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Catalysis Today 26 (1995) 255–265

CATALYSIS TODAY

Heterogeneous/homogeneous reactions and transport coupling for catalytic combustion systems: a review of model alternatives

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Abstract

In applying catalysis to real combustor applications the modeling of transport and chemistry interactions can be key to understanding combustion characteristics. For example the effect of boundary-layer flow and heterogeneous/homogeneous chemistry can determine product selectivity for catalytically promoted oxidation of chlorinated hydrocarbons. In this paper we discuss parameter regions where different flow models including lumped-parameter-transport laminar boundary-layer and full two-dimensional models can be used for obtaining design insights. The degree of detail required in the gas phase chemistry models and surface chemistry models depends both on the system and the properties to be predicted. Definition of different regimes of operation and limits of applicability for parametric scaling relationships are key to the design of catalytic combustors for incineration or power generation. In addition, a theoretically-based rational strategy for applying catalytic boundary conditions in turbulent flow models would provide a valuable design tool. Examples of alternative modeling strategies are given below along with possible applications for the design of practical catalytic combustion systems.

Keywords: Combustion; Transport coupling; Review

1. Introduction

Designs for gas turbine engines having reduced emissions with extended lean limits at high inlet combustor velocities are made possible by catalytic combustion. In our catalytic combustion experiments, we have demonstrated that the inclusion of active catalytic surfaces can serve to provide heat and reactive species to the gas phase thereby extending the lean stability limit (for example, [1]). Designs have also recently been successfully tested for moderate scale stationary gas turbine engines where $>90\%$ of fuel conversion takes place on the catalyst [2]. Catalytic combustor designs where the majority of conversion takes place either on the surface or in the gas phase can both yield significant reduction in pollutant emissions. For example, NO_x reduction is directly related to both combustion temperature and the fraction of fuel converted on the catalyst surface. Issues related to the degree of complexity of surface chemistry, gas phase chemistry and transport description required to produce a predictive model are important and an intimate function of how the catalyst is incorporated into the combustor design. In traditional monolith burner designs where a large fraction ($\gg 50\%$) of the fuel is converted to CO_2 on the catalyst surface, relatively simple models are adequate design tools. These models use simple surface reaction kinetic models and plug-flow reactor/lumped-parameter transport formulations. Examples of

SSDI 0920-5861(95)00147-6

these models can be found in Refs. [3] and [4]. Detailed 2D transport models coupled with either a simple or detailed surface reaction models can also be used to provide a design tool for monolith reactors where only surface reactions are important [5]. Modern computational tools also allow efficient solution of the full 2D transport problem with detailed chemical mechanism for gas phase methane combustion [6]. Fundamental analysis of when specific approximations are valid is discussed in this article.

Use of catalysts in hybrid gas turbine applications where only a portion of the fuel conversion takes place on the catalyst may provide a more near-term approach to the use of catalytic combustion in commercial applications when compared to conventional monolith designs. Scale-up and design issues relating to these hybrid catalytic combustors, however, require a model capable of resolving coupling of catalytic reactivity and gas phase chemistry and transport simultaneously. Many configurations of this concept have been explored, including adding additional fuel and/or air downstream of the catalyst.

2. Numerical models

2.1. Numerical simulation of transport/chemical interactions

An important aspect of applying catalytic boundary conditions in steady-state flow models is the degree of complexity required to obtain meaningful parametric scaling information. In the section below the equations and solution method for the laminar boundary-layer parabolic model are described from the work of Karim et al. [4], and Markatou et al. [7]. The rationale behind the use of lumped parameter models for approximation of radial flux terms is described along with the use of this type of model for qualitative interpretation. Since the catalyst is supported on a solid surface in a combustor, boundary-layer models can sometimes provide useful design information even for turbulent combustion cases. Near the wall u'v' goes to zero and thus the laminar boundary-layer solution can provide an asymptotic solution for correlating rates for creation and transport of surface reaction products to the turbulent core. Early on, however, researchers [8,9] recognized that turbulent flow in a pipe is statistical in nature all the way to the wall itself. Thus, the dimensionless mass transport coefficient (the Sherwood number, Eq. 12 below) can deviate appreciably from the laminar solution. For design purposes 'effective' heat and mass transfer coefficients and thus boundary-layer thicknesses can be developed for use in lumped parameter models that are predictive over limited parameter regimes [9,10]. Heat release in a boundary-layer stabilizes turbulent fluctuations making the use of the 2D averaged transport equations for transport near the wall more realistic. Heat release in the boundary layer also, however, limits the applicability of simple lumped parameter transport formulations. This point along with other implications inherent in the use of lumped parameter transport schemes are discussed below. It should be noted that detailed turbulent reacting flow models are not capable of correctly handling detailed turbulence/chemistry interactions and, for cases in which these interactions are key to stabilization of combustion in the turbulent core, other approaches must be developed for understanding and estimating parametric sensitivities.

In hybrid catalytic combustor designs fuel and air are partially reacted over a catalyst with downstream completion of the reaction taking place in the gas phase. The downstream combustion rate of the prereacted fuel-air mixture is governed by the degree of prereaction and how the downstream mixing takes place. An important goal is the characterization of how catalytic activation of a part of the fuel affects downstream gas phase reactivity in order to develop scaling relationships for application of catalytic boundary conditions in turbulent combustor designs. Two limiting cases that can be considered numerically are defined by the Damköhler number (ratio of reaction to transport rate) that governs the reactivity surface of the products in the gas phase: (1) *the fully 'micro-*

mixed’ regime (reaction slow compared to transport) here, concentration gradients of reactants near the wall are minimal so either simple or detailed surface reaction models can be coupled to a well-stirred reactor or conventional turbulence model and (2) *the laminar flamelet regime* (reaction fast compared to transport) where the effect of catalytic prereaction on the stability of a strained laminar flamelet can be studied. Most hybrid catalytic combustors operate in the laminar flamelet regime. The strain imposed on the laminar flamelet by the turbulent flow field can significantly influence the structure of the flamelet. Use of a model of a burner configuration consisting of a cold premixed fuel air stream impinging on a hot catalytically prereacted fuel-air stream allows the study of the effect of catalytic reaction on flame stability and for the laminar flamelet regime will likely yield a useful first model for correlation and sensitivity studies. A closely related problem that has been addressed numerically by Smooke and coworkers [11] is the opposed jet methane/air flame with a hot prereacted jet opposed to a cold premixed unreacted jet. This configuration provides a convenient tool for studying the influence of strain imposed by the flow on the structure of laminar flamelets as discussed below.

In summary, in order to further develop design tools for catalytic combustors, it is important to define different regimes of operation and thus limits of applicability for various models and parametric scaling relationships. This includes definition of parameter regions where different flow models including lumped-parameter-transport, laminar boundary-layer, full 2D and turbulent flow models can be used for obtaining design insights as well as understanding why/when simple or complex chemical kinetic mechanisms are required. Hybrid catalytic combustor designs where mixing a hot partially prereacted mixture into a colder fuel/air stream intimately affects combustion characteristics pose special modeling problems as they operate in a non-premixed turbulent ‘laminar flamelet’ regime where chemical kinetics and transport are coupled. Description of some of the various model approaches are given below followed by suggestions for application for the design of specific practical systems.

2.2. *Description of the laminar boundary-layer model*

For catalytic combustion inside the tubular reactor in a laminar flow regime the following equations describe the conservation of momentum, total energy, and chemical species for a steady process applying the boundary-layer approximation (diffusion in the principal direction of flow is negligible compared to convection):

Continuity Equation:

$$\frac{\partial(r\rho v)}{\partial r}+\frac{\partial(r\rho u)}{\partial x}=0 \qquad (1)$$

Axial Momentum:

$$\rho v\frac{\partial u}{\partial r}+\rho u\frac{\partial u}{\partial x}+\frac{\partial p}{\partial x}-\rho g-\frac{1}{r}\frac{\partial}{\partial r}(\mu r\frac{\partial u}{\partial r})=0 \qquad (2)$$

Radial Momentum:

$$\frac{\partial p}{\partial r}=0 \qquad (3)$$

Species Equation:

$$\rho v\frac{\partial y_i}{\partial r}+\rho u\frac{\partial y_i}{\partial x}+\frac{1}{r}\frac{\partial}{\partial r}(r\rho y_i V_{ir})=w_i W_i \qquad (4)$$

Energy Equation:

$$\rho u c_p\frac{\partial T}{\partial x}+\rho v c_p\frac{\partial T}{\partial x}-\frac{1}{r}\frac{\partial}{\partial r}(r\lambda\frac{\partial T}{\partial r})$$
$$+\Sigma_i^{II}\rho y_i V_{ir} c_{pi}\frac{\partial T}{\partial r}+\Sigma_i^{II} w_i W_i h_i=0 \qquad (5)$$

Equation of State:

$$\rho=\frac{PW}{RT}\ where\ \frac{1}{W}=\Sigma\frac{y_i}{W_i} \qquad (6)$$

The radial momentum balance was derived by assuming the radial pressure gradient to be negligible. In the energy equation the compressive and viscous dissipation terms were neglected. In all the above Eqs. r refers to co-ordinate direction perpendicular to flow and x to the direction of flow; u and v are the velocities of gas mixture in the axial and radial direction; ρ is the density of gas mixture; λ is the thermal conductivity of the mixture; μ is the viscosity of the mixture; c_p is the specific heat of the mixture; W is the molecular weight of the mixture; y_i is the mass fraction of species i, C_{pi} is the specific heatcapacity of species i; h_i is the specific enthalpy of species i; V_{ir} is the ith component of the diffusion velocity in r direction; W_i is the molecular weight of ith species i, w_i is the molar production rate per unit volume of the ith species and is given by:

$$w_i = \Sigma v_{ki} q_k \qquad (7)$$

where v_k is the stoichiometric coefficient of species i in the kth reaction and q_k is the progress variable for the kth reaction.

Initial and boundary conditions

The initial condition is given for the x coordinate direction, at the entrance of the tube. The initial condition for the axial velocity variable is a fully developed profile:

$$u = U_{\max}\left(1 - \left(\frac{r}{\text{radius}}\right)^2\right) \qquad (8)$$

where $U_{\max}$ is the velocity at the center of the tube or twice the average velocity inside the tube. For temperature $T = T_{\text{inlet}}$ is specified. For the species $y_i = y_{i,\text{inlet}}$ is specified where $y_{i,\text{inlet}}$ are the mass fractions of reactant chemical species as given by the inlet equivalence ratio for the mixture. The following are the boundary conditions for the axial velocity, temperature, species.

$$\frac{\partial u}{\partial r} = 0, \frac{\partial T}{\partial r} = 0, \frac{\partial Y_i}{\partial r} = 0, \text{ at } r = 0 \qquad (9)$$

The other boundary conditions are specified at the wall. For temperature $T = T_{\text{wall}}$ is specified throughout the length of the wall except for a small length near the inlet where the temperature is made to linearly increase from inlet temperature to wall temperature. Axial velocity of $u = 0$ is specified. For species taking part in the surface reaction (either reactant or product) the condition specified is: $\rho_i Y_i V_{ir} + w_{is} = 0$; and for the non-reacting species $V_{ir} = 0$ is specified. The measured surface reaction rate in a Langmuir-Hinshelwood formulation is used to calculate w_{is}. A full 2D model is necessary where a fully developed boundary-layer is not achieved and also allows solution of the wall energy balance and more detailed surface chemistry models where justified.

3. Method of solution

The conservation Eqs. 2–5 and boundary conditions are transformed by introducing the stream function ϕ (von Mises transformation [7]) as an independent variable, defined as:

$$\frac{\partial \varphi}{\partial x} = -\rho r v, \frac{\partial \varphi}{\partial r} = \rho r u. \qquad (10)$$

This facilitates the solution procedure by eliminating the convective derivative in the radial direction and also satisfying the continuity equation automatically. The transformed equations are discretized by finite difference method and a modified Newton method was used to solve the nonlinear discretized equations. The discretization technique, modified Newton method, adaptive gridding, and adaptive x stepping are all discussed in full detail by Markatou and coworkers [7]. It takes approximately 11 h on an HP-735 machine to obtain numerical solution for a tube of 13.5 cm long and cold inlet velocity of 170 cm/s. Fully 2D models with detailed gas phase chemistry are also tractable [6] and are desirable for cases where a fully developed boundary-layer is not achieved. In addition full 2D models allow more complex surface chemistry models to be easily implemented without additional numerical complexity. Although this is not always necessary for lean methane combustion, steady state solutions near the leading edge can be influenced by 2D effects for flow conditions typical in catalytic combustors (dependent on both Re and Damköhler numbers (Dam)). Fig. 1 shows both boundary layer and full 2D solutions for methane combustion

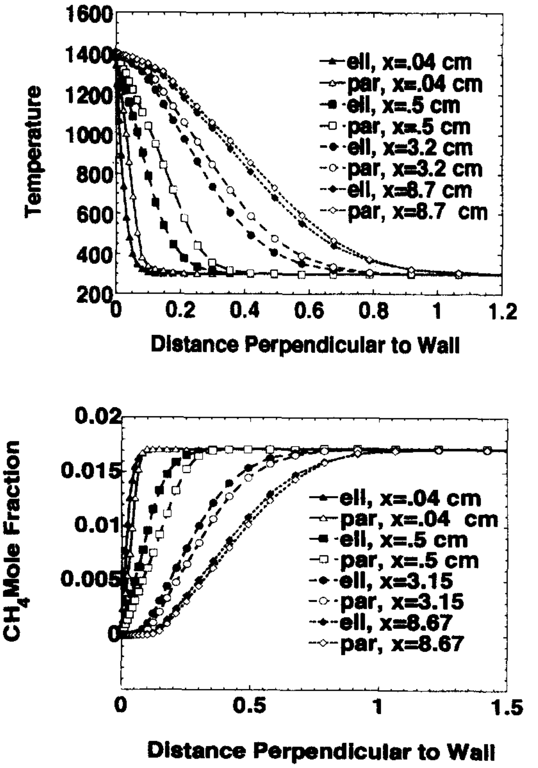

Fig. 1. Temperature and methane profiles for combustion of methane in air over an isothermal polycrystalline Pt-coated surface, ($\phi = 0.3$, $T_s = 1\,400$K).

($\phi = 0.3$) over a heated flat surface coated with a polycrystalline Pt film. Steady-state temperature and methane concentration as a function of position are shown the boundary layer solution is referred to as 'par' for parabolic and the full 2D solution by 'ell' for elliptic. The linear cold (298 K) inlet flow velocity was 1 m/s. The methane surface reaction rate was handled in an overall form as reported in Markatou et al. [7]. Near the leading edge of the plate for these conditions, the steady-state degree of conversion varies significantly between the two models whereas further downstream the solutions are similar. For richer stoichiometries, coupling occurs between transport and surface/gas reaction mechanisms. The steady-state solution in these cases can be strongly affected by 2D effects even far from the leading edge of the reactor.

The detailed boundary-layer or fully 2D Navier-Stokes transport model can be used effectively for laminar and near turbulent lean premixed catalytic combustor design when both surface and gas phase reactions are important. Further simplifications are possible when the surface reaction products do not react significantly in the gas-phase boundary-layer and the surface kinetics over the parameter range of interest can be expressed in terms of a simple Langmuir-Hinshelwood form. For these cases the simple lumped-parameter transport models discussed below are adequate for design calculations.

3.1. Plug flow and lumped parameter models

In the plug flow model there are no gradients in the r direction and isobaric conditions are assumed yielding the species equation:

$$\frac{\mathrm{d}Y_i}{\mathrm{d}t} = \frac{w_i W_i}{\rho} \tag{11}$$

For a plug flow model, the catalytic reaction products are mixed uniformly at each differential volume stepping down the tube. In lumped parameter formulations, radial convection is neglected and radial diffusion in the heat and mass equations (Eqs. 3 and 4) are represented by a flux at the wall as estimated by the product of a transfer coefficient (h_t for heat, k_2 for mass) and a linear driving force between the bulk and wall (see for example [9,10,12,13]). These transfer coefficients can be obtained either by correlation from experimental data or derived by solution of uncoupled energy and species equation with appropriate assumptions and boundary conditions. This approach is illustrated in Table 1 by a derivation of the dimensionless heat transfer coefficient (Nu_h) for fully developed laminar flow in a tube with uniform heat generation (G) in the bulk. It should be noted that the heat transfer coefficient scales with the generation term (G) so that any lumped parameter heat transfer coefficient is directly related to chemical reactivity in the boundary-layer and thus heat and mass transfer processes are coupled. This illustrates a general problem inherent in lumped parameter formulations: heat mass and momentum processes can be critically coupled. This means that transport coef-

Table 1
Development of the Nusselt number for fully-developed laminar flow, uniform wall cooling j''_k and uniform generation (G)

The Nusselt number for no generation:

$$\mathrm{N}_k=\frac{2j''_k a}{\lambda(T_m-T_w)}=48/11$$

The Nusselt number for uniform volumetric generation

$$\frac{\lambda}{r}\left(\frac{\partial}{\partial r}r\frac{\partial T}{\partial r}\right)+G=u\rho c_p\frac{\partial T}{\partial x} \quad \text{(I)}$$

$$\frac{u}{u_m}=2\left(1-\frac{r^2}{r_w^2}\right) \quad \text{(II)}$$

$$\left(\frac{\partial T}{\partial r}\right)_{r=r_w}=\frac{-j''_k}{\lambda} \quad \text{(III)}$$

From I, II, III:

$$T-T_w=\frac{Gr_w^2}{8\lambda}\left(1-\frac{r^2}{r_w^2}\right)^2+\frac{r_w j''_k}{4\lambda}\left(3-4\frac{r^2}{r_w^2}+\frac{r^4}{r_w^4}\right)$$

$$T_m-T_w=\int\frac{u}{u_m}(T-T_w)\mathrm{d}(r/r_w)^2$$

$$=\frac{Gr_w^2}{16\lambda}+\frac{11}{24}\frac{r_w j''_k}{\lambda}$$

$$\mathrm{N}\alpha\frac{1}{G}$$

ficients arrived at for one operating condition may not be meaningful at other operating conditions especially where significant heat release occurs in the gas phase.

Models for parametric analysis of tubular reactor systems for moderate Reynold's numbers can be based on the solution of the coupled boundary-layer or full 2D Navier Stokes equations. For cases where turbulent transport is important or where gas phase heat release is not significant lumped-parameter models can be useful for model simplification with the following cautions. The dimensional mass transport parameter is called the Nusselt number for mass transport ($\mathrm{Nu}_{m,0}$) or the Sherwood number (Sh):

$$Sh=Nu_m=\frac{j''_{i,w}}{A_w\rho D_i\dfrac{(y_{i,w}-y_{i,\infty})}{\delta_{m,0}}} \quad (12)$$

where A_w, $\delta_{m,0}$ is the area and thickness of mass boundary-layer when no reaction is present, across which mass flux $j''_{i,w}$ diffuses, D_i is the diffusivity, $y_{i,w}$ and $y_{i,\infty}$ is wall and bulk mass fraction of species. From heat/mass transfer analogy, the correlation developed for Nu_h can be used for $\mathrm{Nu}_{m,0}$ for equivalent boundary conditions (e.g constant T or y_i at the wall) provided the concentration of species is dilute, no reaction occurs in the bulk phase. For laminar flow in tube and no bulk reaction $\mathrm{Nu}_{m,0}=\mathrm{Nu}_h=3.657$ [12], for constant wall concentration/temperature and $\mathrm{Nu}_{m,0}=\mathrm{Nu}_h=48/11$ [12], for constant wall flux. When homogeneous reaction occurs in the gas boundary-layer then the y_i profile will be distorted, thereby increasing/decreasing the diffusional flux at the wall [see examples, [13]]. For this case, a correction factor F(reaction) can be introduced such that:

$$\mathrm{Sh}=\ \mathrm{N}_m=F(\text{reaction})\ \mathrm{N}_{m,0} \quad (13)$$

The function F(reaction) depends primarily on the Dam which is the ratio of predominant transport and reaction time scales for reactive species. For the case of a first order reaction with rate constant k''' which is a sink for the diffusing species:

$$F(\text{reaction})=\frac{\mathrm{Dam}^{1/2}}{\sinh(\mathrm{Dam})} \quad (14)$$

where $\mathrm{Dam}=\dfrac{k'''\delta_{m,o}^2}{D_i}$.

In a general catalytic combustion system there are several relevant Dams; one for the surface reaction and others for reactions important for fuel consumption in the gas phase boundary-layer. These two Dams are not independent because the surface reaction products can significantly accelerate or retard fuel conversion in the gas phase. If only heterogeneous chemical reactions occur, it is often assumed that $\mathrm{Nu}_m=\mathrm{Nu}_{m,0}$. The wall boundary condition also affects the Nu_m number. The ambiguities relating to boundary conditions and the effect of reaction on the transport process often leads researchers to obtain the $j''_{i,w}/\mathrm{A}_w$ used in the correlation Eq. 12, from experiments. These correlations can often be quite different from the theoretically derived expressions (due to unclear boundary conditions and assumptions which do not match) and must be used with caution because in cases where transport rates are strongly affected by reaction the scaling often does not hold far from the condition where the correlation was originally obtained except for limiting cases (see e.g. [9,10,12,13]). The key parameter in these scaling relationships is the relevant Dam because it represents the ratio between the dominant reaction and transport rates. The problem is significantly simplified in systems where a large portion of the fuel conversion occurs on the surface.

3.2. *Opposed jet burner models*

In hybrid catalytic combustor designs of combustion taking place fuel and air are partially reacted over a catalyst with downstream completion in the gas phase. The downstream reaction rate of the prereacted fuel-air mixture is governed by both the degree of prereaction and mixing downstream with additional fuel and/or air. Reaction is generally fast compared to transport meaning that these burners operate in the laminar flamelet regime. Parametric studies of strained, premixed laminar flames can be useful for modeling turbulent reacting flows which are in the laminar flamelet regime (see Peters [14] and Williams [15]). The strain imposed on a laminar flamelet by a turbulent flow field can interact with the structure of the flamelet even to the point where it can cause the flamelet to extinguish. Counterflow flame configurations provide a system where the effect of strain on a laminar flamelet can be studied in a controlled manner. This has led to many studies using this system, both experimental (e.g. [16–18]) and numerical (e.g. Smooke and coworkers [11] and Rogg [19]) providing a standard for comparison.

The opposed jet configuration is an essentially 2D structure and is modeled by the 2D elliptic form of the Navier-Stokes equations shown in parabolic form above. Smooke and coworkers [11] use a similarity transformation to simplify the problem to a set of non-linear boundary value equations in the axial direction. They explored the case of opposed hot and cold partially premixed jets of methane in air to understand reactivity of mixing layers in turbulent combustion. This concept is directly applicable to developing parametric scaling relationships for hybrid designs as a hot catalytically activated jet can be opposed with a cold jet of varying stoichiometry at varying strain rates. An indication of combustion enhancement is the increased strain rate at extinction demonstrated in hot/cold opposed jet models. The reciprocal of the strain rate at extinction is a time constant proportional to the well stirred reactor (CSTR) residence time required for combustion stabilization. This is a useful concept as many gas turbine manufacturers use simple network reactor models for design purposes consisting of CSTR and plug flow reactor segments.

4. Modeling applications

4.1. *Example 1: the oxidation of ultra-lean methyl chloride in air over a Mn-based catalyst*

The first example is for the total oxidation of ultra-lean ($\phi = 0.035$) methyl chloride in air over a Mn-based catalyst as reported in our earlier work [20–22]. This example is especially interesting because of the chemical coupling between the surface and gas phase reactivity which make lumped parameter models unusable for some flow conditions even though this is an ultra-lean system. The detailed gas phase reaction mechanism used in this study was taken from our previous study of non-catalytic oxidation of fuel lean CH_3Cl [21] and recent thermodynamic data, initial kinetic models and transport data were used from the literature [23–25]. The gas phase mechanism consist of 47 species and 240 homogeneous reactions. The heterogeneous reaction was used as a wall boundary condition in the parabolic model and products were assumed to be uniformly mixed across each differential volume in the plug flow model. The mechanism and rate of the heterogeneous reactions $2CH_3Cl \rightarrow C_2H_6 + 2Cl$ was measured under differential reactor conditions and parameters were not adjusted in the study [26].

Conversion of CH_3Cl fuel in a Mn coated tube (geometric surface area catalyst, $S/V = 25\ cm^{-1}$)

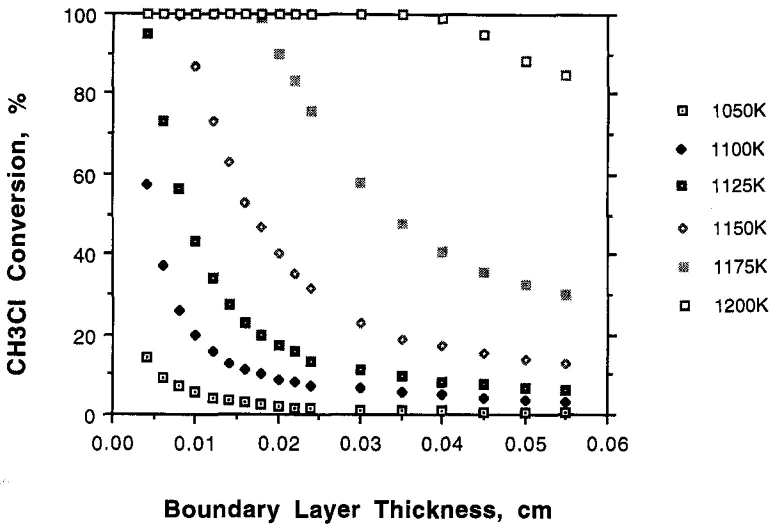

Fig. 2. CH_3Cl conversion for a mean residence of 25 ms as predicted by the lumped parameter model as a function of boundary layer thickness δ_m, tube diameter = 0.158 cm.

at cold (298 K) inlet velocities of 170 and 510 cm/s was modeled using the boundary layer (parabolic), plug flow and lumped parameter transport models discussed above. The 0.16 cm diameter tube was considered to have an isothermal section of 13.5 cm. At the slower velocity of 170 cm/s, there is no observable difference in product species profiles as a function of reaction temperature predicted by the plug-flow or parabolic model. At this velocity, the predictions of both models compare well with the experimental data for CH_3Cl conversion, slightly under predicting at low conversions. The models and experiment show significant (1%) CH_3Cl conversion occurring at 950 K with complete conversion achieved just below 1 200 K. At the higher flow velocity of 510 cm/s the mass transport limitation was noted for the surface reaction and the temperature at which 99% conversion occurred was increased by approximately 100 K. The plug-flow model predicted greater conversions at lower temperatures than the laminar flow model. This was expected because the higher flow velocity yields a shorter gas phase residence time and with surface area fixed this means less surface reaction per gas volume at a given surface temperature. This effect increases the surface temperature required for ignition increasing both Dams and making transport limitations more predominant and more accurate transport modeling important.

Fig. 2 shows calculated CH_3Cl conversion for a range of surface temperatures as a function of mass-transfer-boundary-layer thickness, (related to the mass transfer coefficient through Eq. 12) using a segregated flow lumped parameter model and a tube diameter of 0.16 cm. Residence time is fixed at 25 ms unlike the experimental conditions described above where the tube length was constant. For this particular chemical system where significant coupling exists between the surface and gas phase chemistry, the flow model used can significantly affect calculated conversion. It should be emphasized that a priori estimation of the mass transfer coefficient or δm for these conditions is only qualitatively possible because the appropriate Dam to be used in Eq. 14 changes with the contribution from the surface reaction (a function of both surface temperature and flow condition).

A key feature of this chemical reaction system is the coupling between surface and gas phase chemistry which makes the gas phase Dam dependent on surface reactivity. Fig. 3 shows predicted CH_3Cl conversion for gas phase chemistry only, surface reaction only, and with both chemistries included in the model. We observe that the

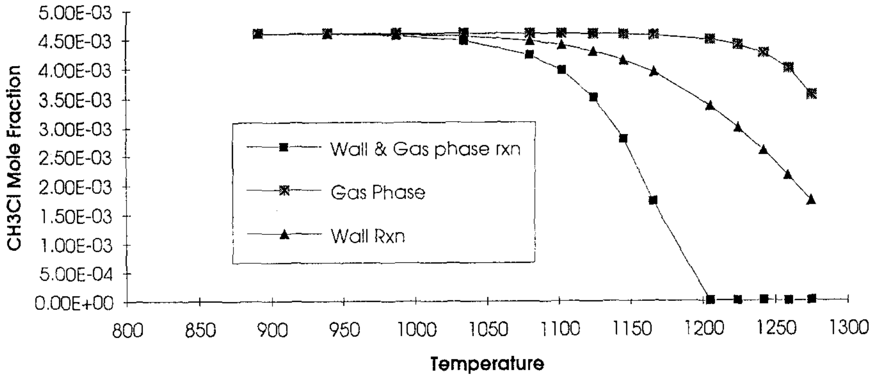

Fig. 3. Comparison of predicted CH_3Cl profile as function of temperature for gas chemistry only, surface reaction only and with both chemistries for the cold velocity of 170 cm/s.

surface reaction products significantly accelerate the gas phase destruction of CH_3Cl and that both detailed gas phase chemistry and surface reaction model must be included to accurately model the system.

4.2. Example 2: methane oxidation over precious metal catalysts

Boundary-layer effects can also affect selectivity to CO or CO_2 in the purely catalytic oxidation of methane over Pt or Pd. Using lumped parameter transport models, Hickman and Schmidt [27] have recently shown for near-stoichiometric mixtures of methane in air over precious metal gauze catalysts, flow conditions can strongly affect the ratio of CO/CO_2 produced. CO_2 was favored for slower velocities where the transport rates are low compared to chemical reaction rates. Transport can affect the surface chemistry mechanism by influencing the local reactant concentrations at the wall, which affects surface coverages. The implication for catalytic combustion applications is that surface product character can be for particular reactant conditions be engineered through appropriate reactor design.

Modeling chemistry/transport interactions becomes more difficult where gas phase reactions are important and reaction rates are fast with respect to mixing of products from catalytic reaction into the free stream. This is the case for many hybrid catalytic combustor designs. As discussed above, the opposed jet configuration is a tool for investigating this combustion regime. Smooke and coworkers [11] have explored the case of opposed hot and cold partially premixed methane/air jets to understand reactivity of mixing layers in turbulent combustion. As a measure of combustion enhancement by partial reaction/preheating, the strain rate imposed by the flow at extinction of the flame was calculated. Interestingly we have some experimental evidence that this type of model can predict features observable in experimental hybrid catalytic combustors that were not predictable using conventional computation fluid dynamics codes. For example, in hybrid catalytic combustor designs it has been observed experimentally that there exist parameter regimes where a sharp extinction will not occur as the flow rate is increased. This behavior was also observed in the model predictions of Smooke et al. [11] where for certain parameter regimes the stability envelope as a function of strain rate tailed off at high strain rates. In addition, the results of the numerical calculations of a methane-air double flame (two counterflowing streams of premixed reactants) at moderate and high values of the strain showed the concentration of the radicals, especially that of H, OH, and O, to be large at the plane of symmetry implying that there is significant interaction between the reaction zones. This work is directly applicable to hybrid catalytic combustors where a hot jet of catalytically activated mixture is mixed with a cold jet of varying stoichiometry at various strain rates imposed by the flow. An indication of combustion enhancement by prereaction/preheating is the calculated strain rate at extinction.

The results of the opposed jet burner computations for the hot prereacted opposed to cold premixed case may also be used to address which are the important variables to handle in a detailed fashion when implementing injection of prereacted mixtures into various locations in engine designs as modeled using turbulent combustor packages. Another interesting possible application of the opposed jet model would be as an chemical overlay model for use with a turbulent reacting flow model. In addition as noted above, the reciprocal of the strain rate at extinction is a time constant proportional to the CSTR residence time required for combustion stabilization. This concept can be used to develop scaling relationships or used directly in simple network reactor models of gas turbine engines.

5. Conclusions

Parametric scaling for catalytic combustion in quasi-laminar and low-turbulence catalytic monolith combustors can be well modeled using laminar boundary-layer or full 2D Navier Stokes flow models with detailed chemical models. For cases where most of the reaction occurs on the surface and very little heat release occurs in the gas phase, lumped parameter correlation schemes for the Sherwood number and simplified chemical models can be used effectively for both steady-state and transient models. For cases where chemical coupling with gas phase reactions is important or where a large proportion of the heat-release occurs in the boundary-layer these correlations break down. Most monolith-type reactors can be designed using the above strategies. The use of catalysts in hybrid or staged designs, however, will require the development of strategies for coupling near wall transport/reaction models with combustion in the turbulent core. A first step in this work is the understanding of how detailed a chemical model is required to describe chemical/turbulence interactions initiated by catalytic reaction products transported to the turbulent core. Opposed jet burner calculations of a hot prereacted flow opposed with a cold premixed unreacted stream may provide insights that will guide the development of future models.

Acknowledgements

The original catalytic flat-plate boundary-layer model was the PhD thesis work of Dr. Penelope Markatou co-supervised by Dr. Mitchell Smooke at Yale. The methyl chloride model discussed here, and the full 2D model development is part of the Ph.D. thesis work of Hasan Karim co-advised by Dr. Mitchell Smooke. I would also like to acknowledge the Physical Sciences Department of the Gas Research Institute for providing financial support on contract 5086-260-1249 and State of Connecticut for partial funding for this work and the many useful discussions with Dr. Stephen Hung (currently at GE, Schenectady) who carried out the methyl chloride oxidation experiments.

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