A homogeneous-heterogeneous reaction model for heat fluid flow in the stagnation region of a plane surface

Hang Xu

Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration (CISSE), State Key Lab of Ocean Engineering, School of Naval Architecture, Ocean and Civil Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

ARTICLE INFO

ABSTRACT

A simple model of chemical reactions for heat fluid flow in the stagnation-point region of a flat sheet is constructed. It is assumed that the heterogeneous reactions taking place on the wall surface are given by isothermal cubic autocatalator kinetics and the homogeneous reactions occurring in the ambient fluid are governing by first order kinetics. The steady-state problem is then reduced to a set of coupled ordinary differential equations via similarity reduction in the case that the diffusion coefficients of reactant and autocatalyst are equal. The multiple solutions of this system are obtained numerically with the help of hysteresis bifurcations.

1. Introduction

Catalysts are usually expected to improve on efficiencies of chemical reactions in many industrial processes. In earlier studies, researchers [1–5] mainly paid their attention to understand mechanisms of catalyst-driven chemical aspects of heterogeneous reactions on the catalyst surface. While Williams et al. [6], Song et al. [7] and Williams et al. [8] noticed that the chemical reaction could occur not only on the catalyst surface (heterogeneous reactions), but also in the bulk (homogeneous reactions). Inspired by Williams et al. [6], Chaudhary and Merkin [9,10] established a mathematical model on homogeneous-heterogeneous reactions near a forward two-dimensional stagnation-point of a flat surface with the assumption that the autocatalytic reaction is isothermal cubic. Note that the homogeneous-heterogeneous model is usually associated with the stagnation flows near a prescribed geometry, whose configuration can be found in the papers of Hsiao [11–13]. It is known that when chemical reaction processes operating in the combined forced and free convective flow regime, the overall mass and/or heat transfer rates could be influenced significantly, or vice versa, the overall reactant conversion rates may be affected significantly by transport phenomena. Therefore, a detailed analysis for accurate evaluation of the transport effects on performance of various processes in the presence of both heterogeneous and homogeneous reactions in a combined flow regime is very desirable. As far as we know, such analyses have seldom been done in the literature. This work tries to meet such a need.

2. Mathematical descriptions

Following Chaudhary and Merkin [9,10], we assume that the reaction in the bulk is isothermal cubic autocatalytic, given by

$$A + 2B \to 3B, \quad \text{rate} = k_1 C_a C_b^2, \tag{1}$$

while on the catalyst surface, the reaction is single, isothermal, first order, governed by

$$A \to B, \quad \text{rate} = k_s C_a, \tag{2}$$

where A and B are two different kinds of autocatalysts, C_a and C_b are their concentrations respectively. k_1 and k_s are constants associated with the homogeneous and heterogeneous reactions. To satisfy physical requirements, it is assumed that the reactant B does not exist in the external flow and the reactant A has a constant concentration C_{a0}. Note that the correlation Eq. (1) indicates that the reaction rate at far field is zero, so does it at the outer edge of the boundary layer. We then assume that the chemical reactions cause heat release, which means that the effects of thermal expansion will not be ignored in the boundary-layer due to the reactions. With those assumptions, we write the governing equations in the following forms (refer to [9,14]):

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0, \tag{3}$$

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \nu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right), \tag{4}$$

E-mail address: hangxu@sjtu.edu.cn.

$$u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} = \alpha\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) + k_1 C_a C_b^2\left(\frac{-\Delta H_h}{\delta_A}\right)\left(\frac{1}{\rho C_p}\right),$$

(5)

$$u\frac{\partial C_a}{\partial x} + v\frac{\partial C_a}{\partial y} = D_A\left(\frac{\partial^2 C_a}{\partial x^2} + \frac{\partial^2 C_a}{\partial y^2}\right) - k_1 C_a C_b^2,$$

(6)

$$u\frac{\partial C_b}{\partial x} + v\frac{\partial C_b}{\partial y} = D_B\left(\frac{\partial^2 C_b}{\partial x^2} + \frac{\partial^2 C_b}{\partial y^2}\right) + k_1 C_a C_b^2,$$

(7)

subject to the following boundary conditions

$$u = v = 0, \quad -k_T\frac{\partial T}{\partial y} = (k_s C_a)\left(\frac{\Delta H_s}{\delta_A}\right), \quad D_A\frac{\partial C_a}{\partial y} = -D_B\frac{\partial C_b}{\partial y} = k_s C_a,$$

at $y = 0$,
$$u \to ax, \quad v \to 0, \quad T \to T_\infty, \quad C_a \to C_\infty, \quad C_b \to 0, \quad as \quad y \to \infty.$$

(8)

where u and v are velocity components in x- and y-axes respectively, p is the pressure, ν is the kinematic viscosity, T is the fluid temperature, α is the thermal diffusivity, ΔH_h is the homogeneous heat reaction, δ_A is the stoichiometric coefficients for heterogeneous reaction of species A, ρ is the fluid density, C_p is the heat capacity, D_A and D_B are the respective diffusion coefficients of species A and B, k_T is the thermal conductivity, and a is a constant.

To make Eqs. (3)–(7) dimensionless, we define the following similarity variables

$$\psi(x, y) = (a\nu)^{1/2}xf(\eta), \quad \theta(\eta) = \frac{T - T_\infty}{\Delta T}, \quad \phi(\eta) = \frac{C_a}{C_\infty}, \quad \vartheta(\eta)$$

$$= \frac{C_b}{C_\infty}, \quad \eta = \left(\frac{a}{\nu}\right)^{1/2}y.$$

(9)

This leads to the reduced governing equations for the momentum, thermal energy and chemical reaction in the following form

$$f''' + ff'' + 1 - f'^2 = 0,$$

(10)

$$\frac{1}{Pr}\theta'' + f\theta' + R_H\phi\vartheta^2 = 0,$$

(11)

$$\frac{1}{S_c}\phi'' + f\phi' - K\phi\vartheta^2 = 0,$$

(12)

$$\frac{\varepsilon}{S_c}\vartheta'' + f\vartheta' + K\phi\vartheta^2 = 0,$$

(13)

subject to the boundary conditions

$$f(0) = f'(0) = 0, \quad \theta'(0) = -K_T\phi(0), \quad \phi'(0) = -\varepsilon\vartheta'(0) = K_S\phi(0),$$
$$f'(\infty) = 1, \quad \theta(\infty) = 0, \quad \phi(\infty) = 1, \quad \vartheta(\infty) = 0,$$

(14)

where Pr is the Prandtl number, R_H is the homogenous reaction heat parameter, S_c is the Schmidt number, K is the strength coefficient of the homogenous reaction, ε is the ratio of the diffusion coefficients, K_T is the thermal conductivity due to homogenous reaction, K_S is the strength parameter due to heterogeneous reaction, which are defined by

$$Pr = \frac{\nu}{\alpha}, \quad R_H = k_1\left(\frac{\Delta H_h}{\delta_A}\right)\left(\frac{1}{\rho C_p}\right)\left(\frac{C_\infty^3}{a\Delta T}\right), \quad S_c = \frac{\nu}{D_A}, \quad K = \frac{k_1 C_\infty^2}{a},$$

$$\varepsilon = \frac{D_B}{D_A}, \quad K_T = \frac{k_s C_\infty}{k_T\Delta T}\left(\frac{\Delta H_s}{\delta_A}\right)\left(\frac{a}{\nu}\right)^{-1/2}, \quad K_S = \frac{k_s}{D_A}\left(\frac{a}{\nu}\right)^{-1/2}.$$

(15)

In practical, it is expected that the diffusion coefficients of reactants A and B are comparable. We therefore assume that D_A and D_B are equal, which is not against physical requirement (refer to [9]). In such case, we can combine Eqs. (12) and (13) to write

$$\phi(\eta) + \vartheta(\eta) = 1.$$

(16)

From above equation, it is known that we only need to calculate one

Table 1
Comparison of $f''(0)$ with the previous works.

Hiemenz [15]	1.2326
Wang [16]	1.232588
Kimiaeifar et al. [17]	1.23258762
Bachok et al. [18]	1.2325877
Present work	1.2325877

function ($\phi(\eta)$ or $\vartheta(\eta)$), the other equation can be obtained via Eq. (16) correspondingly. We substitute Eq. (16) into Eqs. (11) and (12), obtaining

$$\frac{1}{Pr}\theta'' + f\theta' + R_H\phi(1 - \phi)^2 = 0,$$

(17)

$$\frac{1}{S_c}\phi'' + f\phi' - K\phi(1 - \phi)^2 = 0.$$

(18)

3. Result analysis

Solutions to Eqs. (10), (17) and (18) can be easily obtained by numerical techniques. Here we use the fourth-order shooting technique to give solutions with the integration step $\Delta\eta = 0.05$ and the computational error being less than 1.0×10^{-8} for all considered cases. Further to check the accuracies of our results, we compare $f''(0)$ with published results, very good agreement is found, as shown in Table 1. We also notice that our results for $\phi(0)$ agree well with those given by Chaudhary and Merkin [9] (which are obtained by depicting points from their Fig. 1), as shown in Table 2.

We start our discussion by considering solution diversities of the nonlinear systems. It can be seen from Fig. 1, for a prescribed value of K_s, solutions for $\theta(\eta)$ and $\phi(\eta)$ could exist for a large range of K. Particularly, multiple solutions are in existence when the set values of K_s and K are properly chosen. It is also found in the figures that for a sufficiently strong surface reaction rate K_s, the temperature on the surface $\theta(0)$ decreases monotonously as K enlarges. While as K_s becomes weaker, a bifurcation point (K_s^b) appears. Multiple solutions can be expected for $K_s < K_s^b$ in a certain range of K. Our computational results shows that the maximum value of K_s^b is slightly greater than 0.1 for $S_c = 0.1$. One can also find from the figures that when there is no bulk (homogeneous) reaction and $K = 0$, the surface reaction can be persisted with the concentration of reactant $C_a = C_a^*$ being lower than the ambient value. It is also revealed from the figures that ϕ_s tends to 1 as K_s approaches to 0.

We then fix K and check the influence of K_s on the surface temperature $\theta(0)$. It is seen from Fig. 2 that when K is small (e.g. $K = 2$, Fig. 2a), only unique solution can be found for different values of K_s. It is also seen from Fig. 2, solutions could be possible for $K_s < 0$, which correspond to the purely homogenous reaction. Such solutions could be used to describe the autoignition of the system in practical. In this situation, the autocatalytic homogeneous reaction is strong enough to keep itself running. Therefore, the autocatalyst due to the first-order surface reaction is not necessary to be fed into this system. As K becomes sufficiently large, multiple solutions start to appear. The region of K_s for existence of multiple solutions enlarges continuously as K increases, as shown in Fig. 2b–d. Physically, one knows that the dimensionless concentrations of species ϕ must be less than 1 due to the relation defined in Eq. (16). As a result, solutions for $\phi(0) > 1$ (corresponding to $\theta(0) > 1.7529551$ in the figures) have no real physical meaning. We further find that the surface temperature $\theta(0)$ with physical sense (the lower branch) decreases with K_s increasing for any prescribed value of K.

Mathematically, the bifurcation point is of practical interest. It is usually a critical point corresponding to solutions with different behaviours. As shown in Fig. 3, the hysteresis point bifurcation for $\theta(0)$ is illustrated with the upper line corresponding to the upper turning