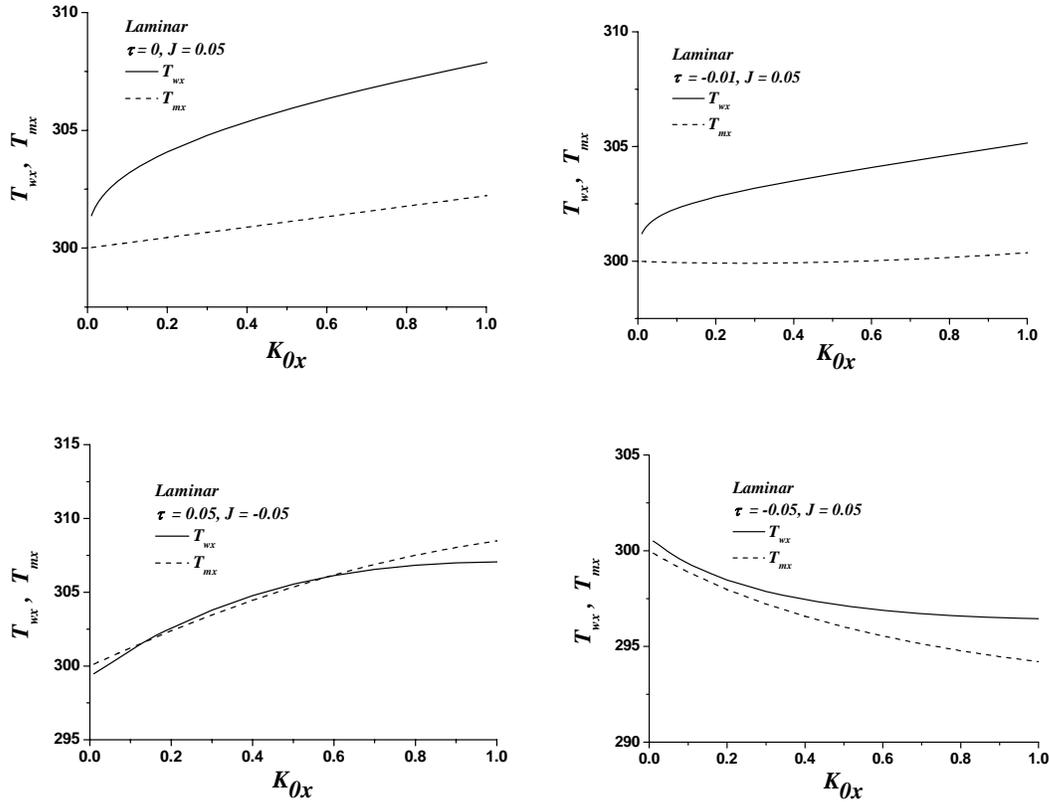


Figure 4. Longitudinal Temperature Profiles for Laminar Flow

computational error. The moderately close approach in the lower-right plot for the converse case is in agreement with the strong non-chaotic enhancement that may be observed in Fig. 3. It should be noted that the scale of the ordinate differs in these plots.

Numerically calculated values of T_{wx} and T_{mx} for turbulent flow are plotted versus K_{0x} in Fig. 5 for four representative cases. The upper-left plot is for non-reactive flow and corresponds to the numerically computed values of Nu_{x0} in Table 2. The upper-right plot for $\tau = 0.05$ and $J = -0.1$ results, as can be seen in Fig. 3, in a strong attenuation, but the abbreviated abscissa does not include the crossing of the curves required by the transition from attenuation to enhancement. (The range of the abscissa was restricted to values that might be utilized in practice.) The lower-left plot for $\tau = -0.01$ and $J = 0.15$ produces a moderate single-peaked enhancement in Nu_x , while the close approach in the lower-right plot for $\tau = -0.01$ and $J = 0.05$ produces the strong double-peaked enhancement in Nu_x in Fig. 3. Again, the different scales of the ordinates in Fig. 4 should be noted. Although the plots of T_{wx} and T_{mx} in Figs. 4 and 5 provide considerable insight they too fail to provide a physical explanation for the enhancements and attenuations.

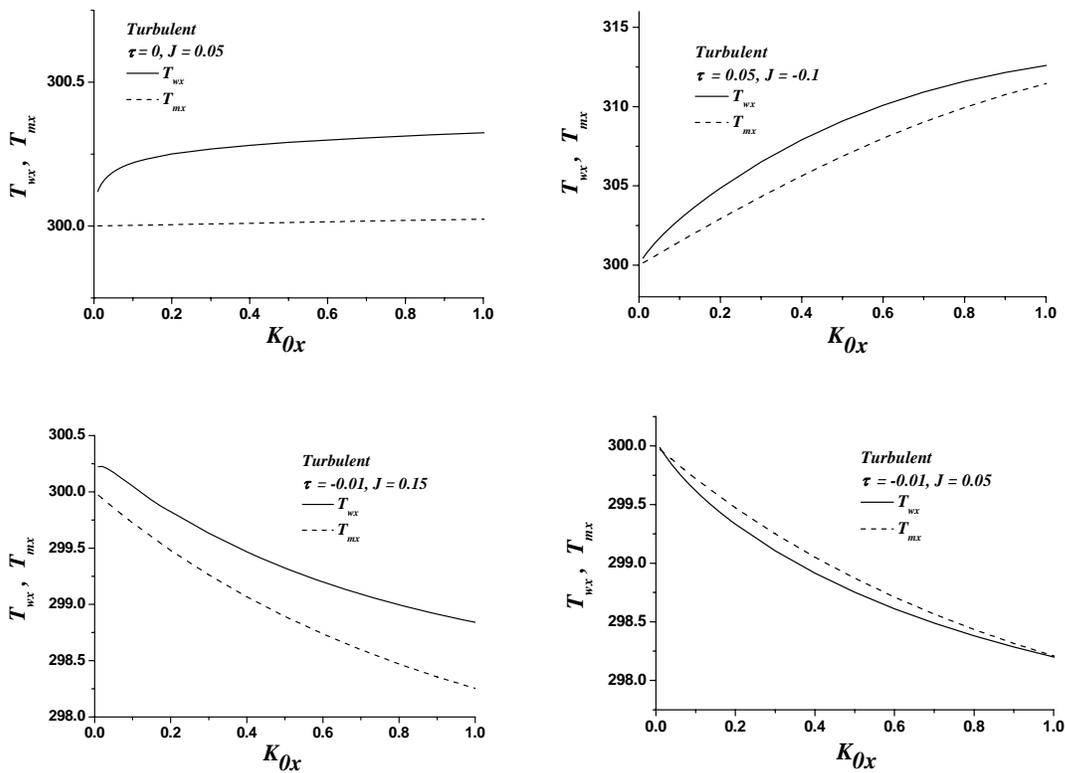


Figure 5. Longitudinal Temperature Profiles for Turbulent Flow

An Explanation in Terms of the Radial Temperature Profile

The most convincing physical explanation for the enhancement of Nu_x by an energetic chemical reaction is the preferential generation of the heat reaction near the wall or preferentially near the centerline. In the instance of an exothermic reaction (and a positive thermicity) the radial temperature profile is skewed upward relative to that for no reaction. Such behavior is illustrated in Fig. 6 for laminar flow, $\tau = 0$ and 0.05 , $K_{0x}=1$, $J = -0.05$, and the otherwise common conditions herein. The temperature may be noted to be skewed

upward over the whole cross-section by the exothermic reaction. It is obvious by inspection, or by a mental integration that the difference between the mixed-mean temperature and the wall temperature is decreased by the reaction. The effect of cooling at the wall for a fixed thermicity is illustrated in Fig. 7 for $J = -0.05$ and -0.10 with $\tau = 0.05$, and otherwise the same conditions as for Fig. 6. In the instance, a decrease in the rate of cooling increases the relative effect of the reaction and skews the radial temperature profile in much the same way as in Fig. 6, again reducing the difference between the mixed-mean temperature and the wall temperature, and in this instance enhancing the magnitude of Nu_x . However, as may be inferred from the upper curve, it is possible for T_{mx} to be less than T_{wx} at some values of K_{0x} (as in the lower left plot of Fig. 4, resulting a negative value of Nu_x even though the heat flux density is outward and dT/dr is negative at the wall. (The absolute values of Nu_x were actually plotted in Fig. 2 to avoid displaying this seeming anomaly.) The scale of the abscissa of Fig. 7 should be noted to differ from that of Fig. 6.

The rate of release of the exothermic heat of reaction is proportional to the rate of reaction which is dependent on the local composition and temperature. The conversion at any radius and axial distance is a consequence of these factors but primarily of the local velocity of the fluid. The fluid near the wall moves much more slowly than near the centerline and therefore may rise more rapidly in temperature and reach a higher temperature, other factors being equal. All aspects of this behavior vary with distance down the tube. For example, as the conversion near the wall approaches unity, the release of the heat of reaction will shift toward the centerline where the velocity is higher and the conversion is less. This explains the variation of the enhancement with length. These conclusions are applicable with proper modification for endothermic reactions and heating at the wall as well. Indeed, the behavior of Nu_x for all of the cases plotted in Figs. 2 and 3 can be deduced from the radial temperature profiles as a function of length.

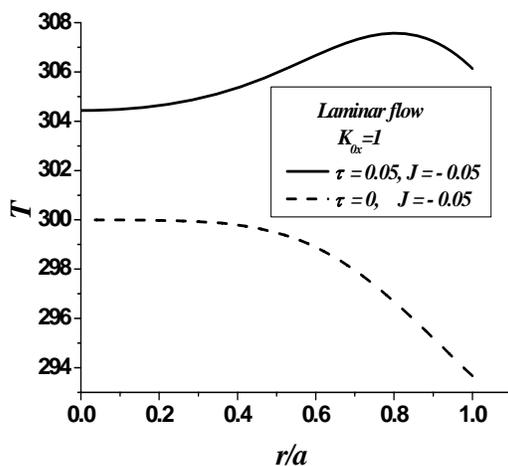


Figure 6. Radial Temperature Profiles for an Exothermic and a Non-Energetic Reaction

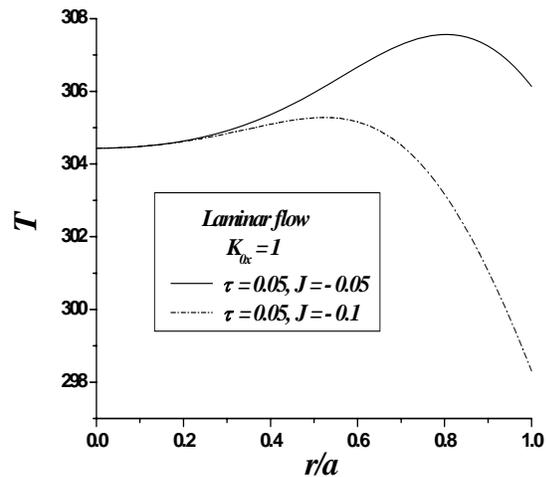


Figure 7. Radial Temperature Profiles for an Exothermic Reaction with Two Different Rates of External Cooling

Interpretation

The preferential release (or absorption) of the heat of reaction near the wall or near the centerline and the consequent skewing of the radial temperature profiles provides a physical explanation for enhancement and attenuation of the Nusselt number, including the sometimes chaotic variation with distance through the reactor/exchanger. This explanation is, however, qualitative as contrasted with the analytical explanations provided by Eqs. (2) and (10).

It should be noted that the rate of heat transfer between the fluid and the wall in terms of j_w or J is not enhanced or attenuated, only the Nusselt number. Furthermore, if the energy and material balances partial differential form are solved numerically as was done to obtain the values plotted and tabulated herein, the heat transfer coefficient and the Nusselt number are dependent not specified variables. Why then has the variation of the Nusselt number with the several dependent variables been sought herein? There are two primary reasons. The first is understanding; the Nusselt number gives insight into the complexity of the combined process of reaction and heat exchange that would otherwise not be realized, and indeed this interaction has been generally overlooked in the fields of both reaction engineering and heat transfer. The second reason arises from the conventional process of design for reactor/heat exchangers; such design calculations have traditionally been carried out with a lumped parameter model that incorporates a heat transfer coefficient. Such a model together with the conventional (non-reactive) correlations for the Nusselt number may yield predictions that are grossly in error.

Finally, it should also be noted that the postulate of plug flow, which is often made in modelling chemical reactors, excludes all of the very real effects of combined reaction and convection that are examined herein. This a further, if redundant, reason to abandon outright the very concept of plug flow, which occurs in the real world only for semi-solid materials such as ice cream pushed through a tube by a wooden rod.

Summary and Conclusions

1. Prior numerical calculations and experimental work, although scattered and incoherent, suggest that heating or cooling the wall of a tubular reactor might produce orderly perturbations of the chemical conversion but irregular and extreme perturbations of the Nusselt number. These perturbations are unmentioned in the standard textbooks and handbooks on heat transfer and reaction engineering.

2. The coherent numerical results presented herein for a uniform heat flux density at the wall confirm that an energetic reaction may indeed produce great perturbations in the magnitude of the Nusselt number, as well as a highly irregular variation in the axial direction. (See Figs. 2 and 3.) It should be noted in this context (See Fig.1) that, even though the mixed-mean conversion is critically dependent on the local radial and longitudinal variations in temperature, its variation with axial distance does not echo the drastic excursions in the Nusselt number.

3. These results were obtained by finite-difference solution of the partial differential equations of conservation for energy and species for fully developed laminar and turbulent

flow. The modelling is limited to a first-order irreversible equimolar reaction, a single, temperature-dependent reaction-rate constant, and single values of Pr and Sc . Numerical solutions for a uniform wall temperature will be presented in a separate paper in the interests of clarity.

4. If solutions of the partial differential equations for the conservation of energy and species are carried numerically, as they were in this investigation, the heat transfer coefficient and the Nusselt number do not appear in the model and their extreme and chaotic variation are only of intrinsic interest. However, if the reactor/heat exchanger is modelled in terms of ordinary differential equations with lumped parameters (for example, the mixed-mean velocity, composition, and temperature) the neglect of the enhancement and/or attenuation in the Nusselt number may lead to gross errors.

5. The common postulate of “plug flow” in reactor design excludes the enhancement and/or attenuation and thereby may also produce erroneous predictions for combined reaction and heat transfer.

6. An important aspect of the investigation was to explain the gross effects of an energetic chemical reaction on the Nusselt number. The search for such an explanation followed three different paths that each proved to have limitations.

First, the predictions of the recent new analogy devised in the course of the overall investigation were examined in this respect. Since the coefficient β was found to be relatively invariant for a wide range of conditions, Eq. (2) provides a rationalization and a theoretical structure for correlation of the magnitude and longitudinal variation of the enhancement and attenuation. However, because of its speculative origin, Eq. (2) does not provide a physical explanation, and because β is empirical, it falls short of quantitative *a priori* predictions.

Next, Eq. (10), which is based on the difference between the mixed-mean and wall temperatures, was examined in terms of explanation and prediction. The enhancement and attenuation can be explained or at least rationalized on the basis of the variation of this difference (see, Figs. 4 and 5), but the wall temperature is not predictable *a priori*.

Finally, the radial profiles of temperature were examined (see Figs. 6 and 7). These plots indicate that the preferential release or absorption of the heat of reaction near the centerline or near the wall is the root cause of the enhancement and attenuation. This is the sought-after physical explanation.

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Nomenclature

a	radius of tube, m
a^+	$a(\rho\tau_w)^{1/2}/\mu$
c	specific heat capacity, J/kg K
C_A	concentration of species A , J kg-mol / /m ³
C_M	molar heat capacity, J/kg-mol K
E	energy of activation, J/ kg-mol
D_f	diffusivity, m ² /s
Gz	Graetz number $wc/\lambda x = \pi K_{0a} Re Pr / 2 K_{0x} = \pi a Re Pr / 2 x$
j_w	specified heat flux density at wall, W/m ²
J	specified dimensionless heat flux = $aj_w/\lambda T_0$
k	reaction–rate constant, s ⁻¹

k_{∞}	frequency factor for reaction mechanism, s^{-1}
K_{0a}	dimensionless reaction-rate constant = $k_0 a / u_m$
K_{0x}	dimensionless distance from inlet = $k_0 x / u_m$
Nu	Nusselt number = $2j_w a / \lambda (T_w - T_m)$
Pr	Prandtl number = $c\mu / \lambda$
Pr_t	turbulent Prandtl number
q_M	molar heat of reaction, J/kg-mol
q_V	heat input from reaction per unit volume, J/m ³
Q	heat input from reaction/ heat flux at wall per unit length of reactor
r	radial coordinate, m
R	universal gas constant, J/kg-mol K
Re	Reynolds number = $2au_m\rho/\mu$
Sc	Schmidt number = $\mu/\rho D_f$
Sc_t	turbulent Schmidt number
T	absolute temperature, K
u_m	mixed-mean velocity, m/s
u'	temporal fluctuation in u , m/s
$\overline{u'v'}$	time-average of product of fluctuations in velocity, m ² /s ²
$(\overline{u'v'})^{++}$	dimensionless shear stress due to turbulence = $-\rho(\overline{u'v'})/\tau$
v	velocity component normal to wall, m/s
v'	temporal fluctuation in v , m/s
x	distance from inlet, m
Z	fractional conversion of species A

Greek symbols

α	arbitrary coefficient in Eq. (7)
β	arbitrary coefficient in Eq. (2)
γ	arbitrary coefficient in Eq. (7)
λ	thermal conductivity
μ	dynamic viscosity
ζ	dimensionless collective parameter = $\tau Re Pr K_{0a} / 4J$
ρ	specific density
σ	arbitrary coefficient in Eq. (7)
τ	thermicity = $q_M / c_M T_0 = C_{A0} q_M / \rho c T_0$; or shear stress,
χ	arbitrary coefficient in Eq. (7)

Subscripts

em	effective-mean
m	mixed-mean
o	for no reaction
x	at distance x from let
w	at wall
0	at inlet

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