Toward simulation of full-scale monolithic catalytic converters with complex heterogeneous chemistry

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Computational fluid dynamic (CFD) modeling of full-scale catalytic converters with realistic chemistry has remained elusive primarily due to the extreme computational requirements. In this work, a new low-memory coupled implicit solver, based on the conservative unstructured finite-volume method, was utilized to simulate laboratory-scale catalytic converters with implicit coupling between fluid flow, heat transfer (including conjugate heat transfer), mass transfer, and heterogeneous chemical reactions. Steady-state calculations were performed for a catalytic methane–air combustion process with 24 reaction steps and 19 species (8 gas-phase species, 11 surface-adsorbed species), and a three-way catalytic converter process with 61 reaction steps and 31 species (8 gas-phase species, 23 surface-adsorbed species). Both calculations were conducted on a single processor for a monolith with 57 channels discretized using 354,300 control volumes. The catalytic combustion simulation was completed in 19 h and required 900 MB of memory, while the three-way conversion simulation required 6 days and 1 GB of memory, indicating that the complexity of the surface reaction mechanism dominates the overall CPU time requirements. Subsequently, the solver was parallelized, and the same catalytic combustion case was simulated for a monolith with 293 channels discretized using 1.27 million control volumes. A 4-node cluster was utilized for the parallel computations, and the parallelization efficiency was found to be about 80%.

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1. Introduction

Despite tremendous progress in computer technology in recent years, simulation of full-scale monolithic catalytic converters has remained elusive. Such simulations require extreme computational resources (Mazumder, 2007), to be discussed shortly. Literature review reveals numerous publications on two- and three-dimensional computational fluid dynamic (CFD) modeling of a single channel of the monolith (Canu & Vecchi, 2002; Chatterjee, Deutschmann, & Warnatz, 2001; Deutschmann, Maier, Riedel, Stroemmann, & Dibble, 2000; Grimm & Mazumder, 2008; Groppi, Belloli, Tronconi, & Forzatti, 1995; Holder, Bolliga, Anderson, & Hochmuth, 2006; Mantzaras, Appel, & Benz, 2000; Papadias, Zwinkels, Edsberg, & Bjormborg, 1999; Raja, Kee, Deutschmann, Warnatz, & Schmidt, 2000; Sallamie & Koshkanab, 2003; Young & Finlayson, 1976, among many others). Currently, due to lack of better alternatives, the knowledge gained from the simulation of a single channel is extrapolated to the entire catalytic converter. Since the channels are coupled to each other through heat transfer, and individual channels may encounter different flow rates, extrapolation of the results of a single channel to the entire converter is not always accurate, and may lead to flawed designs (Tischer, Correa, & Deutschmann, 2001). Also, some catalytic combustors use a design in which catalytic reactions take place only in alternate channels (Carroni, Griffin, Mantzaras, & Reinke, 2003) to manage peak temperatures and thermal gradients, leading to considerable variations from channel to channel. Another important issue that is not addressed by such extrapolations is the impact of scale-up or scale-down of a catalytic converter, i.e., what happens if the overall size (diameter) of a catalytic converter is increased or decreased while keeping the channel dimensions unchanged? With a trend towards miniaturization of next-generation energy conversion devices, this is a critical question that needs to be answered by modeling and simulations in order to keep design costs low.

In recent years, in realization of the need to address variations of flow and temperature within the monolith of a catalytic converter, many research groups have attempted to model full-scale monolithic catalytic converters. Broadly, the approaches used can be categorized into two types. The first approach is one where the monolith is modeled as a porous medium, as is done traditionally for packed-bed reactors. The second approach is one where a “representative” number of channels within the monolith are modeled, and the results are coupled through thermal network-type models. Pertinent work using these two approaches is discussed next.

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Monolithic reactor was modeled as an anisotropic porous medium. Mazumder and Sengupta (2002) used a sub-step reaction and the catalytic monolith was modeled as a porous medium. The surface reaction model was used to identify the representative channels in a monolith. Two-dimensional, steady-state results of reactive flow in these representative channels were coupled with three-dimensional transient models of energy transport in the solid structure of the monolith. In their study, around 10 channels were chosen as representative channels.

While the two approaches, just discussed, represent improvement over modeling a single channel, the accuracy (in the case of the porous medium approach) and the numerical robustness (in the case of loose coupling using network models) of such approaches remains questionable. Ideally, it is desirable to model the entire monolithic catalytic converter using a CFD approach in which all pertinent length scales are resolved by the mesh, and no assumptions are made with regard to the relative magnitude of the length and times scales of the underlying physical and chemical processes.

Although CFD calculations with full implicit coupling between the various physical phenomena and length scales are desirable, from a numerical standpoint, such large-scale calculations pose several challenges. The core of a simple cylindrical catalytic converter is shown in Fig. 1. Estimates by Mazumder (2007) show that modeling such a converter with approximately 500 channels will require about 5 million grid points and more than 200 h of CPU time on a single processor even if a simple one-step reaction mechanism is used to describe the chemistry. Another challenge is keeping memory requirements within reasonable limits, so that such computations can be performed using desktop computers and/or parallel clusters with a few nodes, rather than supercomputers or massively parallel clusters.

The objective of the present study is to demonstrate the effectiveness of a new implicit coupled solver for such large-scale catalytic converter computations with complex heterogeneous chemistry. One of the key attributes of the solver to be demonstrated is that it solves all the species conservation equations simultaneously, rather than in a segregated manner. As demonstrated by past research (Mazumder, 2006; Venkateswaran & Olsen, 2003), coupled solution of the species conservation equations is

![Fig. 1. Monolithic core of a catalytic converter.](image-url)
desirable to attain robust and rapid convergence for reactive flow computations with complex chemistry and/or multi-component diffusion. To the best of the authors’ knowledge, the present article reports the first instance where CFD calculations with complete coupling between all relevant phenomena, and with resolution of all relevant length scales by the mesh has been performed for a full-scale catalytic converter with complex heterogeneous chemistry.

2. Governing equations and solution

2.1. Governing conservation equations

The governing equations to be solved are the equations of conservation of mass (both overall and individual species), momentum and energy, and are written as (Bird et al., 2001; Kuo, 1986; Mazumder, 2007):

- **Overall mass:**
  \[ \frac{\partial}{\partial t}(\rho) + \nabla \cdot (\rho \mathbf{U}) = 0 \]  
  (1)

- **Momentum:**
  \[ \frac{\partial}{\partial t}(\rho \mathbf{U}) + \nabla \cdot (\rho \mathbf{U} \mathbf{U}) = -\nabla p + \nabla \cdot \mathbf{T} + \rho \mathbf{B} \]  
  (2)

- **Energy:**
  \[ \frac{\partial}{\partial t}(\rho h) + \nabla \cdot (\rho \mathbf{U} h) = -\nabla \cdot \mathbf{q} + \dot{S}_h \]  
  (3)

where \( \mathbf{q} \) is the heat flux vector and \( \dot{S}_h \) is the rate of production of enthalpy. The species mass conservation equation is written as (Bird et al., 2001):

\[ \frac{\partial}{\partial t}(\rho X_k) + \nabla \cdot (\rho \mathbf{U} X_k) = -\nabla \cdot \mathbf{J}_k + \dot{S}_k \]  
  (4)

where \( X_k \) is the mole fraction of species \( k \) and \( \dot{S}_k \) is the rate of production of enthalpy due to homogeneous chemical reactions. The total mass of gas-phase species in the system is denoted by \( M \).

In a reacting flow, mass is always conserved while moles are not. Thus, it is advantageous to re-write Eq. (11) in terms of mass fractions rather than mole fractions. Using the conversion relation \( Y_k = X_k M_k / M \), Eq. (11) may be written as (Mazumder, 2006; Wangard, 2001, 2004, 2005):
The boundary conditions for the mass and momentum conservation equations are the no-slip conditions at walls, and appropriate mass flux or pressure boundary conditions at inflow and outflow boundaries. These boundary conditions and their numerical implementation are well known (Ferziger & Peric, 1999) and need no further discussion. The focus of this sub-section is the boundary conditions for species and energy associated with heterogeneous chemical reactions at fluid-solid interfaces.

At a reacting surface, the diffusion flux of species is balanced by the reaction flux since the surface cannot store any mass. At the heart of surface reaction processes is adsorption and desorption of species at the surface, the treatment of which requires inclusion of so-called surface-adsorbed species (Coltrin, Kee, & Rupley, 1991). At steady-state, the net production rate of the surface-adsorbed species is zero. In the absence of etching or deposition of material from the surface (i.e., zero Stefan flux), the reaction-diffusion balance equation at the surface may be written as (Coltrin et al., 1991; Mazumder & Lowry, 2001)

\[ \dot{R}_k = M_k \dot{R}_k \quad \forall k \in \text{gas-phase species} \]

where \( R_k \) is the molar production rate of species \( k \) due to heterogeneous chemical reactions, \( \dot{R}_k \) is the molar concentration of species \( k \) at the fluid–solid interface, and \( \dot{R}_k \) is the outward unit surface normal. Since \( \dot{R}_k \) is an extremely nonlinear function of the molar concentrations (or mass fractions) (Coltrin et al., 1991; Mazumder & Lowry, 2001), Eq. (17) represents a nonlinear set of differential algebraic equations (DAE). The solution of this stiff set of nonlinear DAE is generally obtained using the Newton method, but requires special pre-conditioning to address stiffness and ill-posed-ness in the case of steady-state solutions. Details pertaining to these numerical issues may be found elsewhere (Mazumder & Lowry, 2001). The solution of Eq. (17) provides the near-wall mass fractions and mass fluxes [represented by the left hand side of Eq. (17a)] of all gas-phase species, which appear as sources/sinks for control volumes adjacent to the surface in a finite-volume formulation (Mazumder & Lowry, 2001).

The balance of energy at the surface yields the following equation:

\[
- kVT + \dot{q}_R + \sum_{k=1}^{N} J_k h_k \cdot \hat{n} = -kVT + \dot{q}_R \hat{n} \cdot \hat{n}
\]

where the subscript ‘F’ denotes quantities on the fluid side of the fluid–solid interface, while the subscript ‘S’ denotes quantities on the solid side of the same interface. The solution of Eq. (18), which is also a nonlinear equation, yields the temperature at the fluid–solid interface, and subsequently provides the flux of energy at the interface, which can then be used as a source/sink for the cells adjacent to the interface after appropriate linearization. In this enthalpy formulation, the heat of surface reaction actually manifests itself through the sum \( \sum J_k h_k \) term.

Eqs. (1)–(4), along with Eq. (16), when solved along with the appropriate boundary conditions described in the preceding sub-section, will produce flow, temperature and mass fraction distributions of all species within the computational domain. In the present study, the equations were discretized using the standard conservative unstructured finite-volume procedure (Date, 2005; Mathur & Murthy, 1997), which is well documented in the literature and is, in fact, in use in the vast majority of commercial CFD codes.

2.2. Boundary conditions

The formulation for the multi-component diffusion model can be attained with a small fraction of the computational cost incurred by the multi-component diffusion model (Eq.(12)). Further details on both models are available in Kumar and Mazumder (2008).

2.3. Solution of governing equations

Since our primary interest is in low-speed reacting flow applications, a pressure-based solver was chosen (over a density-based solver) and developed for solution of the Navier–Stokes equations. The SIMPLEC algorithm (Van Doormal & Raithby, 1984) was used to resolve velocity–pressure coupling. A co-located mesh was
used, and the pressure-weighted interpolation method (Miller & Schmidt, 1988; Rhie & Chow, 1983) was used to damp checkerboard pressure oscillations. The species equation solver was kept separate from solution of the Navier–Stokes and energy equations. The momentum equations, the pressure correction equation, and the enthalpy equation (in correction form) were solved in a segregated manner using full-field conjugate gradient (for momentum and energy equations) and algebraic multi-grid (for pressure correction equation) solvers. For simplicity, heat transfer by radiation is neglected. Overall outer iterations were performed to couple all the conservation equations, and to address non-linearities in the governing equations, which were all solved in appropriate linearized form.

The species conservation equations were solved in a coupled manner. As discussed earlier, this is desirable from the point of view of numerical stability and convergence. The approach used here was to sub-divide the computational domain into sub-domains that are small enough such that for each of these sub-domains a fully implicit solution of the governing equations is affordable from a memory standpoint. The rationale is that this approach will enable spatial as well as species-to-species implicit coupling, and the extent of spatial coupling is to be dictated by memory constraints.

The development of the coupled solver for the species conservation equations entailed three major steps, as follows:

1. The computational domain was decomposed into smaller groups of cells that are geometrically contiguous—a process termed Internal Domain Decomposition (IDD). This is a one-time preprocessing step.

2. For each sub-domain, an iterative solver based on Krylov subspace iterations (i.e., the restarted and pre-conditioned Generalized Minimum Residual Solver or GMRES (Saad, 2003)) were employed to obtain the solution at all nodes within the sub-domain and for all species simultaneously. Other sub-domains adjacent to the sub-domain in question were treated explicitly, and ghost (or virtual) boundary conditions were applied at interfaces between sub-domains to transfer information between sub-domains.

3. An overall (or outer) iteration was performed within which the preceding step is repeated until convergence. Iterations are necessary not only to resolve the explicit coupling between sub-domains, but also to resolve non-linearities in the governing equations.

The overall algorithm is depicted in Fig. 2, and details pertaining to each of the above three steps may be obtained from Kumar and Mazumder (2007, submitted for publication). The coupled species equation solver is henceforth referred to as the IDD + GMRES solver.

2.4. Solver parallelization

Parallelization of the solver was performed to enable calculations on a larger scale by dividing the computational load across multiple processors. It also keeps the memory requirement for each processor tractable. The computational domain was divided into various zones using domain decomposition. Two different decomposition strategies were implemented: (a) multi-graph-based partitioning algorithm METIS (Karypis & Kumar, 1998), and (b) domain partitioning along predefined axes \((x, y \text{ or } z)\) axes. The number of parallel zones and the number of processors have to be equal in both cases.

If there are \(N_z\) parallel zones (and hence \(N_z\) processors), there will be \(N_z\) cells in the \(i\)-th parallel zone. All data (connectivity data, geometry data, values of variables at cell centers, and all other data needed for CFD calculations) on those \(N_G\) cells is stored on the \(i\)-th processor. In addition to the cells in the \(i\)-th parallel zone, ghost cells from the neighbors of the \(i\)-th zone are also mapped to the \(i\)-th processor. Therefore, a particular processor stores the data of the cells in its own zone as well the data of the ghost cells from all its neighboring zones. However, a given processor solves for the variables only in the \(N_G\) cells belonging to the corresponding parallel zone. Computations of variables in the ghost cells are performed by the neighboring processors. Since data in the ghost cells are needed to discretize governing equations at the zonal boundaries, data is exchanged between neighboring processes. The Message Passing Interface (MPI\textsuperscript{TM}) based communication strategy was used for exchange of data between different processors. The frequency of MPI communication calls between neighboring processes is an important parameter to consider. Values in the ghost cells are the only mode of exchange of information between various parallel zones. In any CFD calculation, it is beneficial to have as much implicitness as possible in the solution procedure. It is well recognized that the lack of implicitness can lead the solution to stagnate for steady-state calculations. In terms of the use of the IDD + GMRES solver, the zonal interfaces are treated as a Dirichlet boundary condition with the values in the ghost cell treated as known from the previous iteration. One parallel zone is typically divided into multiple sub-domains within the IDD + GMRES solver. All sub-domains in a given parallel zone are solved sequentially within the IDD + GMRES algorithm. Since different parallel zones are solved independent of each other using different processes, it is possible that a sub-domain \(S_1\) in zone \(i\) is solved after sub-domain \(S_2\) in zone \(j\). If sub-domains \(S_1\) and \(S_2\) are neighbors too, then updating the values in ghost cells after \(S_2\) has been solved for, leads to latest zonal boundary information being used in solution of sub-domain \(S_1\). Use of the latest results instead of results from previous iteration increases the implicitness and improves the convergence behavior. Recognizing this fact, values in the ghost cells were exchanged each time a sub-domain solution is performed in any of the parallel zones. This algorithm maximizes the chance of implicitness in the solution procedure and has been implemented for the parallel version of the IDD + GMRES solver.

3. Sample calculations and results

Prior to exploration of the solver for large-scale catalytic conversion simulations, it was validated against results reported by Raja et al. (2000), and then tested for 5 different problems with either homogeneous or heterogeneous chemistry of various levels of com-
plexity. Both two-dimensional and three-dimensional test cases were considered, with mesh sizes ranging from 20,000 to 80,000 cells. In all cases, robust convergence was attained. A full description of these relatively simple test cases and their results may be found in Kumar and Mazumder (2007, submitted for publication).

In this study, three test cases, directly related to the application in question, are considered:

- **Case 1**: heterogeneous (catalytic) combustion of methane using 24-step chemistry (8 gas-phase species) in a 3D catalytic converter comprised of 57 channels with 354,300 mixed (hexahedra and prisms) cells.
- **Case 2**: heterogeneous three-way catalytic conversion using 61-step chemistry (8 gas-phase species) in a 3D catalytic converter comprised of 57 channels with 354,300 mixed (hexahedra and prisms) cells.
- **Case 3**: heterogeneous (catalytic) combustion of methane using 24-step chemistry (8 gas-phase species) in a 3D catalytic converter comprised of 293 channels with 1.27 million mixed (hexahedra and prisms) cells.

The first two cases were computed on a single processor (2 GHz Intel Xeon 5130 processor with 4 GB of RAM) machine, while the third case was computed on a 4-node parallel cluster with each node having exact same specifications as the single processor mentioned above. In each case, convergence was deemed to have been attained when the residuals ($L_2$norm) of all the conservation equations decreased by 5 orders of magnitude.

### 3.1. Case 1: catalytic combustion of methane in 57-channel converter

The first test case considered is that of steady-state heterogeneous (catalytic) combustion of a premixed methane–air mixture on platinum in a catalytic converter monolith with multiple channels. A cylindrical monolith with diameter of 1.84 cm and length 10 cm is considered. The monolith geometry has two planes of symmetry and therefore only a quarter of the device is modeled. The geometry, mesh, and boundary conditions are shown in Fig. 3. The channels have a square cross-section of dimension $1.6 \times 1.6$ mm. Channel walls have a thickness of 0.4 mm. As shown in Fig. 3, 19 channels are modeled, implying a catalytic reactor with 57 total channels, corresponding to a channel density of 140 cpsi. The monolith support in many catalytic monoliths is made of cordierite. Thermal conductivity of cordierite has been reported in the range of 2–5 W/(m K) (Lynch, 1975). A value of 5 W/(m K) is used as the thermal conductivity of the monolith solid support in the present study. The inlet gas temperature is 400 K, and the external walls of the converter are fixed at 1300 K, following simulation conditions used by Raja et al. (2000). The Reynolds number based on the channel width is 130 (corresponding to a velocity of 0.9 m/s at the inlet), and the inlet equivalence ratio is unity, yielding the following mass fractions of the various species at the inlet: $CH_4 = 0.05$, $H_2 = 0.001$, $O_2 = 0.215$, $N_2 = 0.734$. The reaction mechanism used for this test calculation is a 24-step reaction mechanism (Deutschmann, Behrendt, & Warnatz, 1994). This particular mechanism has been validated and widely used for hydrogen-assisted catalytic combustion of methane (Deutschmann et al., 2000). A value of $2.7 \times 10^{-8}$ kmol/m² has been used for the surface site density, which is the value used in the literature when platinum is the catalyst dispersed in alumina washcoat for a catalytic loading of 40 g/ft³ (Deutschmann et al., 2000). The computational mesh is comprised of 354,300 cells, leading to approximately 4.6 million unknowns (pressure, 3 velocity components, enthalpy, and 8 gas-phase species at each node). The two-dimensional mesh of the cross-section of the converter is shown in Fig. 3(b). When extruded in the third direction, it results in a hybrid mesh comprised of hexahedral and prismatic elements.

For this particular test case, computations were performed with the new IDD + GMRES solver on a single processor. The convergence plot obtained using the IDD + GMRES solver is shown in Fig. 4. It is clear from the convergence plot that despite the large number of unknowns and the complexity of the chemistry, the convergence
is robust. The convergence of the enthalpy equation is the slowest. This is most likely because conjugate heat transfer is accounted for, and the disparate thermal conductivity of the fluid and the solid results in a relatively stiff system of equations. Results of the computations are shown in Fig. 5. Even though the same mass flow rate and inlet temperature are used in each channel, the results clearly depict the effect of external heat transfer on temperature and species concentration distributions, both of which are strongly non-uniform. These results clearly emphasize the importance of full-scale simulations. Overall, this particular calculation required 19 h of CPU time for five orders of magnitude convergence. The solver required 900 MB of memory.

To put matters in perspective, it is worthwhile comparing the results of these calculations with another state-of-the-art fully implicit reacting flow solver, MPSalsa (Shadid et al., 1998). MPSalsa is general-purpose implicit finite-element code for reacting flow applications (Shadid et al., 1998; Shadid, Tuminaro, Devine, Hennigan, & Lin, 2005). It uses an inexact Newton iteration technique in conjunction with a parallel GMRES solver to solve the final discrete algebraic equations. Due to the fact that the coupling between the unknowns is attained through Newton-type iterations, the method requires calculation and storage of a Jacobian matrix, at least partially. Thus, computations using this method require large amounts of memory. For example, a chemical vapor deposition reactor was modeled with just 3 chemical species (i.e., a total of 8 unknowns at each node: 3 velocity components, temperature, pressure, and 3 mass fractions) on a fine mesh, resulting in a total of 4.8 million unknowns. Computations were performed on a 64-node parallel cluster (each node was a 3 GHz Intel Pentium IV processor) and required about 2200 s of CPU time. Even if linear parallel scaling (best case scenario) is considered, this implies that such computations would require about 140,000 s (≈39 h) on a single processor. In contrast, the present calculation with 4.6 million unknowns required 19 h of CPU on a comparable single processor. With single-step chemistry described by 5 species, the same computation takes only 6 h with the IDD + GMRES solver. While the two problems solved by the two solvers are not the same, it appears that the solver used in the present study is not only significantly more memory efficient, but also computationally more efficient than existing state-of-the-art reacting flow solvers.

3.2. Case 2: three-way catalytic conversion in 57-channel converter

The second test case considered is that of steady-state three-way catalytic conversion of combustion exhaust products in a catalytic converter monolith with multiple channels. The geometry used in this case is the same as the first test case. The inlet temperature is 400 K, and the external walls of the converter are fixed at 700 K, in keeping with typical temperatures for such processes (Brinkmeier, 2006). The Reynolds number based on the channel width is 130. The composition of the inlet mixture corresponds to combustion of a stoichiometric air–gasoline mixture as measured experimentally (Brinkmeier, 2006), yielding the following mass fractions of the various species at the inlet: \( \text{C}_3\text{H}_6 = 6.74 \times 10^{-4}, \ \text{CO} = 0.0142, \ \text{NO} = 0.00107, \ \text{O}_2 = 0.00879, \ \text{and N}_2 = 0.975266 \). Propene \((\text{C}_3\text{H}_6)\) is considered as the representative unburnt hydrocarbon in this case because it is usually the final product that results from the thermal decomposition of larger hydrocarbon molecules (Braun et al., 2002; Chatterjee et al., 2001). Oxidation of carbon monoxide and propene, and reduction of nitric oxide is modeled using a 61-step reaction mechanism (Chatterjee et al., 2001). This mechanism considers a total of 31 chemical species, including 23 surface-adsorbed species and 8 gas-phase species. Surface reactions are considered on two kinds of catalytic surface reaction sites, Platinum (Pt) sites and Rhodium (Rh) sites. The reaction mechanism consists of three parts, namely a mechanism for oxidation of propene on Pt, a mechanism for reduction of NO on Pt, and a mechanism for NO reduction and CO oxidation on Rh. The catalyst loading is taken from literature as 50 g/ft\(^3\), with Pt and Rh being mixed in the weight ratio 5:1. Using the data from literature, the ratio of platinum and rhodium surface areas is taken to be 3:1 for a weight ratio 5:1. A value equal to \( 2.72 \times 10^{-8} \) kmol/m\(^2\) has been used for the overall surface site density, which is the value used in the literature when Pt/Rh is the catalyst dispersed in alumina washcoat (Chatterjee et al., 2001).
For this particular test case also, computations were performed with the new IDD + GMRES solver on a single processor. The convergence plot obtained using the IDD + GMRES solver is shown in Fig. 6. Once again, robust convergence is observed, although it is somewhat slower than the catalytic combustion case because of the additional complexity of the surface reaction mechanism in this particular case. Results of the computations are shown in Fig. 7. The results, once again, clearly depict non-uniformities from channel to channel, emphasizing the importance of full-scale simulations. Overall, this particular calculation required 156 h of CPU time for five orders of magnitude convergence. The solver required 1 GB of memory.

A comparison of the two test cases, just described, reveals that the second test case (catalytic three-way conversion) requires about 8 times more CPU time than the first test case (catalytic combustion), even though the same number of conservation equations (≈13) are solved in each case on the same mesh. Further examination of this issue revealed that the complexity of the surface reaction mechanism used in the second test case is responsible for this discrepancy. The second test case uses a 61-step reaction mechanism with 31 species, while the first test case uses a 24-step mechanism with 19 species. Careful examination of the CPU budget revealed that about 80% of the total CPU time is spent in surface reaction calculations for the second test case, i.e., in solving Eq. (17). As mentioned earlier, Eq. (17) represents a system of stiff non-linear differential algebraic equations, whose solution is numerically challenging. When the number of species is large, the solution of this equation is also very computationally expensive because it has to be performed for all reacting boundary faces and at each outer iteration.

3.3. Case 3: catalytic combustion of methane in 293-channel converter

The third test case considered is identical to the first test case, except that the geometry used is much larger: 293 channels are sim-
ulated rather than 57 channels. The physical conditions considered in this case are identical to that of the first test case. Since the geometry considered in this case is much larger than the first test case, and the first test case already required 900 MB of memory, this particular case was solved on a 4-node parallel cluster. The geometry (including zonal partitions), boundary conditions, and the computational mesh are depicted in Fig. 8. The whole computational domain has 1.272 million cells, and considering that there are 13 unknowns on each cell, there are a total of 16.5 million unknowns. Computations were performed on a 4-node parallel cluster, each node being an Intel Xeon 5130 processor. Zonal interfaces of the four zones can be clearly seen in Fig. 8. Each zone has roughly 318,000 cells, which is approximately the same number of cells that were present in the geometry considered for the first test case. The calculation converged in approximately 24 h and 1867 iterations (Fig. 9),
representing approximately 80% parallel efficiency. The physical results are shown in Fig. 10. In this case, the core of the converter has a more uniform temperature than the smaller converter simulated earlier (Case 1) because the surface-to-volume ratio is larger for the smaller converter, implying relatively more heat loss to the ambient. The effect of scaling of the catalytic converter (Case 1 vs. Case 3) is best understood by comparing the species concentration profiles in Figs. 5 and 10. In the larger converter (Case 3), CH$_4$ is depleted more in the central core than in the small converter (Case 1), indicated by the fact that in the larger converter, only one shade of blue is seen in the central core (Fig. 10), while two shades of blue are observed in the central core for the smaller converter (Fig. 5). Similarly, more CO$_2$ is produced in the central core of the larger converter, as indicated by the saturated pink color (Fig. 10), while two shades of pink are observed in the central core for the smaller converter (Fig. 5). Post-processing of the results in the two cases further indicates that the conversion fraction in the larger converter is 91%, as opposed to 86% in the smaller converter. These results emphasize not only the importance of performing full-scale simulations to understand non-uniformity effects, but also the fact that these simulations clearly delineate the impact of scaling of the overall converter size.

4. Summary and conclusions

Computational analysis of full-scale catalytic monolithic reactors is necessary to capture thermal and flow non-uniformity effects on the overall performance of the device. Such modeling is also vital for understanding scale-up or scale-down issues. To date, modeling of full-scale catalytic converters has been pursued using two approaches. The first approach is one where the monolith is modeled as a porous medium. The second approach couples detailed transport-chemistry models within a few representative channels to a three-dimensional thermal model. Both approaches have serious shortcomings. The first approach is not always accurate and requires calibration of several free parameters (Mazumder et al., 2002), while the second approach is not always robust. To the best of the authors’ knowledge, this article represents the first successful attempt at computational fluid dynamics (CFD) calculations of full-scale catalytic converters with complex chemistry. In this approach, all relevant length scales are resolved by the mesh, and two-way implicit coupling between fluid flow, heat transfer, mass transfer, and heterogeneous chemical reactions is manifested. Although the number of channels considered here (~100) are representative of laboratory-scale catalytic converters, the methodology presented and demonstrated here is directly applicable to truly full-scale catalytic converters with ~1000 channels if a larger parallel cluster with more compute nodes is utilized. With modern-day multi-core processors, such simulations, as shown here, are quite feasible.

A new coupled implicit solver for the species transport equations that solves the species conservation equations in a coupled (rather than segregated) manner was developed and coupled to the flow and energy equation solver. The overall simulation tool was then used to solve three test problems, namely catalytic combustion of methane in a 57-channel catalytic converter, three-way conversion of an automotive exhaust stream in a 57-channel converter, and catalytic combustion of methane in a 293-channel converter. The first and third test cases employed a 24-step reaction mechanism with 19 species, while the second test case employed a 61-step reaction mechanism with 31 species. The first two cases were solved on a mesh comprised of 354,300 cells (4.6 million unknowns) on a single processor, while the third case was solved on a mesh comprised of 1.27 million cells (16.5 million unknowns) on a 4-node parallel cluster. In each case, robust convergence was attained. Comparison of the performance of the solver to comparable state-of-art solvers, including available commercial codes, revealed that the solver is superior both from a memory as well as efficiency standpoint—sometimes by more than one order of magnitude. While preliminary, the results presented here clearly demonstrate the feasibility of using direct numerical simulation of laboratory-scale catalytic converters with realistic chemistry.

Future work will be directed towards enhancing the efficiency of the core solver using better pre-conditioning techniques, multi-grid techniques, and better approaches for parallelization, which will be necessary for simulation of full-scale catalytic converters with ~1000 channels. One of the findings of this study is that the CPU time taken for such calculations is strongly dictated by the complexity of the reaction mechanism used (specifically, the number of reaction steps and species). Work is already ongoing in adapting the In Situ Adaptive Tabulation (ISAT) algorithm (Pope, 1997) for surface chemistry. While some preliminary work has been done in this direction (Mazumder, 2005), coupling of ISAT for surface chemistry with the current Chemistry is still incomplete, and is currently being pursued. Once the chemistry calculations have been accelerated, efforts will also be directed towards performing unsteady calculations for fundamental understanding of phenomena such as ignition and blowout. While the approach presented here is directly applicable to unsteady simulations, refinements, such as adaptive time-stepping, will be necessary to capture a large spectrum of time-scales. Further, unsteady simulations will generate a large quantity of data, and effective post-processing techniques will be necessary to extract relevant information from this large volume of data. When all these pieces of the puzzle are finally in place, it should be possible to simulate truly industrial-scale catalytic converters with complex chemistry using direct CFD analysis rather than approximate or loosely coupled methods.

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References


