COMPUTATIONAL OPTIMIZATION AND SENSITIVITY ANALYSIS OF FUEL REFORMER

Arman Raoufi¹, Sagar Kapadia², James C. Newman III³

SimCenter: Center of Excellence in Applied Computational Science and Engineering
University of Tennessee at Chattanooga

ABSTRACT

In this study, the catalytic partial oxidation of methane is numerically investigated using an unstructured, implicit, fully coupled finite volume approach. The nonlinear system of equations is solved by Newton's method. The catalytic partial oxidation of methane over rhodium catalyst in a coated honeycomb reactor is studied three-dimensionally, and eight gas-phase species (CH_4 , CO_2 , H_2O , N_2 , O_2 , CO , OH and H_2) are considered for the simulation. Surface chemistry is modeled by detailed reaction mechanism including 38 heterogeneous reactions with 20 surface-adsorbed species for the Rh catalyst. The numerical results are compared with experimental data and good agreement is observed. Effects of the design variables, which include the inlet velocity, methane/oxygen ratio, catalytic wall temperature, and catalyst loading on the cost functions representing methane conversion and hydrogen production, are numerically investigated. The sensitivity analysis for the reactor is performed using three different approaches: finite difference, direct differentiation and an adjoint method. Two gradient-based design optimization algorithms are utilized to improve the reactor performance.

¹ Corresponding author, Ph.D Candidate, 701 E. M.L. King Blvd., Chattanooga, TN 37403, ar.raoufi@gmail.com

² Research Assistant Professor, 701 E. M.L. King Blvd., Chattanooga, TN 37403, Sagar-Kapadia@utc.edu

³ Professor, 701 E. M.L. King Blvd., Chattanooga, TN 37403, James-Newman@utc.edu

INTRODUCTION

Catalytic reactors are widely used in fuel reforming processes and have engineering applications such as in automotive catalytic converters, gas turbines, and for portable radiant heaters. These reactors are mainly required for environment concerns with regards to reducing pollutants and emission levels. There are many different structures for catalytic reactors, such as packed bed and monolith, which depend on the particular application and other parameters.

The monolith or honeycomb reactor is a commonly used configuration in the fuel reforming industry. With the catalyst being coated on the channel walls, these structures consist of a number of parallel passageways through which the gas flows. These catalytic monolithic reactors are generally characterized by the complex interaction of various physical and chemical processes. Figure 1 illustrates the physics and chemistry in a catalytic monolith reactor. The flow field includes the complex transport of momentum, energy, and chemical species. Because of the complexity and coupled interaction between mass and heat transfer, design and optimization of catalytic reactors is challenging. Computational fluid dynamics (CFD) can be used to simulate and understand the physical and chemical interactions within the reactor. Moreover, this predictive capability may then be utilized to perform reactor design or offer design alternatives. However, an enabling technology is the need to development robust and reliable numerical methods to model the fluid mechanics which includes the complex chemical reactions. The use of detailed models for chemical reactions is exceedingly challenging due to the large number of species involved, nonlinearity, and multiple time scales arising from the complex reacting systems. The resulting partial differential equations (PDEs) tend to be very large and stiff systems, with highly nonlinear boundary conditions [1].

In addition to design and optimization, CFD can be used to support experimental testing of these catalytic reactors. For example, Hettel *et al.* (2013) developed a numerical model to study the in situ effect of probe insertion on the velocity and species profiles [2]. Therefore, numerical modeling combined with experimental measurements together should be used to provide a comprehensive and detailed understanding of catalytic reactors.

Modeling of monolithic reactors can be broadly divided in two categories: single-channel modeling that considers just one channel of the monolith and full-scale modeling that considers

the whole reactor comprised of several hundred channels [3]. Simulations for a single-channel have been previously performed using one-, two- and three-dimensional models. One-dimensional (1D) models ignore radial and angular gradients in temperature, concentration, and velocity, and consider only axial variations. These models, which use lumped heat and mass coefficients, are widely used because of their simplicity, ease of implementation, and computational efficiency. The resulting one-dimensional model is typically referred to as the plug-flow model. In the monolith channel, the catalytic reaction occurs in the washcoat on the channel wall. There are two choices for incorporating the catalyst reaction into the heat and mole balance equations: pseudo-homogeneous model and heterogeneous model. In the pseudo-homogeneous model, the wall temperature and concentrations are assumed to be the same as the fluid, and the reaction rate is incorporated directly into the conservation equations. For the heterogeneous model, the gas-solid interface at the wall is assumed to be discontinuous and separate mole and energy balance equations are solved for the solid. These equations are coupled to the fluid equations through mass and heat transfer coefficients. The catalytic reactor results presented in this report utilize the heterogeneous model for surface chemistry.

Since no diffusive terms remain, the plug-flow equations form a differential-algebraic-equation (DAE) initial-value problem for the axial variation of the mean species composition [4]. The catalytic partial oxidation of hydrogen was previously investigated by Cerkowicz *et al.* (1977) [5] with simplified chemistry and by Kramer *et al.* (2002) [6] with detailed kinetics. Two and three-dimensional models are more complex but provide more realistic results than the one-dimensional models. These models are developed based on both boundary-layer equations and the Navier-Stokes equations. In boundary-layer approximations, axial (flow-wise) diffusive transport is neglected, but detailed transport to and from the channel walls is retained. Deutschmann *et al.* (2000) [7] and Dogwiler *et al.* (1999) [8] utilized two-dimensional Navier-Stokes models with detailed heterogeneous and homogeneous chemistry for the simulation of catalytic partial oxidation. The catalytic partial oxidation of methane-air has been studied by Markatou *et al.* (1993) [9] using a two-dimensional boundary layer model. Raja *et al.* (2000) [4] investigated the efficiency and validity range of the Navier–Stokes, boundary-layer, and plug-flow models in a catalytic monolithic channel. That research demonstrated that boundary-layer models provide accurate results with low computational cost. Kumar (2009) [3] developed a new implicit solver for species conservation equations and investigated the flow field in a full-scale

three-dimensional catalytic converter. The catalytic partial oxidation of iso-octane over rhodium catalysts was studied by Hartmann *et al.* (2010) [10]. In that research, detailed surface chemistry including 17 surface species and 58 surface reactions was utilized in the simulation. In the current study, the effect of considering homogeneous reaction mechanisms in the numerical model is investigated. Maestri and Cuoci (2013) [11] have used the open-source CFD solver OpenFOAM [12] to simulate heterogeneous catalytic systems three-dimensionally with the detailed kinetics schemes. The catalytic partial oxidation (CPOX) of methane over a honeycomb reactor was numerically studied by Hettel *et al.* (2015) [13], where OpenFOAM and DETCHEM [14] were coupled to model a large-scale CPOX reactor. Raoufi *et al.* (2016) [15] developed a fully coupled numerical model to investigate the catalytic partial oxidation of methane over a honeycomb-structured Rh/Al₂O₃ coated catalyst. In that work, the governing equations for fluid and solid regions of the monolithic reactor are solved simultaneously. Table 1 illustrates a summary of the literature review, and presents the numerical studies that have been carried out in the field of the catalytic partial oxidation.

Many researchers have numerically studied the effects of reactor parameters, such as the velocity inlet, temperature, and fuel concentration, on the performance of catalytic systems. In those works, the dependency of reactor performance on different design variables was obtained via parametric studies. That is, simulating the reactor performance at baseline values, then systematically changing the parameter values and reevaluating the performance. This method provides valuable information for reactor design, however, when the number of design variables is large, this procedure may become computationally prohibitive. Furthermore, utilizing parametric studies to investigate design alternatives has proven extremely valuable in practice, but this process does not provide a direct nor rigorous manner in which to arrive at an optimal design. This is the underlying motivation for the combination of computational fluid dynamics with numerical optimization methods. Moreover, the use of sensitivity analysis represents a more computationally efficient alternative for parametric studies as well as for optimization purposes. To this end, Minh (2005) [16] developed numerical methods for the simulation and optimization of complex processes in catalytic monoliths for two practical applications: catalytic partial oxidation of methane and conversion of ethane to ethylene. In that work, the optimization was formulated as an optimal control problem constrained by a system of PDEs describing the chemical fluid dynamics process. Minh *et al.* (2008) [17] then investigated the optimization of

the oxidative dehydrogenation of ethane to ethylene over platinum using this optimal control problem. In that study, a two-dimensional model was used to simulate the single monolith channel.

In the current research, a three-dimensional fully implicit unstructured model is developed to solve the transport of mass, momentum, energy and species in a methane reformer simultaneously. The surface chemistry is solved using the mean-field approximation model to obtain the surface coverage and reaction rates. Effects of the different parameters on the reactor performance are investigated using discrete sensitivity analysis. Sensitivity derivatives are computed and validated using three different approaches: finite difference, direct differentiation and an adjoint method. Finally, a fuel reforming reactor is numerically optimized using gradient-based design algorithms.

NOMENCLATURE

c_t	Total molar mixture concentration
D_{ij}	Binary mass diffusion coefficient of species i into species j
D_i^{kn}	Knudsen diffusion coefficient
$\vec{F}_e$	Inviscid flux vector
$\vec{F}_v$	Viscous flux vector
e_i	Species internal energy
e_t	Specific total energy (total energy per unit mass)
h_i	Species enthalpy
J_i	Mass diffusion flux vector for species i
$\tilde{k}$	Heat transfer coefficient
MW	Mean molecular weight of the mixture
MW_j	Molecular weight of species j
N_i	Diffusion molar flux

ns	Number of species
p	Pressure (mixture)
p_i	Partial pressure
$\vec{Q}$	Conservative flow variables
$\hat{q}$	Heat flux vector
R_i	Gas constant
R_u	Universal gas constant
$\vec{S}$	Source term vector
T	Temperature
u	x-velocity
U_i	Species diffusion velocity
v	y-velocity
w	z-velocity
X_j	Mole fraction of species j
Y_i	Mass fraction of species i
Greek symbols	
ρ	Mixture density
ρ_i	Species density
Ω_μ	Collision integral value for viscosity
Ω_{ij}	Collision integral
μ	Dynamic viscosity (mixture)
τ	Shear stress tensor
$\dot{\omega}_i$	Reaction rate source term for the species i
σ	Lennard-Jones collision diameter

GOVERNING EQUATIONS AND NUMERICAL SOLUTION

The time-dependent Reynolds Averaged Navier-Stokes equations for chemically reacting flows can be written in conservative-law form as:

$$\frac{\partial \vec{Q}}{\partial t} + \nabla \cdot (\vec{F}_e(\vec{Q}) - \vec{F}_v(\vec{Q})) = \vec{S}(\vec{Q}) \quad (1)$$

The conservative flow variables $\vec{Q}$, the inviscid flux vector $\vec{F}_e$, the viscous flux vector $\vec{F}_v$ and source term vector $\vec{S}$ are defined as:

$$\vec{Q} = \begin{bmatrix} \rho_1 \\ \rho_2 \\ \vdots \\ \rho_{ns} \\ \rho u \\ \rho v \\ \rho w \\ \rho e_t \end{bmatrix} \quad \vec{F}_e = \begin{bmatrix} \rho_1 u \\ \rho_2 u \\ \vdots \\ \rho_{ns} u \\ \rho u^2 + p \\ \rho uv \\ \rho uw \\ (\rho e_t + p)u \end{bmatrix} \hat{i} + \begin{bmatrix} \rho_1 v \\ \rho_2 v \\ \vdots \\ \rho_{ns} v \\ \rho uv \\ \rho v^2 + p \\ \rho vw \\ (\rho e_t + p)v \end{bmatrix} \hat{j} + \begin{bmatrix} \rho_1 w \\ \rho_2 w \\ \vdots \\ \rho_{ns} w \\ \rho uw \\ \rho vw \\ \rho w^2 + p \\ (\rho e_t + p)w \end{bmatrix} \hat{k} \quad (2)$$

$$\vec{F}_v = \begin{bmatrix} J_{1x} \\ J_{2x} \\ \vdots \\ J_{nsx} \\ \tau_{xx} \\ \tau_{xy} \\ \tau_{xz} \\ u\tau_{xx} + v\tau_{xy} + w\tau_{xz} - \hat{q}_x \end{bmatrix} \hat{i} + \begin{bmatrix} J_{1y} \\ J_{2y} \\ \vdots \\ J_{nsy} \\ \tau_{xy} \\ \tau_{yy} \\ \tau_{yz} \\ u\tau_{xy} + v\tau_{yy} + w\tau_{yz} - \hat{q}_y \end{bmatrix} \hat{j} \quad (3)$$

$$+ \begin{bmatrix} J_{1z} \\ J_{2z} \\ \vdots \\ J_{nsz} \\ \tau_{zx} \\ \tau_{zy} \\ \tau_{zz} \\ u\tau_{zx} + v\tau_{zy} + w\tau_{zz} - \hat{q}_z \end{bmatrix} \hat{k}$$

$$\vec{S} = \begin{bmatrix} \dot{\omega}_1 \\ \dot{\omega}_2 \\ \vdots \\ \dot{\omega}_{ns} \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (4)$$

The modified Stephen-Maxwell equation is used to compute the diffusion molar flux [18]. The binary diffusion coefficients are obtained by using the Chapman–Enskog theory [19], and the Wilke’s mixing rule is used for estimation of the mixture viscosity [19].

The governing equations are discretized using a node-centered finite volume method on an unstructured mesh. That is, the field is discretized into control volumes defined by the median dual centered on the mesh point vertices. A Green-Gauss formula is used for gradient evaluation at vertices, which results in second-order spatial accuracy. The residual for each control volume is approximated by quadrature of the fluxes passing through the boundaries of the control volume faces. The convective flux terms are calculated using the Roe-scheme [20]. The Roe averaged variables are constructed using a density weighted average of the flow variables on either side of the control volume face for a multi species mixture [21]. The Roe averaged flux Jacobian is computed using the eigensystem described in references [21] and [22]. The complex Taylor series expansion (CTSE) method is used for accurate linearization of the residual to form the Jacobian derivatives [23] [24]. The viscous flux contribution is evaluated using the average of the flux vectors on either side of the control volume faces. A robust iterative solution process based on Newton’s method is used to solve the highly coupled, nonlinear partial differential equations. The GMRES algorithm is utilized for the solution to the linear systems arising at each Newton iteration [25]. An ILU(K) preconditioner is used to improve convergence of the linear solver. Parallelization of the solution algorithm is afforded via Message Passing Interface (MPI) libraries. METIS [26] is utilized to decompose the computational domain and create the sub-domain connectivity for parallel communications. METIS converts the computational mesh into a graph, and then uses a graph partitioning technique to split the graph into sub-domains. METIS uses multilevel graph partitioning technique that first partition a coarser graph. After the coarse partitioning is complete, the graph is un-coarsened to obtain the partition for the full graph. This technique leads to better quality partitions and higher computational efficiency. METIS decomposition improved the scalability of the code since it minimizes load imbalance and edgcut simultaneously. The currently used distributed memory paradigm for parallelization is somewhat standard within the CFD community and may be readily found in the literature (e.g. [27]).

MODELING THE SURFACE CHEMISTRY

The heterogeneous and homogeneous chemical reaction mechanisms are key components of reacting flow modeling. The mechanism of heterogeneously catalyzed gas-phase reactions can be described by the sequence of elementary reaction steps including adsorption, surface diffusion, chemical transformations of adsorbed species, and desorption. Several modeling approaches are available to compute the reaction rates of heterogeneous reactions. Different approaches, such as Ab-initio calculation, density function theory (DFT), and kinetic Monte Carlo modeling have been used to include the molecular aspects of heterogeneous catalysis. In the power-law kinetic approach, the rate of the catalytic reaction is calculated by fitting empirical equations to experimental data. In the last two decades mean-field approximation has been used improve upon the much simpler Langmuir-Hinshelwood or even power-law approaches as well as to include some of the elementary aspects of catalysis into models suitable for numerical simulation of catalytic reactors [28]. In the mean-field approximation, rate equations similar to homogeneous reactions are used to model heterogeneous reactions.

In the mean-field model, the chemistry source terms, $\dot{s}_i$, of gas-phase species due to adsorption/desorption and surface absorbed species are given by [29]:

$$\dot{s}_i = \sum_{k=1}^{K_s} v_{ik} k_{fk} \prod_{j=1}^{N_g+N_s} [X_j]^{v_{jk}'} \quad (i = 1, \dots, N_g + N_s) \quad (5)$$

where K_s is the number of elementary surface reactions (including adsorption and desorption), and N_s is the number of species adsorbed. The heterogeneous flux on the surface is then obtained by:

$$Flux_{het} = MW_i \dot{s}_i \quad (6)$$

Since the catalyst is dispersed as small particles in the reactor support, the active catalyst area is usually much larger than the geometric surface area. The ratio of these two values is defined as:

$$F_{cat/geo} = \frac{A_{catalyst}}{A_{geometric}} \quad (7)$$

To account for the pore diffusion within the catalyst coating layer, the effectiveness factor, η , is defined. With $F_{cat/geo}$ and η determined experimentally, the heterogeneous flux formula can be written as:

$$Flux_{het} = F_{cat/geo} \eta MW_i \dot{s}_i \quad (8)$$

The time variation of the surface coverage, used for transient simulations, is obtained by [29]:

$$\frac{\delta \Theta_i}{\delta t} = \frac{\dot{s}_i}{\Gamma} \quad (9)$$

where Γ is the surface site density (mol/m²) which describes the maximum number of species that can be adsorb on a unit surface area. The surface site densities are of the order of 10⁻⁹ mol/cm² (approximately 10¹⁵ adsorption sites per cm²) [30]. Equation (9) assumes that the total surface site density Γ is constant. In steady-state calculations, the surface species concentrations (or site fractions) remain constant with time [29], which results in:

$$\dot{s}_i = 0 \quad (i = N_g + 1, \dots, N_g + N_s) \quad (10)$$

Hence, at steady-state the surface species concentrations must adjust to be consistent with the adjacent gas-phase species concentrations in order to satisfy this condition. Therefore, the solutions of equations (5) and (10) provide the surface coverages and the surface molar concentrations. Once these values are obtained, the source terms for the governing equations can be computed. The system of equations generated by equations (5) and (10) is considered to be extremely stiff. A C-language version of VODE, CVODE, which is included in the Sundials package, is chosen for solving these stiff equations. For coupling with CVODE an interface based on Cantera [31] is used. The structure of this interface is illustrated in Figure 2. In the solution algorithm, the domain was decomposed first and the information of control volumes and the reacting surface boundary cells was transferred to the corresponding processor. Each processor computes and solves the flow field and surface chemistry related to itself and then communicates with other processors. Based on the application, a Cantera input file is written which includes the definition of the gas and surface phases and detailed chemical reactions. Input from this file is used to create and allocate the Cantera gas, surface and interface objects at the beginning of the simulation. During simulation, the flow simulation solver provides the gas phase to Cantera. This information includes the temperature, pressure, and mole fractions of the species. Cantera specifies the required parameters, which is then provided to the CVODE solver. The surface coverages and reaction rates are computed and communicated back to the flow simulation solver to use as the chemical source terms. The surface computations are performed

on demand for every reacting surface cells within each Newton iteration using the information from the flow solver for temperature, pressure and mole fractions.

SENSITIVITY DERIVATIVES

In many engineering design applications, sensitivity analysis techniques are useful in identifying the design parameters that have the most influence on the response quantities. This information is helpful prior to an optimization study as it can be used to remove design parameters that do not strongly influence the responses. In addition, these techniques can provide assessments as to the behavior of the response functions which can be invaluable in algorithm selection for optimization, uncertainty quantification, and related methods. In a post-optimization role, sensitivity information is useful in determining whether or not the response functions are robust with respect to small changes in the optimum design point [32]. The sensitivities are obtained by computing gradients or derivatives of the solution with respect to the set of design variables. There are many methods for computing and obtaining sensitivities derivatives. A review of these methods may be found in [33]. Finite difference, direct-differentiation and adjoint methods have been widely used in the literature for this purpose. The finite difference method is the simplest approach to compute sensitivity derivatives. For a design variable β and a cost function $I(\beta)$, the sensitivity derivatives are obtained from a central difference as following:

$$\frac{\partial I}{\partial \beta} \approx \frac{I(\beta + \Delta\beta) - I(\beta - \Delta\beta)}{2\Delta\beta} \quad (11)$$

which has second-order truncation error and is subjected to subtractive cancellation. This method is computationally expensive for a large number of design variables because two fully converged nonlinear flow solutions are required for every design parameter.

The direct-differentiation method is obtained by use of the chain rule. The residual may be expressed in terms of explicit and implicit dependencies on the design variables as:

$$R = R(\beta, \vec{Q}(\beta), X(\beta)) \quad (12)$$

Applying the chain rule yields:

$$\frac{dR}{d\beta} = \frac{\partial R}{\partial \beta} + \frac{\partial R}{\partial Q} \frac{\partial Q}{\partial \beta} + \frac{\partial R}{\partial X} \frac{\partial X}{\partial \beta} \quad (13)$$

At convergence the residual and therefore the total differential are zero, that is $\frac{dR}{d\beta} = 0$, and therefore the above may be solved for the sensitivity of the conserved variables as:

$$\left[\frac{\partial R}{\partial Q}\right]\left\{\frac{\partial Q}{\partial \beta}\right\} = -\frac{\partial R}{\partial \beta} \quad (14)$$

In this linear system the Jacobian and sensitivity matrices, $\partial R/\partial Q$ and $\partial R/\partial \beta$, are evaluated using the CTSE method. Applying the chain rule to the cost function, assuming in general that this function has both explicit and implicit dependencies on the design variables, yields:

$$\frac{\partial I}{\partial \beta} = \frac{\partial I}{\partial \beta} + \frac{\partial I}{\partial X} \frac{\partial X}{\partial \beta} + \frac{\partial I}{\partial Q} \frac{\partial Q}{\partial \beta} \quad (15)$$

The linearization of the cost function can be evaluated analytically or using the CTSE method. Direct differentiation requires the solution to a linear system of equations for each design variable and, thus, provides an efficient method when the number of design variables is relatively small.

In the adjoint method a constraint term, which is proportional to the residual through a Lagrange multiplier [34], is added to the cost function:

$$I(\beta, \vec{Q}(\beta), X(\beta)) = I_c(\beta, \vec{Q}(\beta), X(\beta)) + \lambda^T R(\beta, \vec{Q}(\beta), X(\beta)) \quad (16)$$

where I_c is the initial cost function, λ is an arbitrary vector of Lagrange multipliers, and T is the transpose operator. Linearizing the above with respect to the design variables yields:

$$\frac{dI}{d\beta} = \frac{\partial I_c}{\partial \beta} + \frac{\partial I_c}{\partial Q} \frac{\partial Q}{\partial \beta} + \frac{\partial I_c}{\partial X} \frac{\partial X}{\partial \beta} + \lambda^T \left(\frac{\partial R}{\partial Q} \frac{\partial Q}{\partial \beta} + \frac{\partial R}{\partial X} \frac{\partial X}{\partial \beta} + \frac{\partial R}{\partial \beta} \right) \quad (17)$$

Rearranging this equation to isolate the sensitivity of the conserved variables gives:

$$\frac{dI}{d\beta} = \left[\frac{\partial Q}{\partial \beta}\right]^T \left\{ \left[\frac{\partial R}{\partial Q}\right]^T \lambda + \frac{\partial I_c}{\partial Q} \right\} + \left\{ \frac{\partial I_c}{\partial \beta} + \left[\frac{\partial X}{\partial \beta}\right]^T \frac{\partial I_c}{\partial X} \right\} + \left\{ \left[\frac{\partial R}{\partial \beta}\right]^T + \left[\frac{\partial X}{\partial \beta}\right]^T \left[\frac{\partial R}{\partial X}\right]^T \right\} \lambda \quad (18)$$

Since the Lagrange multipliers are arbitrary they are chosen to eliminate the first term on the right hand side resulting in:

$$\left[\frac{\partial R}{\partial Q}\right]^T \{\lambda\} + \left\{ \frac{\partial I_c}{\partial Q} \right\} = 0 \quad (19)$$

Once the Lagrange multipliers have been obtained by solving the above linear system, sensitivity derivatives can be obtained from:

$$\frac{dI}{d\beta} = \frac{\partial I_c}{\partial \beta} + \left[\frac{\partial X}{\partial \beta}\right]^T \frac{\partial I_c}{\partial X} + \lambda^T \left\{ \left[\frac{\partial R}{\partial \beta}\right] + \left[\frac{\partial R}{\partial X}\right] \left[\frac{\partial X}{\partial \beta}\right] \right\} \quad (20)$$

As can be seen, evaluation of the Lagrange multipliers only requires solution to one linear system of equations for a given cost function. Therefore, the adjoint method is more efficient than the direct differentiation approach for a large number of design variables.

RESULTS AND DISCUSSION

To organize and present the current research, the computational results are divided into a number of sections. For the catalytic partial oxidation of methane, these sections specifically address the parallel performance of the developed methodology, validation with experimental data, parametric study of design parameters, sensitivity analysis, and design optimization.

Parallel performance

The parallel performance of the currently developed methodology is assessed using the simulation for the catalytic partial oxidation of methane. The details concerning this simulation are presented in the following section, and are not presently required to assess algorithmic performance. The developed methodology utilizes standard Message Passing Interface (MPI) libraries, and the scalable performance is examined over an increasing range of processors. The simulations are performed on an in-house SimCenter cluster. This cluster has 325 dual-processor dual-core machines (1300 cores total), E1200 Gigabit Ethernet switches, and a cluster performance of 7.7 terraflops (TF).

Considering 10 Newton iterations, the execution time for 1, 2, 4, 8, 16, 32, 64 and 128 processors are shown in Fig. 3. As illustrated in the figure, run time is decreased with increased number of processors. However, for evaluating the parallel efficiency, it more useful to ascertain how much performance gain is achieved by parallelizing a given problem over a serial implementation. The speedup is a measure that captures the relative benefit of solving a problem in parallel. Speedup is defined as the ratio of the time taken to solve a problem on a single processor to the time required to solve the same problem on a parallel system [35]:

$$Speedup = \frac{T_{serial}}{T_{parallel}} \quad (21)$$

The speedup for the current case is presented in Fig. 4. As indicated, the speedup is decreasing with increasing the number of the processors. The computing speedup is close to the ideal speedup for the number of processors less than 10. With increasing the number of processors for a fixed size problem, the communication overheads are increased and which lead to decreasing speedup. This result is typical in that for a given discretization, the amount of computational work is fixed, and as the number of processors is increased the communication

costs become more proportional. For larger problem sizes, the theoretical speedup is achieved for a larger number of processors.

Validation for the catalytic partial oxidation of methane

In this section, the catalytic partial oxidation of methane over Rh/Al₂O₃ coated honeycombs is numerically investigated. Honeycomb-structured reactors are widely used in many engineering applications such as fuel reformers, catalytic converters, and gas turbine combustors. The experimental study conducted by Hettel *et al.* [13] is selected for validation purposes. In the experimental study the reactor is a 2 cm diameter cylinder, with 260 channels, and a channel density of 600 cpsi (channels per square inch). The initial and boundary conditions are summarized in Table 2. The simulations are performed with the detailed heterogeneous oxidation mechanism proposed by Deutschmann *et al.* [36], and include 38 heterogeneous reactions and 20 surface-adsorbed species. The site density is assumed to be $2.79 \times 10^{-9} \text{ mol/cm}^2$, and the kinetic data of the surface-reaction mechanisms are taken from the literature. Eight gas-phase species (CH₄, CO₂, H₂O, N₂, O₂, CO, OH and H₂) are considered for the simulation, with the surface chemistry modeled using the mean-field approximation. Since it has no the significant effect on the flow field for this test case and operating conditions, the homogenous combustion in the gas phase is ignored in this study [37]. The computational grid is comprised of 122,208 tetrahedral cells, and the parallel simulation performed over 64 processors. Figure 5 depicts the surface grid for one channel of the monolith. The grid is refined in the regions near the catalytic wall to accurately resolve the boundary layer. The “inflow” boundary condition is used at the channel inlet and a fully developed boundary condition is considered for the outlet. The no-slip boundary condition with catalytic reaction source term is applied at the channel walls. The temperature of the catalytic wall is assumed to be constant along the channel. The nonlinear system of equations obtained from the discretization is solved using Newton’s method, and the convergence history of the solution is shown in Figure 6.

Figure 7 illustrates the comparison between the numerical results and experimental data for the species mole fractions as a function of position in the reactor. As seen, overall good agreement is observed. At the inlet of the reactor methane oxidation begins, and in the experimental test set-up the temperature is increased gradually to 1000 K in this initial section of reactor. Therefore, due to difficulties in replicating these precise conditions, the greatest

difference between the numerical and experimental data is visible in this region. Furthermore, as expected, oxygen is completely consumed in the first few millimeters of the reactor.

Parametric study

In this section, the effect of the different design parameters on the fuel reformer performance is investigated. These design parameters can be related to the shape/size of the reformer as well as the operating conditions and catalyst material. In this work the inlet methane/oxygen ratio, inlet velocity, and catalytic wall temperature are considered as variables for parametric study. Note that by using the inlet velocity as one of the parameters, the effect of different Reynolds numbers is also studied indirectly on reformer performance.

The baseline conditions for this study are shown in Table 3. Figure 8 shows the comparison of the mole fraction of species along the symmetry axis of the reformer with two different inlet velocities of 0.5 and 2 m/s. The conversion of methane is predicted to decrease with increasing inlet velocity. The rate of oxygen consumption along the reactor is also decreased and therefore the peak of H₂O concentration is shifted towards the middle of the channel for the higher inlet velocity. Mole fraction contours of the different species for the reactor with inlet velocity of 2 m/s are illustrated in Fig. 9. The influence of the catalytic wall temperature on species conversion rates is shown in Fig. 10. The numerical results predict that the conversion of methane increases from 90% at 1070 K to 96% at 1170 K. Additionally, hydrogen production is increased by approximately 10% at the higher temperature.

The inlet methane-oxygen ratio represents another important design parameter. To investigate the influence of this ratio, two different simulations were performed. These consisted of methane-oxygen ratios of 1 ($x_{CH_4} = 0.1$ and $x_{O_2} = 0.1$) and 1/3 ($x_{CH_4} = 0.05$ and $x_{O_2} = 0.15$). The numerical results are shown in Fig. 11, which compares the aforementioned cases with a baseline methane-oxygen ratio of approximately 2 ($x_{CH_4} = 0.133$ and $x_{O_2} = 0.067$). Figure 11 demonstrates the influence of the methane-oxygen ratio on reformer performance. As seen, the size of the active methane conversion region increases with higher methane-oxygen ratios at the inlet. The hydrogen production reaches the highest level for the richest mixture. Hydrogen production for the mixture ratio of 1/3 is minimal and CO, CO₂ and H₂O are the main products, as can be seen from the mole fraction contours illustrated in Fig. 12.

Catalyst loading is an import factor in the design and optimization of catalytic reactors. The heterogeneous flux with catalyst loading effects has been previously given in equation (8). For considering the effect of catalyst loading, two parameters $F_{\text{cat/geo}}$ (ratio of catalytic surface area to geometric surface area) and η (effectiveness factor) are considered. As shown in Fig. 13, the methane conversion increases for high catalyst loading. The methane conversion increases from 57% at $F_{\text{cat/geo}}\eta = 0.5$ to 98% at $F_{\text{cat/geo}}\eta = 2$, and the hydrogen production at $F_{\text{cat/geo}}\eta = 2$ increases about 7% relative to the baseline case. Additionally, oxygen is almost completely consumed by surface reactions in the first millimeter of the reactor length for all three cases. For $F_{\text{cat/geo}}\eta = 0.5$ the contours of the concentrations of species along the length of the reactor are shown in Fig. 14 to illustrate the variations within the channel.

Sensitivity Analysis

For the parametric studies, the dependencies of the reformer performance on design variables were obtained by comparing baseline solutions to those with variations. An alternative approach to assessing these effects is through the use of sensitivity analysis. In this method, the sensitivities are obtained by computing gradients or derivatives of the solution with respect to the set of design variables. These sensitivity analysis methods, having widely varying implementation costs, provide a precise sensitivity measure at roughly the same cost as a function evaluation [33]. As previously discussed, there are several methods for computing sensitivity derivatives.

The typical use of sensitivity analysis is for computational design whereby the cost function is to be either minimized or maximized. To improve the cost function, gradient-based optimization algorithms require information on how the cost function changes with respect to the design variables; that is, $dI/d\beta$. Furthermore, sensitivity derivatives may be used to identify the variables that have the most significant impact on design performance. Design variables of the inlet velocity, methane density, oxygen density, catalytic wall temperature, and catalytic area ratio are considered for sensitivity analysis in this study. The mean value of H_2 concentration at the outlet boundary is considered as the cost function. For verification purposes, sensitivity derivatives obtained using the adjoint and direct differentiation approaches are compared with those computed using a central finite-difference method. For the central finite-difference method,

a perturbation value of 1×10^{-5} is used for the simulation. The baseline conditions for this study have been previously given in Table 2. Sensitivity derivative results are presented in Table 4. As illustrated in Table 4, the sensitivity derivatives obtained by the direct differentiation and adjoint methods show good agreement, and match up to 9 digits. Additionally, it may be observed that the methane concentration, followed by oxygen density, plays the most significant roles in the mean value of H_2 concentration. Differences are observed in comparisons with the central finite-difference method. These discrepancies may be attributable to the highly nonlinear response of the cost function to the design variables and due to subtractive cancellation errors in the finite-difference method. To ascertain a better understanding on the sources of errors, a more detailed step-size study for the finite-difference method is warranted.

Optimization

In gradient-based optimization algorithms, sensitivity derivatives are utilized in determining a search direction that will maximize or minimize the cost function. One potential drawback to these methods is the added complexity and computational costs associated with evaluating these gradients. However, sensitivity analysis requires solutions to linearized systems of equations, whereas finite-difference methods necessitate the solution to nonlinear systems for each design variable perturbation. Furthermore, as noted previously, the discrete adjoint eliminates the dependence of the sensitivity of the cost function with respect to the state-vector and, therefore, represents an efficient means to evaluate sensitivity derivatives for large number of design parameters. Since the number of design variables is small in this case, there is no significant advantage of using the adjoint method relative to the direct differentiation. Thus, the direct differentiation method is utilized.

Computational optimization is the minimization (or maximization) of a function subjected to constraints on its variables. The optimization problem can be defined as

$$\begin{aligned} & \min I(\boldsymbol{\beta})_{\boldsymbol{\beta} \in \mathbb{R}^n} \\ & \text{Subject to:} \quad g_i(\boldsymbol{\beta}) \leq 0 \quad i \in J \\ & \quad \boldsymbol{\beta}^L \leq \boldsymbol{\beta} \leq \boldsymbol{\beta}^U \end{aligned} \tag{22}$$

where $I(\boldsymbol{\beta})$ is the objective or cost function, $g_i(\boldsymbol{\beta})$ is the vector of inequality constraints, and $\boldsymbol{\beta}^L$ and $\boldsymbol{\beta}^U$ the lower and upper side-constraints on the design variable, respectively. Numerous

algorithms have been developed for solving this standard optimization problem and, moreover, are available in software packages.

In the current research, the DAKOTA toolkit is used. DAKOTA (Design Analysis Kit for Optimization and Terascale Applications) was developed at Sandia National Laboratories [32]. DAKOTA's optimization capabilities include a wide variety of gradient-based and nongradient-based optimization methods. It includes many external optimization libraries such as the OPT++ library [38], CONMIN and DOT libraries [39], and an interface to link with third-party routines that provide the function evaluations and sensitivity information.

Initially, to demonstrate the numerical optimization procedure, three design parameters including inlet velocity, inlet methane concentration, and catalytic wall temperature are studied. For this optimization, the mean value of CH₄ concentration at the outlet boundary is considered as the cost function, and the initial conditions on the design parameters of inlet velocity, inlet methane concentration, and catalytic wall temperature are 0.7 m/s, 0.05, and 1000 K, respectively. The initial concentration for oxygen and nitrogen are 0.15 and 0.8, respectively. All other conditions are the same as found in Table 2. Note that since the values of the design variables have different orders of magnitude, scaled values are used within the optimization for methane concentration and catalytic wall temperature. Additionally, side-constraints are imposed on these design variables and are listed in Table 5.

The optimization is performed using two gradient-based algorithms: the Fletcher-Reeves conjugate gradient (frcg) method (from DAKOTA's CONMIN library) and a quasi-Newton method (from DAKOTA's OPT++ library). OPT++'s quasi-Newton method is based on the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [40] variable-metric algorithm. Both Opt++'s quasi_newton and DOT's frcg methods used the same line searching approach, which is based on the algorithm by More and Thuente [41]. Furthermore, both methods are initiated with a steepest descent search and, therefore, the first approximation to the inverse of the Hessian for the BFGS algorithm is the identity matrix. It should be noted that the use of Newton's method and, thus, the direct evaluation of the analytic Hessian is prohibitively expensive for high-fidelity simulation. However, it was shown by Sherman et al. [42] that a combination of the direct-differentiation and the adjoint method may be utilized for evaluation of the Hessian. Depending on the number of design variables and cost functions required in the optimization problem formulation, the methods presented in [42] may be utilized to mitigate some of the computational burden.

Both methods achieve the same local optimal point of 0.3 m/s, 0.0825, and 1200 K for inlet velocity, methane concentration, and catalytic wall temperature, respectively. Note that in this case, the lower side-constraint for inlet velocity and the upper side-constraint for catalytic wall temperature are active. For this particular optimization, as seen in Table 6, the quasi-Newton algorithm requires significantly more function evaluates and design cycles as compared to the Fletcher-Reeves conjugate gradient method. Figure 15 shows a comparison of methane concentration along the centerline of the reactor using baseline and optimized conditions.

While the previous case optimized the methane conversion, the main goal of reformer design is to maximize the hydrogen production. In some cases, although methane is almost completely consumed for the given conditions, the main products of the chemistry are species other than hydrogen. For this reason, a cost function representing the hydrogen concentration at the outlet boundary may be defined as

$$Cost\ function = \frac{1 - \iint_{Outlet\ BC} \rho_{H_2} dA}{0.09} \quad (23)$$

Based on the previous optimization results using high-fidelity analysis, the Fletcher-Reeves conjugate gradient method is selected for this case. Again, the design variables of inlet velocity, wall temperature and inlet methane concentration are used. The initial conditions on the design parameters of inlet velocity, inlet methane concentration, and catalytic wall temperature are 0.7 m/s, 0.082, and 1000 K, respectively. The initial concentration for oxygen and nitrogen are 0.118 and 0.8, respectively. For this optimization, the 20 objective function evaluations and 5 gradient calculations were required to obtain the local minimum point of 0.545 m/s, 0.13, and 1200 K. A comparison of hydrogen concentration along the centerline of the reactor using baseline and optimized conditions is shown in Figure 16.

CONCLUSIONS

The complex interaction of chemical and physical processes inside a methane reformer is numerically studied with an implicit, unstructured finite volume based multi-species Navier-Stokes solver. The surface chemistry, heterogeneous combustion and coverages are computed and solved by coupling the high-fidelity simulation with Cantera. Coupling with the Cantera package enabled solving the stiff system of equations encountered while modeling the surface chemistry. For validation, numerical results are compared with experimental data and good

agreement is observed for the catalytic partial oxidation. To assess the effect of various parameters on reactor efficiency, a parametric study was performed. This study indicated that the conversion of methane decreases with increasing inlet velocity and, therefore, Reynolds number. Moreover, the methane and hydrogen production increases with increasing catalytic wall temperature, the methane conversion decreases with increasing methane/oxygen ratio, and hydrogen production is higher at more rich mixtures. Sensitivity analysis was additionally used to assess the effect of design parameters on reactor performance. Verification of these sensitivity derivatives was performed using finite-difference, direct differentiation, and adjoint formulations. From sensitivity analysis it was observed that the methane concentration, followed by oxygen density, play the most significant roles in the mean value of H_2 concentration. Finally, utilizing the sensitivity analysis capability, computational design was performed with a gradient-based optimization algorithm. Considering the inlet velocity, wall temperature and inlet methane concentration as design variables, two optimization cases were performed. The first optimization selected the mean value of CH_4 concentration at the outlet boundary as the objective function, and compared the numerical performance of Fletcher-Reeves conjugate gradient and quasi-Newton algorithms. The second optimization case selected hydrogen concentration at the outlet boundary as the objective function, and demonstrated significant reactor improvement over the baseline design.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research (ONR) Grant No. N00014-10-1-0882 and the Tennessee Higher Education Commission (THEC) Center of Excellence in Applied Computational Science and Engineering (CEACSE). This support is greatly appreciated.

REFERENCES

- [1] H. D. Minh, Numerical Methods for Simulation and Optimization of Chemically Reacting Flows in Catalytic Monoliths, PhD Thesis, University of Heidelberg, 2005.
- [2] M. Hettel, C. Diehm, B. Torkashvand and O. Deutschmann, “Critical Evaluation of In-situ Probe Techniques for Catalytic Honeycomb Monoliths,” *Catalysis Today*, vol. 216, 2013.

- [3] A. Kumar, Physical Models and Computational Algorithms for Simulation of Catalytic Monolithic Reactors, PhD Thesis, Ohio State University, 2009.
- [4] L. L. Raja, R. J. Kee, O. Deutschmann, J. Warnatz and L. D. Schmidt, "A critical evaluation of Navier–Stokes, boundary-layer, and plug-flow models of the flow and chemistry in a catalytic-combustion monolith," *Catalysis Today*, vol. 59, no. 1-2, pp. 47-60, 2000.
- [5] A. E. Cerkowicz, R. B. Cole and J. G. Stevens, "Catalytic Combustion Modeling; Comparisons With Experimental Data," *ASME. J. Eng. Power*, vol. 99, no. 4, pp. 593-600, 1997.
- [6] J. F. Kramer, S. A. Reihani and G. S. Jackson, "Low Temperature Combustion of Hydrogen on Supported Pd Catalysis," in *29th International Symposium on Combustion*, Japan, 2002.
- [7] O. Deutschmann, L. I. Maier, U. Riedel, A. H. Stroemman and R. W. Dibble, "Hydrogen assisted catalytic combustion of methane on platinum," *Catalysis Today*, vol. 59, no. 1-2, pp. 141-150, 2000.
- [8] U. Dogwiler, P. Benz and J. Mantzaras, "Two-Dimensional Modelling for Catalytically Stabilized Combustion of a Lean Methane-Air Mixture with Elementary Homogeneous and Heterogeneous Chemical Reactions," *Combustion and Flame*, vol. 116, pp. 243-258, 1999.
- [9] P. Markatou, L. D. Pfefferle and M. D. Smooke, "A computational study of methane-air combustion over heated catalytic and non-catalytic surfaces," *Combustion and Flame*, vol. 93, no. 1-2, pp. 185-201, 1993.
- [10] M. Hartmann, L. Maier, H. D. Minh and O. Deutschmann, "Catalytic partial oxidation of iso-octane over rhodium catalysts: An experimental, modeling, and simulation study," *Combustion and Flame*, vol. 157, no. 9, pp. 1771-1782, 2010.
- [11] M. Maestri and A. Cuoci, "Coupling CFD with detailed microkinetic modeling in heterogeneous catalysis," *Chemical Engineering Science*, vol. 96, pp. 106-117, 2013.
- [12] "www.openfoam.org," OpenFOAM, The Open Source CFD Toolbox, 2014. [Online].

- [13] M. Hettel, C. Diehm, H. Bonart and O. Deutschmann, "Numerical simulation of a structured catalytic methane reformer by DUO: The new computational interface for OpenFOAM® and DETCHEM™," *Catalysis Today*, vol. 258, no. 2, pp. 230-240, 2015.
- [14] O. Deutschmann, S. Tischer, C. Correa, D. Chatterjee, S. Kleditzsch, V. M. Janardhanan, N. Mladenov, H. D. Minh, H. Karadeniz and M. Hettel, "www.detchem.com," DETCHEM Software Package, 2014. [Online].
- [15] A. Raoufi, S. Kapadia and J. C. Newman III, "Computational Simulation of Thermal and Chemical Phenomena for a Honeycomb-Structured Catalytic Reforming Reactor," in *229th ECS meeting*, San Diego, CA, 2016.
- [16] H. D. Minh, Numerical Methods for Simulation and Optimization of Chemically Reacting Flows in Catalytic Monoliths, PhD Thesis, University of Heidelberg, 2005.
- [17] H. D. Minh, H. G. Bock, S. Tischer and O. Deutschmann, "Optimization of Two-Dimensional Flows with Homogeneous and Heterogeneously Catalyzed Gas-Phase Reactions," *AIChE journal*, vol. 54, no. 9, pp. 2432-2440, 2008.
- [18] D. Arnost and P. Schneider, "Dynamic transport of multicomponent mixtures of gases in porous solids," *The Chemical Engineering Journal*, vol. 57, pp. 91-99, 1995.
- [19] M. Coltrin, R. Kee and F. Rupley, "Surface chemkin: A general formalism and software for analyzing heterogeneous chemical kinetics at gas-solid interfaces," *Int. J. Chem. Kinet*, vol. 23, p. 1111, 1991.
- [20] P. L. Roe, "Approximate Reimann Solvers, Parameter Vectors and Difference Schemes," *Journal of Computational Physics*, vol. 43, pp. 357-372, 1981.
- [21] M. Busby, Steps Toward More Accurate and Efficient Simulations of Reactive Flows, Ph.D. Thesis, Mississippi State University, 1997.
- [22] S. Kapadia, Computational Design and Sensitivity Analysis of Solid Oxide Fuel Cells, Ph.D Thesis, University of Tennessee at Chattanooga, 2008.
- [23] J. C. Newman, W. K. Anderson and D. Whitfield, "Multidisciplinary sensitivity derivatives using complex variables," Technical Report MSSU-COE-ERC-98-09, Engineering Research Center Report, Mississippi State University, 1998.
- [24] W. K. Anderson, J. C. Newman, D. Whitfield and E. Nielsen, "Sensitivity analysis

for the navier-stokes equations on unstructured meshes using complex variables,” *AIAA Journal*, vol. 39, p. 56–63, 2001.

- [25] Y. Saad and M. H. Schultz, “GMRES: A Generalized Minimal Residual Algorithm for Solving Nonsymmetric Linear Systems,” *SIAM J. Sci. Stat. Comput.*, vol. 7, pp. 856-869, 1986.
- [26] METIS, [Online]. Available: <http://glaros.dtc.umn.edu/gkhome/views/metis>.
- [27] D. G. Hyams, "An Investigation of Parallel Implicit Solution Algorithms for Incompressible Flows on Unstructured Topologies," Ph.D Dissertation, Mississippi State University, 2000.
- [28] O. Deutschmann, Modeling and Simulation of Heterogeneous Catalytic Reactions, Wiley-VCH, 2012.
- [29] R. J. Kee, M. Coltrin and P. Glarborg, Chemically Reacting Flow: Theory & Practice, John Wiley & Sons, 2003.
- [30] C. Diehm, H. Karadeniz, C. Karakaya, M. Hettel and O. Deutschmann, "Spatial Resolution of Species and Temperature Profiles in Catalytic Reactors: In Situ Sampling Techniques and CFD Modeling," in *Advances in Chemical Engineering: Modeling and simulation of heterogeneous catalytic processes*, vol. 45, A. G. Dixon, Ed., Academic Press, 2014, pp. 41-96.
- [31] D. G. Goodwin, H. K. Moffat and R. L. Speth, “Cantera: An object- oriented software toolkit for chemical kinetics, thermodynamics, and transport processes,” 2015. [Online]. Available: <http://www.cantera.org>.
- [32] B. M. Adams, L. E. Bauman, W. J. Bohnhoff, K. R. Dalbey, M. S. Ebeida, J. P. Eddy, M. S. Eldred, P. D. Hough, K. T. Hu, J. D. Jakeman, L. P. Swiler and D. M. Vigil, “DAKOTA, A Multilevel Parallel Object-Oriented Framework for Design Optimization, Parameter Estimation, Uncertainty Quantification, and Sensitivity Analysis: Version 5.2 User's Manual,” Sandia Technical Report SAND2010-2183, 2009.
- [33] C. E. Burdyslaw, Achieving Automatic Concurrency Between Computational Field Solvers and Adjoint Sensitivity Codes, Ph.D dissertation, University of Tennessee at Chattanooga, 2006.

- [34] L. C. Elliott, Solid Oxide Fuel Cell Simulation and Design Optimization with Numerical Adjoint Techniques, Ph.D dissertation, University of Tennessee at Chattanooga, 2008.
- [35] A. Grama, A. Gupta, G. Karypis and V. Kumar, Introduction to Parallel Computing, Second, Ed., Pearson, 2003.
- [36] O. Deutschmann, R. Schwiedemoch, L. I. Maier and D. Chatterjee, "Natural Gas Conversion in Monolithic Catalysts: Interaction of Chemical Reactions and Transport Phenomena," *Studies in Surface Science and Catalysis*, vol. 136, pp. 251-258, 2001.
- [37] O. Deutschmann and L. D. Schmidt, "Modeling the Partial Oxidation of Methane in a Short-Contact-Time Reactor," *AIChE Journal*, vol. 44, no. 11, pp. 2465-2477, 1998.
- [38] J. C. Meza, R. A. Oliva, P. D. Hough and P. J. Williams, "OPT++: an object oriented toolkit for nonlinear optimization," *ACM Transactions on Mathematical Software*, vol. 33, no. 2, pp. 126- 136, 2007.
- [39] "DOT Users Manual, Version 4.20," Vanderplaats Research and Development, Inc., Colorado Springs, CO, 1995.
- [40] C. Meza, "OPT++: An object-oriented class library for nonlinear optimization," Sandia National Laboratories, Rep. SAND94-8225, 1994.
- [41] J. J. More and D. J. Thuente, "Line Search Algorithms With Guaranteed Sufficient Decrease," *ACM Transactions on Mathematical Software*, vol. 20, pp. 286-307, 1994.
- [42] L. L. Sherman, A. C. Taylor III, L. L. Green, P. A. Newman, G. W. Hou and V. M. Korivi, "First- and Second-Order Aerodynamic Sensitivity Derivatives via Automatic Differentiation with Incremental Iterative Methods," *Journal of Computational Physics*, vol. 129, no. 2, pp. 307-331, 1996.

LIST OF FIGURES

Figure 1 Catalytic combustion monolith and physical and chemical process occurring in the monolith reformer

Figure 2 Data exchange between the solver and Cantera through the interface

Figure 3 The total run times for the different number processors

Figure 4 The speedup for solving the problem

Figure 5 Grid generated for the channel of reactor

Figure 6 Convergence history of the solution

Figure 7 Comparison between the numerical results and experimental data for the partial oxidation of methane

Figure 8 The comparison of the mole fraction of species along symmetry axis of the reformer with the different inlet velocities 0.5 and 2 m/s

Figure 9 The mole fraction contour for the reactor with the inlet velocity 2 m/s

Figure 10 The comparison of the mole fraction of species along symmetry axis of the reformer for the different catalytic wall temperature

Figure 11 The influence of the variation of methane/oxygen ratio on the reformer performance

Figure 12 The mole fraction contour for the reformer with the methane/oxygen ratio 1/3

Figure 13 The influence of the variation of the catalyst loading on the reformer performance

Figure 14 The mole fraction contour for the reformer with $F_{\text{cat/geo}}\eta = 0.5$

Figure 15 The optimized conditions for methane concentration along the reactor

Figure 16 The comparison between the base condition and the optimized condition for hydrogen concentration along the centerline of the reactor

LIST OF TABLES

Table 1: The literature review and numerical studies were carried out in the field of the catalytic partial oxidation

Table 2: Initial conditions for the catalytic partial oxidation of methane

Table 3: Baseline conditions for the catalytic partial oxidation of methane

Table 4: The sensitivity derivatives for the different design variables

Table 5: Initial values and constrained bounds for the design variables

Table 6: The number of solver and gradients calls for the optimization algorithms

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

a)

b)

c)

d)

e)

Figure 9

Figure 10

Figure 11

a)

b)

c)

d)

e)

f)

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Table 1

Authors	Affiliation	Year	Model	Fuel/catalyst
Cerkanowicz <i>et al.</i>	Exxon Research and Engineering Co.	1977	1D- simplified chemistry	Hydrogen- Pt
Markatou <i>et al.</i>	Yale University	1993	2D Boundary layer-detailed chemistry	Methane -Pt
Deutschmann <i>et al.</i>	University of Stuttgart	1994	1D- detailed chemistry	Methane -Pt
Deutschmann <i>et al.</i>	University of Heidelberg	1996	1D- detailed chemistry	Methane -Pd
O. Deutschmann, L. D. Schmidt	University of Minnesota	1998	2D - detailed chemistry	Methane- Rh-Pt
Dogwiler <i>et al.</i>	Paul Scherrer Institute	1999	2D - detailed chemistry	Methane - Pt
Raja <i>et al.</i>	Colorado School of Mines	2000	2D- detailed chemistry	Methane -Pt
Deutschmann <i>et al.</i>	University of Heidelberg	2000	2D - detailed chemistry	Methane -Pt
Dupont <i>et al.</i>	University of Leeds	2001	1D- detailed chemistry	Methane -Pt
Kramer <i>et al.</i>	University of Maryland	2002	1D- detailed chemistry	Hydrogen -Pt
Minh	University of Heidelberg	2005	2D- detailed chemistry-optimization	Ethane-Pt
Minh <i>et al.</i>	Karlsruhe Institute of Technology	2008	2D- detailed chemistry-optimization	Ethane-Pt
Kumar	Ohio State University	2009	3D- detailed chemistry	Methane -Pt
Hartmann <i>et al.</i>	Karlsruhe Institute of Technology	2010	2D- detailed chemistry	Iso-octane-Rh
Maestri and Cuoci	Politecnico di Milano	2013	3D- detailed chemistry	Iso-octane-Rh
Hettel <i>et al.</i>	Karlsruhe Institute of Technology	2013	3D - detailed chemistry	Methane - Rh
Hettel <i>et al.</i>	Karlsruhe Institute of Technology	2015	3D- detailed chemistry	Methane- Rh
Raoufi <i>et al.</i>	University of Tennessee	2016	3D- detailed chemistry	Methane- Rh

Table 2

Gas inlet velocity	0.329 m/s
Gas inlet temperature	1000 K
Wall temperature	1000 K
Gas inlet compositions (mole fraction)	$x_{\text{CH}_4} = 0.133$, $x_{\text{O}_2} = 0.067$, $x_{\text{N}_2} = 0.8$
Working pressure	1 atm
Channel width	1 mm
Channel length	10 mm

Table 3

Gas inlet velocity	0.5 m/s
Gas inlet temperature	1070 K
Wall temperature	1070 K
Gas inlet compositions(mole fraction)	$x_{\text{CH}_4} = 0.133$, $x_{\text{O}_2} = 0.067$, $x_{\text{N}_2} = 0.8$
Working pressure	1 atm
Channel width	1 mm
Channel length	10 mm
Catalyst	Rh

Table 4

DV	finite difference	direct differentiation	adjoint
Inlet velocity	-0.00571674320	-0.00580817201	-0.00584081720
Inlet methane density	0.10364058231	0.10718769820	0.10718769812
Inlet oxygen density	-0.080342139543	-0.079660588349	-0.079660588319
Catalytic wall temperature	0.00116746547	0.00105843297	0.00105843127
Catalytic area ratio	0.00104274151	0.00113610487	0.00113610454

Table 5

	inlet velocity	methane concentration at inlet	catalytic wall temperature
Lower bound	0.3	0.3	0.8
Upper bound	1.5	1.3	1.2
Initial values	0.7	0.5	1.0

Table 6

Method	function evaluation	gradient calculation
Fletcher-Reeves conjugate gradient method	17	7
quasi-Newton algorithm	17	15