MULTICOMPONENT MASS TRANSFER IN A PLASMA REACTOR: COMPARISON OF THREE DIFFERENT DIFFUSION FLUX FORMULATIONS

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A comparison is made between effective binary, linear and Ramshaw's approximations used in predicting multicomponent diffusion mass flux. The study of an inert flow of a CH_4-H_2-Ar gas mixture at 1200 K reveals the limits of the effective binary approach in the context of multicomponent diffusion. The imposition of a temperature gradient affects significatively the results obtained by the linear approximation. Finally, the results of the Ramshaw's method compare favourably to the exact ones, even in the presence of strong temperature gradients.

Introduction

The modeling of multicomponent reactive flows such as plasma involves the study of the interaction between many physico-chemical phenomena. This interaction is best illustrated by an analysis of the species conservation where convection, diffusion and kinetics simultaneously take place. Therefore, if accurate concentration profiles are desired, one must use adequate flux formulation in combination to appropriate kinetic mechanism. Focussing on the quenching zone of a plasma reactor, this work essentially deals with convection and diffusion phenomena in a complex mixture.

Recent studies [1,2] reveal the importance of diffusion mass transfer in predicting realistic concentration profiles, particularly in systems where hydrogen is present in a significant amount. Takagi & Xu [2] demonstrated the importance of radial diffusion in laminar flames where preferential diffusion of heat and species causing flame tip-opening can be predicted by considering multicomponent effects.

In most previous works treating numerical simulation of reacting flows, little attention has been paid to multicomponent effects. In fact, the treatment of mass transfer is mostly oversimplified [3-5]. Although some approaches have been proposed to consider multicomponent diffusion in complex mixtures [6,7], it is relevant to compare them as they are applied to a common diffusion problem typical of the reactive zone found at the tail of a plasma reactor.

The present paper analyses the effect of three different mass flux formulations used for the diffusion of an ideal and inert gas mixture in a plasma reactor. It essentially compares the results obtained by the different flux approximations to that of an exact formulation. After a theoretical review and a brief presentation of the governing equations and of the associated boundary conditions, the results are discussed in relation to multicomponent effects. The ternary gas mixture studied shows the strengths and the limits of the formulations considered. The main conclusions about the comparison of the different diffusional approaches are finally presented.

Diffusion mass flux formulations

The easiest way to consider multicomponent diffusion is through the use of an effective binary diffusion coefficient, $D_{i,eff}$:

$$\vec{J}_i^* = -c_t D_{i,eff} \vec{\nabla} x_i; \qquad i = 1, ..., n \tag{1}$$

where J_i^*, c_t and ∇x_i represent the molar diffusion flux of species i, the total concentration and the molar fraction gradient respectively.

This method greatly simplifies the mathematical treatment of the mass conservation equations. Simple to implement in a general CFD procedure because of its standard form, it suffers from an inconsistency on the global mass conservation ie. $\Sigma J^*_i \neq 0$.

Ramshaw [6] improves the preceding approach by proposing a correction to be added to the binary velocities. The resulting mass fluxes are then forced to be consistent through the addition of a simple term:

$$\vec{J}_i^* = -c_t D_{i,eff} \vec{\nabla} x_i + x_i c_t \sum_{j=1}^{n} D_{j,eff} \vec{\nabla} x_j \tag{2}$$

where n represents the total number of species present in the mixture studied.

The last approximate method starts with the more rigorous Fick's formulation for ideal gases:

$$\vec{J}_i^* = -\sum_{j=1}^{n-1} c_t D_{ij} \vec{\nabla} x_j; \qquad i = 1, ..., n-1 \tag{3}$$

or in the more concise matrix notation:

$$\left[\vec{J}^*\right] = -c_t [D] \left[\vec{\nabla} x\right] \tag{4}$$

In the preceding equation, $[J^*]$ is a vector containing the n-1 independent species fluxes while [D] represents the matrix of Fick's diffusion coefficients.

Based on the linearized theory of Toor [8], the third method simplifies the resolution of mass conservation equations by assuming a constant matrix of diffusion coefficients. This simplification linearizes the equations to solve that can further be diagonalized by a matrix transformation [9].

Considering the variation of [D], it is also possible to model mass fluxes in their complete Fick's form. This approach which is based on an exact flux formulation is

thus consistent; it assures that the sum of diffusion fluxes gets to zero. Because of its completeness, this last approach is chosen as a basis of comparison for the discussion of the numerical results obtained with the approximations mentioned above.

Governing equations

The geometry of the physical system modeled is shown in Fig. 1; an axisymmetric configuration is adopted. The following assumptions are supposed in the development of the model:

- Steady, laminar, axisymmetric and incompressible flow
- Diffusive species are chemically inert i.e. no chemical reaction is considered

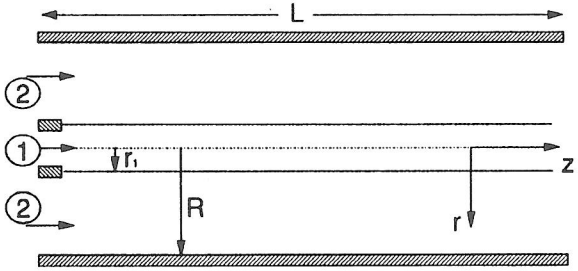


Figure 1: Chemical reactor modeled

① : mixture injected at the center ····· : center line

② : mixture injected in the annular region —— : mixing line

The governing equations to be solved consist of continuity, momentum, energy and species (diffusion) conservation equations for multicomponent fluid mixture.

- Continuity equation:

$$\vec{\nabla}\cdot(\rho\,\vec{u}) = 0 \quad (5)$$

- Momentum equation:

$$\vec{\nabla}\cdot(\rho\,\vec{u}\vec{u}) = -\vec{\nabla}P + \vec{\nabla}\cdot(\mu\,\vec{\nabla}\vec{u}) \quad (6)$$

- Energy equation:

$$\rho\hat{C}_p(\vec{u}\cdot\vec{\nabla}T) = \vec{\nabla}\cdot(\lambda\,\vec{\nabla}T) - \sum_{i=1}^{n}(\vec{j}_i\cdot\vec{\nabla}\hat{h}_i) \quad (7)$$

- Diffusion equation (molar basis):

$$\vec{\nabla}\cdot(c_t\,\vec{u}^*\,x_i) = -\vec{\nabla}\cdot\vec{J}_i^* \qquad i=1,\ldots,n \quad (8)$$

where $\vec{u}$ is the mass-averaged velocity, ρ the gas mixture density, P the pressure, μ the mixture viscosity, T the temperature, $\hat{C}_p$ the mean heat capacity, λ the mixture conductivity, $\vec{j}_i$ the mass diffusion flux of species i, $\hat{h}_i$ the specific enthalpy of species i, $\vec{u}^*$ the molar-averaged velocity, and x_i the molar fraction of diffusing species.

Boundary conditions

The boundary conditions considered for simulations are as follows:

Entrance (z = 0):

$0 < r < r_1$: $u = u_1\left[1-\left(\frac{r}{R}\right)^2\right]$; $v = 0$

$T = 1200K$; $x_i = x_{i1}$

$r_1 < r < R$: $u = u_2\left[1 - \left(\frac{r}{R}\right)^2 + \frac{1-k^2}{\ln(1/k)}\ln\left(\frac{r}{R}\right)\right]$; $v = 0$

$T = 1200K$; $x_i = x_{i2}$

Exit (z = L): $\frac{\partial}{\partial z} = 0$, except for $v = 0$

Centerline (r = 0): $\frac{\partial}{\partial r} = 0$, except for $v = 0$

Wall (r = R): $u = v = 0$, $T = T_w$, $\frac{\partial x_i}{\partial r} = 0$

u_1 and u_2 are defined as maximum velocity in a circular tube of radius r_1 and R respectively. k represents the ratio of the inside radius, r_1, over the outside radius, R. x_{i1} and x_{i2} are the initial molar fraction of species i in the center and in peripheral tube respectively. T_w is the wall temperature, fixed at 300 K or 1200 K, depending if a temperature gradient is present.

Eqns. (5)-(8), submitted to the above boundary conditions, are solved simultaneously by a control volume based numerical procedure called SIMPLER [10]. Transport properties (μ, λ, D_{ij}) are evaluated using the Chapman-Enskog theory with Lennard-Jones potentials.

Results and discussion

The multicomponent effects are studied in a ternary mixture consisting of gaseous methane, hydrogen and argon. An equimolar mixture of CH_4 and Ar is injected (10 l/min) in the center tube while the annular gas is an equimolar flow (40 l/min) of H_2 and Ar. Thus, at the beginning of the reactor, the only diffusing species are H_2 and CH_4 (Fig. 2a). As the diffusion process starts, demixing of Ar is observed (Fig. 2b). This multicomponent effect is caused by the peculiar influence of each diffusing species that exerts a specific force over the initially uniform species, Ar.

Since axial Peclet number exceeds 100, the axial diffusion is far less important than convection. Thus, in order to compare the different flux formulations presented, the focus is rather made on radial mixing by considering radial molar fluxes at the

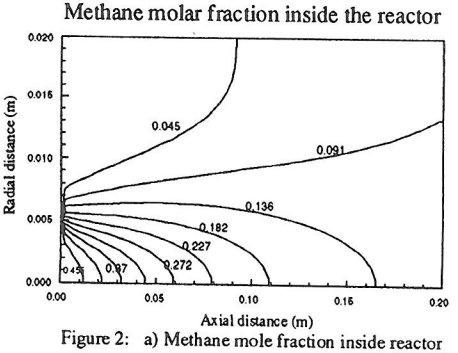
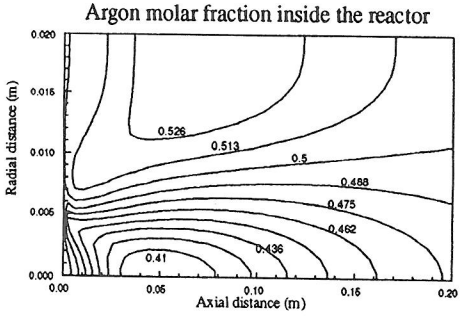


Figure 2: a) Methane mole fraction inside reactor



b) argon molar fraction in reactor

mixing line (cf. Fig. 1) where Peclet number approaches 1. First, the radial flux of a diffusing species, CH_4, is presented in Fig. 3 where the maximum flux is naturally found at the beginning of the reactor. Here, mass flux approximations compare qualitatively well to the exact formulation. However, while linear and Ramshaw's approximations follow the exact curve inside a 5% error, effective binary approach may underestimate or overestimate CH_4 radial flux with an error up to 30%.

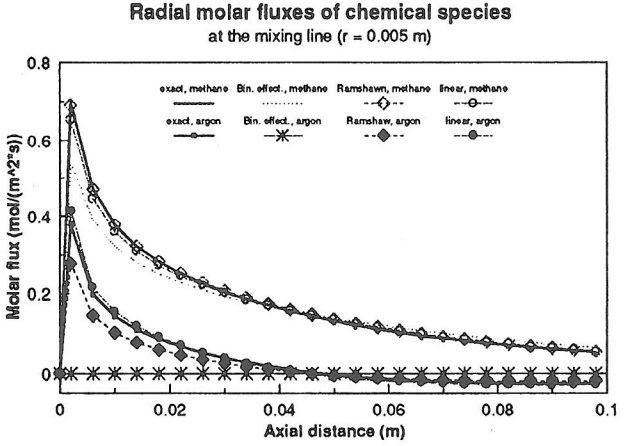


Figure 3: Radial molar fluxes for methane and argon at the mixing line in isothermal reactor

It is also interesting to analyze radial flux of an initially uniform component. Fig. 3 illustrates the results obtained from the different approximations in relation to the radial molar flux of Ar at the mixing line. Again, linear and Ramshaw's approximations predict the general features of the exact curve, though the linear method gives better results. As expected, effective binary approach doesn't present the demixing effect due to multicomponent nature of the diffusion. The initial flux of Ar corresponds to more than half of the CH_4 one, which is not negligible. In that sense, the effective binary approach can't handle multicomponent effect with regard of Ar demixing.

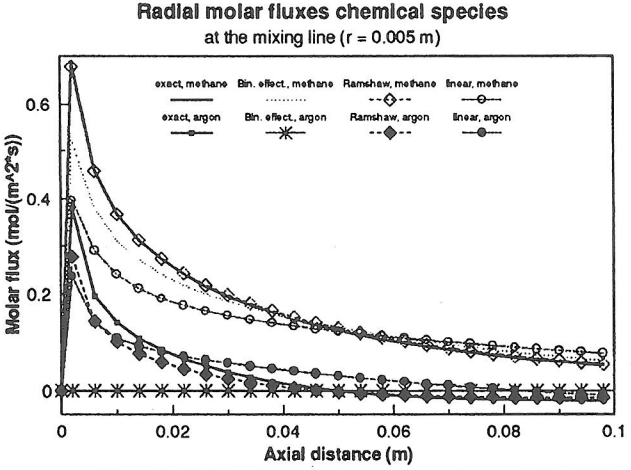


Figure 4: Radial molar fluxes for methane and argon at the mixing line in the presence of temperature gradients

Plasma reactors presenting strong radial temperature gradients, it is thus pertinent to look at the behavior of different approximations when such gradients are considered. Results of Fig. 4, obtained by imposing a wall temperature of 300 K, show that temperature gradients mostly affect the linear method. This can be explained by the error

introduced by estimating the Fick's matrix of diffusion coefficient at the averaged temperature.

Numerical results demonstrate the inadequacy of the popular effective binary approach to predict multicomponent features of a ternary flow. Simple to implement, this method requires the imposition of the flux consistency. The calculation of diffusion flux of one species based only on the gradient of that same species, this method cannot reflect demixing effects like the one observed with Ar. Ramshaw's improvement of the effective binary approximation gives the best results. Consistent, this method also reflects multicomponent effects in an advantageous way, even in presence of temperature gradients. The last approach, the linear one, responds quite well in isotherm simulations. Its sensitivity to temperature gradients and its complexity of implementation limits its applicability.

Conclusion

Three different diffusion flux formulations have been compared to an exact approach in order to evaluate their strengths and limits. A common ternary diffusion problem has been used as a benchmark. Results reveals the inability of the effective binary method to represent the multicomponent features of the ternary flow considered. The linear and Ramshaw's approximations reflect these features in a qualitative way. Nevertheless, Ramshaw's approach appeared more adequate to model diffusion fluxes in the context of plasma flows where important temperature gradients are prekent. At this point, it could be interesting to compare the computing effort associated to each formulation.

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