ACCURATE PREDICTIONS OF CHEMICAL PHENOMENA IN CHEMICALLY REACTING FLOWS

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Abstract. In the past decade, the computational fluid dynamics (CFD) community has put increasing attention on incorporating complex chemistry and physics into CFD simulations. However, for many practicing engineers today there is still much lacking in the effectiveness of reacting-flow simulation. Particularly in the area of combustion, the results can often be either too time consuming, or still too inaccurate to provide practical solutions for applications where chemistry details are critical.

There are important alternatives to forcing such detailed phenomena directly into CFD. Such alternatives leverage CFD advances but also provide more effective and more accurate chemistry capabilities. These approaches build on reduced-geometry models that provide higher fidelity chemistry predictions, while establishing indirect coupling to the transport environment that is well predicted by CFD. The solvers employed in reduced-order models easily handle large chemistry reaction mechanisms and accurately resolve both trace and major species over disparate time scales. Links to CFD can be established through determination of zonal mapping to equivalent reactor networks or through table look-up methods.

Central to these hybrid approaches is the continued advancement of the chemistry accuracy provided by reduced-order models. One area of particular importance is the combustion of large hydrocarbon fuel molecules that results in soot-particle formation. Presented here is a new capability for tracking the formation and destruction of particles dispersed in a gas flow. This capability has been incorporated into models for batch, perfectly stirred, plug-flow, and shear-layer flow reactors. A key advance is the incorporation of general, detailed surface kinetics in the description of particle growth and oxidation processes, together with polyaromatic hydrocarbon (PAH) condensation and particle coagulation. This capability allows kineticists flexibility in hypothesizing and testing competing reaction pathways to more accurately capture the particle-formation process. The implementation in reduced-order models further allows discrimination of important reaction and transport processes and, through comparisons with well controlled experiments, allows testing and verification of competing pathways in a more systematic way than previously possible.
1 INTRODUCTION

For a broad spectrum of industries, including energy, automotive, microelectronics, chemicals, and materials processing, there is an increasing need for more chemistry and physics details in fluid systems. This is in part driven by requirements to reduce emissions and unwanted byproducts under environmental regulations, and in part due to increasing global competition in manufacturing that involves progressively more complex requirements. Emissions can be reduced through abatement, by improvements in process efficiency, or by substitution of lower-emission processes. Simulation can play an important role in all three approaches, provided that there is sufficient knowledge of the chemistry involved. Simulation can also play a key role in improving product performance or yield and in reducing product-development time, when the simulation is sufficiently accurate to adequately address the chemistry-intensive processes.

There are several ways that researchers and commercial-simulation-tool developers have been approaching the need for more accurate chemistry capability in engineering simulations. These include: direct-coupling approaches, where all fluid species considered are transported through solution of a species equation in the CFD simulation; table-lookup methods that attempt to reduce real-time calculations using database storage and access of cell-by-cell results;\(^1\) and flamelet-table methods that try to account for sub-grid-scale phenomena using extraction from a database built by 1-D flame simulations.\(^2,3\) These approaches have had mixed results from the perspective of the engineer attempting to use such simulation in practical design and process-development applications. The main detractors are (1) the long computational time required to transport additional species within the CFD simulation or to build appropriately accurate tables and (2) a great confusion about the accuracy or pitfalls of various methods for handling “turbulence-kinetics” interactions (the accounting of effects on kinetics of sub-grid-scale transport phenomena), and (3) the inadequacy of reduced or global reaction mechanisms that must often be used. Nonetheless, these approaches represent important advances.

Direct coupling of detailed gas and gas-surface chemistry with CFD has been achieved through the commercial product, KINetics,\(^4\) which is available for use with STAR-CD\(^5\) and FLUENT,\(^6\) and through many of the “stiff solvers” recently made available through the native offerings of several CFD vendors (e.g., CD adapco Group, ESI Group, and Fluent, Inc.). This direct coupling approach typically uses a combination of operator-splitting methods in the transport steps and cell-by-cell solution of the kinetics with a stiff-chemistry solver for transient or time-stepping simulations. For steady-state simulation, the KINetics module also incorporates a more sophisticated direct coupling that involves iteration with alternating levels of implicitness for transport and kinetics terms, which provides more computationally efficient simulation compared to pseudo-time-stepping methods.\(^3\) These direct-coupling approaches have been most successfully applied to applications where the size of the appropriate elementary gas-phase chemistry mechanism is relatively small (<50 species), and where kinetics rate limitations dominate the process or where the flow is predominantly laminar. Applications that fit these criteria include chemical vapor deposition (CVD) or atomic-layer deposition (ALD) for materials processing, surface catalytic conversion for
automotive exhaust-gas treatment, as well as laminar-flame studies for small hydrocarbon fuels. Applications driven by surface chemistry can be particularly well treated, because the additional burden of very detailed kinetics on the surface does not cause a great computational burden for the transported species in the fluid phase. However, even for these cases, close attention must be paid to the grid resolution when sharp chemistry-induced gradients are present.

For turbulent combustion flows, such as industrial burners, gas-turbine combustors, or internal combustion engines, this use of elementary kinetics in the gas-phase is still not practicably feasible in CFD when realistic representations of both fuel and geometry are necessary. In these cases, there is increasing emphasis on methods that provide indirect coupling between chemistry-reduced CFD models and geometry-reduced chemistry models. Recent work at the Institut Français du Pétrol, for example, demonstrates a table-lookup method applied to homogeneous-charge compression-ignition and diesel engine-ignition calculations. The CFD simulation solves for one or two auto-ignition delay progress variables and then extracts ignition-delay times from a database generated by a closed-homogeneous reactor model. The advantage of this database-lookup method is that the database can be generated using any level of detail in the gas-phase chemistry (100s of species and 1000s of reactions), although in this case it is limited in application to the specific application of ignition timing.

Another approach applied to large industrial-scale combustion systems uses a combination of CFD simulation to capture geometric details, and an equivalent reactor network to then calculate chemistry details. Here the reactor networks consist of large sets of idealized-flow zones connected through mass and energy flow streams but including elementary kinetics descriptions of the combustion and pollutant-formation chemistry. The equivalent reactor networks have been shown to provide good predictions of NOx concentrations, as well as other pollutants, for glass furnaces, biomass combustors, coal combustors and gas turbine combustors. A number of published studies have consistently achieved NOx predictions within 10% of measurements spanning the range 50-600 ppm. Unlike other approaches, predictions from reactor networks do not require “recalibration” to handle changes in fuel composition, stoichiometric ratio or operating conditions. In addition, several researchers have demonstrated that the equivalent reactor networks can be auto-generated from the CFD results, where a much simpler combustion model is included, using flow-field, temperature, and fuel/oxidizer stoichiometry information from the CFD simulation. In this way, the CFD + equivalent reactor networks simulations can be used to evaluate the results of design and operation changes on pollutant formation.

Both the table-lookup and the reactor-network approaches build on reduced-geometry or reduced-transport models. Examples of such models range from the simplest chemical-equilibrium model, to a kinetically detailed closed-homogeneous or stirred-reactor model, to 1-D models based on similarity transformations of a 3-dimensional flowfield. The basic premise of such methods is that the reduced-geometry models are accurate with respect to the chemistry details, within the constraints of the model assumptions and approximations. This paper explores issues that must be addressed in assuring accurate chemistry solutions and highlights recent advances that improve simulation accuracy and robustness for the specific
2 REQUIREMENTS FOR ACCURATE KINETIC MODELS

CHEMKIN\textsuperscript{13} represents the most widely used collection of idealized-flow or reduced-geometry models, in which any level of chemistry detail may be included. Originally developed at Sandia National Laboratories, this product has been commercially supported and developed by Reaction Design since 1997. Figure 1 shows a screenshot from CHEMKIN 4.1, where the diagram on the right shows an example of a complex reactor network built from component reactor models (listed on the left panel of the user interface). Idealized-flow models have also been developed at several universities that provide similar functionality to some of the basic reactor components within CHEMKIN and that are popular in academic research.\textsuperscript{14,15} Criteria that must be met by such models to assure fidelity to the chemical kinetics are discussed below.

![Figure 1. Screenshot of CHEMKIN 4.1, showing reactor options and an example of a reactor-network diagram.](image)

2.1 Stiff Equation Solvers

Such idealized-flow simulations can be performed at a very small fraction of the computational time for a CFD simulation and with relatively quick user setup. At the same time, the simulations provide a higher level of accuracy for the chemical composition, as resolved in time and space, than would be possible with CFD even under the same
approximations and assumptions of the idealized flow. This is due to the use of transient solution algorithms that have two key features: (1) strict absolute and relative error-tolerance controls for all species in the system (abundant and trace) and (2) adaptive time (or distance) stepping that allows resolution of both extremely fast kinetics processes and slower transport processes. Examples of such transient solvers include the Differential Algebraic Equation solver family DASSL and DASPK, developed by Petzold, et al.\textsuperscript{16,17}

For steady-state solution, computationally efficient solution usually involves careful scaling of equations in the application of a modified Newton iteration algorithm, again with strict error-tolerance controls. In addition, for these iterative methods much computer savings can be achieved through gradual refinement of the problem. For example, a common method for resolving freely propagating flame fronts involves first solving a fixed temperature problem on a coarse grid and then, using this solution as the initial guess, adding the energy equation.\textsuperscript{18} Adaptive grid refinement is also important in making sure that gradients and curvatures of solution variables are properly resolved in the spatial dimension considered, even with extreme changes at flame-front locations or within surface boundary layers. The modified Newton-method solver that is used in the CHEMKIN framework is the TWOPNT solver, originally developed by Grcar.\textsuperscript{19}

2.2 Adaptive gridding and solver-step selection

It is well known that chemical kinetics give rise to “stiff” differential equations, due to the disparate time-scales of kinetics rates and transport processes, as well as to the range of species-concentrations that must be accurately resolved (sometimes ranging more than 9 orders of magnitude). However, it is important to realize that such temporal “stiffness” also often gives rise to spatial stiffness as well. In CFD, temporal stiffness can be handled to some extent through operator-splitting methods, where the chemistry step uses adaptive time-stepping as described above. However, the spatial stiffness is a bigger challenge for CFD, because it imposes severe adaptive-meshing requirements to resolve phenomena such as laminar flame fronts or “light-off” on catalytic surfaces.

A simple example of this is for a 3-way catalytic converter simulation, using the detailed mechanism reported by Chatterjee et al.\textsuperscript{20} A CHEMKIN simulation of the catalytic conversion for the fixed-temperature cases shows very sharp changes in surface site coverage, as shown in Figure 2. The CHEMKIN shear-layer flow model applies a fixed, non-uniform grid in the cross-flow direction and then marches down the channel, neglecting diffusion in the axial direction. The marching algorithm uses a variant of the DASSL transient solver,\textsuperscript{17} which dynamically selects an appropriate step size to maintain the error control and capture the local gradients. In this way, the smallest step size may be eight or nine orders of magnitude smaller than the largest step size. Performing the same simulation with a FLUENT/KINetics,\textsuperscript{6} results in similar predictions, but the gradients can not be as accurately resolved. Figure 3 shows a comparison for the CO conversion in one case, with a uniform mesh as well as with a mesh that has been subsequently adaptively refined. The adaptive refinement brings the CFD solution closer to the CHEMKIN solution, but much more adaptation would be required for exact agreement. When first viewing the differences, one
might be tempted to assume that the differences were due to the idealized-flow model neglecting axial diffusion. However, for these flow conditions (Peclet number > 10), this is not a significant effect. Thus, while CFD simulation can be important in verifying the model approximations and in exploring effects of non-ideal geometries, it is important to recognize what aspects of CFD are inherently accurate and what are not.

Figure 2. Surface site fractions as a function of distance in a three-way catalytic converter

Figure 3. CO profile predicted by CHEMKIN Shear-flow Reactor, compared with FLUENT/KINetics, for a three-way catalytic converter.
2.3 Kinetics data

Using the right chemical kinetics mechanism is critical to accurate predictions in chemically reacting flow simulation. By “mechanism”, we refer to the set of species, reaction paths, reaction-rate coefficients, thermodynamic data, and transport-property data that describe the reacting, multi-component system. However, deciding what is “right” and finding appropriate data is often a huge challenge for engineers performing the simulations. In many cases, the details of the kinetics behavior are still a subject of research. In other cases, there are competing reaction mechanisms reported by researchers using different nomenclatures that are difficult for the non-kineticist to decipher. Particularly in the area of surface chemistry, there is often a dearth of detailed data, forcing the use of empirically derived rate expressions. Nonetheless, the past few decades have seen a steady progression in the knowledge base available for chemical kinetics, in the reduction of the level of expertise required to use computational chemistry methods, and in the ability to automate mechanism generation for new sets of reactants. This progress ensures that those of us involved in reacting-flow simulations will continue to be challenged in the handling of ever-more detailed mechanisms, despite the concurrent increase in available computer power.

For gas-phase reactions, automatic generation of reaction paths and reaction-rate coefficients is becoming increasingly viable. Mechanism-generation schemes rely on a broad range of rule-based algorithms, such as group-additivity methods, as well as the use of more advanced computational chemistry methods. While these methods are very promising in their ability to shorten the development time of mechanisms for reactants that have not been previously studied, such automated schemes tend to generate very large reaction sets. Making these results more useful to the end user will require tools that can help remove extraneous reactions for particular conditions of interest and that will facilitate more systematic validation and comparison of the resulting mechanisms. To this end, there are several efforts underway to populate, validate, and manage comprehensive databases of reaction mechanisms for combustion of fuel surrogates, driven by both government and industry initiatives.

There are similar trends towards more detailed and fundamental treatment of the microkinetics associated with surface-catalyzed processes, with a focus on partial oxidation on rare-metal catalysts for use in chemical processing and exhaust after-treatment. These studies show the predictive advantages of including more detailed kinetics description, such as surface-site competition and coverage-dependent reaction rates. Such approach to surface chemistry has long been popular in the study of chemical vapor deposition in materials processing. In the area of metal catalysts, rule-based methods such as bond-order-conservation are facilitating more automated determination of reaction mechanisms for catalyzed systems.

Advances in kinetics understanding also require reacting-flow simulation tools to handle more complex reaction types. For gas-phase systems, more advanced methods of handling pressure-dependence for multiple-well, multiple-channel reactions are necessary. For surface chemistry, the lack of fundamental understanding creates the need to provide flexibility between empirically derived rates, such as Langmuir-Hinshelwood or Eley-Rideal
lumped-kinetics expressions, as well as detailed, site-specific treatments. Recent work at MIT\textsuperscript{32} demonstrated the importance of maintaining thermodynamic consistency for surface species, requiring the implementation of a heat-of-formation dependence of adsorbed surface species on local site coverage. All of these advances have been recently incorporated into the CHEMKIN software,\textsuperscript{13} to allow continued evaluation and testing of the state-of-the-art chemistry descriptions.

In addition to reaction rates, the accuracy of a chemically reacting flow simulation often depends on the accuracy of the molecular transport in the multicomponent system. This is true for molecular-diffusion-dominated systems (such as laminar diffusion flames) and for regions where transport through a laminar boundary-layer becomes rate-limiting. In such cases, the treatment of a many-species system requires transport properties that are dynamically determined based on local composition and temperatures, that strictly conserve mass, and that account for non-dilute as well as dilute conditions. CHEMKIN transport-property formulations, which were derived from the original work of Dixon-Lewis,\textsuperscript{33} have long represented the state-of-the-art in this area. Paul and Warnatz\textsuperscript{34} advocated a refinement of this approach, although the modest accuracy improvement (~10\% for a flame-speed calculation) was undermined by the need for additional molecular data for each molecule in the system. However, their work served to highlight the need to improve on the fundamental molecular data used in the transport calculations for some systems.

While chemical-kinetics knowledge grows, so do the challenges for handling large elementary mechanisms, even for idealized-flow models. For one-dimensional flame simulations, for example, the use of a mechanism that contains several hundreds of species and many thousands of reactions can easily push the memory requirements to a point where 64-bit indexing is required. This means that there is a continued need to advance the reduced-order models in terms of solution algorithm, memory management, and performance, especially as these models are the work horses in most mechanism-reductions techniques.

4 ADVANCED PARTICLE SIZE TRACKING WITH DETAILED KINETICS

Idealized-flow models continue to serve as a vehicle for developing and testing more comprehensive mechanisms for describing chemically reacting systems. An area of particular industrial importance today is the determination of soot particle formation during and after combustion processes for large hydrocarbon fuels. Development of soot-reduction strategies requires knowledge of how the total mass and size-distributions of soot particles correlate to the operating conditions in the combustion system.

Reaction Design has recently added a new capability for tracking the formation and destruction of particles dispersed in a gas flow. This module has been incorporated into CHEMKIN models for closed homogeneous systems, perfectly stirred reactors, plug-flow reactors, and shear-layer flow reactors.\textsuperscript{13} The particle size-distribution tracking method\textsuperscript{35} builds from the moment method reported by others.\textsuperscript{36-38} It has been extended to allow robust and computationally efficient simulation in both steady-state and transient systems and to accommodate full control by the user over the competing reactions and physical processes considered. In addition, the implementation takes advantage of the general surface-kinetics
capability offered in CHEMKIN to facilitate specification of growth and reduction kinetics on an elementary and site-specific basis. The concept of a “nucleation reaction” is introduced, which allows transition between growth of soot precursors in the gas and the tracking of condensed, dispersed particles on which surface chemistry takes place.

4.1 Particle nucleation from gas-phase species

One of the innovations of the particle-tracking module is the introduction of the nucleation reaction as a special type of gas-surface reaction. The nucleation reaction serves to create bulk and surface species from gas-phase precursors and to set the stage for surface reactions to play a role by creating surface area. The new reaction type is offered as one of CHEMKIN’s surface-chemistry reaction options. Using this formulation, soot nuclei may be generated by collisions between two polyaromatic hydrocarbon species (PAHs), such that the nucleation rate is proportional to the PAH collision frequency. A prototype for such a reaction is shown in Eq. (1).

\[ \text{PAH} + \text{PAH} \rightarrow \sigma_c \text{C(B)} + \sigma_{\text{H}} \text{H(s)} + \sigma_{\text{op}} \text{open(s)} \]  

(1)

Here (s) denotes a surface species and C(B) represents the composition of the soot particle (in this case pure carbon). In this reaction, it is necessary to account for the initial surface state of the newly formed condensed particle. The factors \( \sigma_{\text{H}} \) and \( \sigma_{\text{op}} \) represent stoichiometric coefficients for an H-adsorbed surface site and an open, reactive site, respectively. These terms allow the reaction to be balanced in mass and elements, and also allow the initial surface state to be chemically related to the PAH composition. The factor \( \sigma_c \) determines the initial particle size or “class”, which is simply the number of carbon atoms in the nucleated particle. This process is irreversible and need not conserve surface sites. More than one nucleation reaction can be included for a given condensate.

For example, a soot particle created by dimerization of pyrene can be expressed by the surface reaction given in Eq. (2).

\[ \text{C}_{16}\text{H}_{10} + \text{C}_{16}\text{H}_{10} \Rightarrow 32 \text{C(B)} + 15.5 \text{H(S)} + 2.25 \text{H}_2 \]

NUCL

(2)

The “NUCL” keyword signifies that the surface reaction is a nucleation reaction. This nucleation reaction carries several important pieces of information. It indicates that the soot particles are comprised of bulk species C(B), and the inception class of the soot particle is 32 (its stoichiometric coefficient upon creation). This reaction also shows that the surface of a new soot particle is covered by H(S), and that some gas-phase H\(_2\) is created during nucleation as the soot surface cannot accommodate all of the H atoms from the two pyrene molecules.

4.2 Particle coagulation

After particle inception, the physical process of coagulation can take place. Coagulation does not affect the chemical composition of the particles, but changes the number density and
average size. The rates for the coagulation process are calculated outside of the chemical kinetics calculations, because they are based only on physical properties and relations. Three regimes are treated within the particle-tracking module: the free molecule regime, the continuum regime, and the transition regime. Details of the coagulation models are described by Frenklach and Harris\textsuperscript{37} and by Kazakov and Frenklach.\textsuperscript{39}

4.3 Surface growth and oxidation

Another important aspect of the new particle-tracking module is the ability to express particle growth and oxidation reactions as surface reactions. For example, the H-abstraction-\(\text{C}_2\text{H}_2\)-addition (HACA) soot growth sequence proposed by Frenklach and coworkers\textsuperscript{36,38} can be expressed by the reactions shown in Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Arrhenius Rate Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H} + \text{H(S)} \rightarrow \text{Open(S)} + \text{H}_2)</td>
<td>(4.20\times10^3) 0.0 13000</td>
</tr>
<tr>
<td>(\text{Open(S)} + \text{H}_2 \rightarrow \text{H(S)} + \text{H})</td>
<td>(3.90\times10^2) 0.0 9320</td>
</tr>
<tr>
<td>(\text{Open(S)} + \text{H} \rightarrow \text{H(S)})</td>
<td>(2.00\times10^3) 0.0 0</td>
</tr>
<tr>
<td>(\text{H(S)} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Open(S)})</td>
<td>(1.00\times10^1) 0.139 1430</td>
</tr>
<tr>
<td>(\text{H}_2\text{O} + \text{Open(S)} \rightarrow \text{OH} + \text{H(S)})</td>
<td>(3.68\times10^1) 1.139 17100</td>
</tr>
<tr>
<td>(\text{Open(S)} + \text{C}_2\text{H}_2 \rightarrow \text{H(S)} + 2\text{C(B)} + \text{H})</td>
<td>(8.00\times10^7) 1.56 3800</td>
</tr>
</tbody>
</table>

Table 1. Surface reactions depicting the HACA growth mechanism

Each sweep of the HACA growth sequence will increase the soot-particle class by two, based on the stoichiometry of the C(B) species on the right-hand-side of the last reaction. Expressing the soot growth sequence as a chain of surface reactions has other advantages. As part of a general surface mechanism, it is easy to check for conservation of elements and to perform sensitivity analysis and optimization with respect to these reactions. If information about a certain reaction is available from surface-science experiments, incorporation of such information would be straightforward.

In addition to the acetylene-based HACA mechanism for soot growth, we have developed mechanisms that incorporate growth by PAH condensation on the existing particles in the system. This was suggested as an important growth mechanism by Marr.\textsuperscript{40} Again, with the surface-chemistry formulations, such reactions are easily implemented as additional growth paths, using “sticking” probabilities for the PAH reaction on the particle surface and the calculated collision frequencies between particle and PAH.

We have also explored several different soot-particle oxidation mechanisms that have been reported in the literature, and have developed an initial detailed surface chemistry mechanism based on surface-science data. The surface-science-based mechanism considers oxidation of the surface by several different gas-phase species, including O, OH, O\(_2\), and H\(_2\)O. The adsorption of different oxygen-containing species on the particle surface competes with H addition, allowing self-consistent consideration of both growth and oxidation. The dominant
desorbing species is assumed to be CO, based on experimental observations. The CO desorption rate from carbon surfaces has been measured under a variety of conditions and can be implemented directly in the model. In this way, the balance between adsorption and desorption leading to particle oxidation and burn-out is controlled dynamically by the balance of gas-phase species present in the system and the statistical state of the particle surface.

4.1 Moment method for tracking particle size distributions

The particle-tracking module employs the method of moments to solve for the size distribution, using the concept of particle “class”. The moment equations determine the size distribution by accounting for the initial class from nucleation reaction(s), growth due to particle coagulation, and the net growth due to surface reactions including deposition and oxidation.

The particle size distribution determines the total surface area of the particle cloud. The total surface area is used in energy and mass balances that control transport to and from the particles and the surrounding gas, and to scale the surface reaction rates. The nucleation reaction creates new surface area (based on the bulk density and the assumption of spherical particles) and determines the initial state of that surface. Subsequent processes can modify the surface area. A surface reaction resulting in a net gain in bulk C atoms can grow the size of a soot particle, and the gain in particle class by this reaction, again, is determined by the stoichiometric coefficient of the bulk C atom. Once the relationship between particle class and surface reaction is established, the properties of soot particles can be derived from the particle size (or class) moments. Detailed descriptions of the method of moments can be found in the papers by Frenklach and coworkers.36-38 Specifics on the implementation in the CHEMKIN module are described elsewhere.13,35

The implementation within the particle-tracking module is completely general with regards to the chemistry of the problem. The chemical identity of the nucleation precursor and the composition of the new particle are determined entirely by the surface-chemistry description. In this way, the utilities can be applied to other particle chemistry, such as alumina particulates, by providing the appropriate reaction-mechanism input data.

5 RESULTS AND DISCUSSION

The particle-tracking utility and generalized soot-formation chemistry mechanisms described above have been tested against data from well controlled experiments at MIT for ethylene combustion in a jet-stirred / plug-flow reactor (JSR/PFR) configuration.40 The experiment is modeled as a perfectly stirred reactor feeding into a plug-flow reactor, where the fluid residence time is calculated as a function of channel distance in the PFR. This configuration provides a good basis for comparison of kinetics models, because the effects of diffusive transport are minimized. In these comparisons, we used the gas-phase mechanism describing the combustion of ethylene and the formation of PAHs reported by Frenklach and Wang.38 Figure 4 shows that the gas-phase mechanisms provide reasonably good agreement of the species concentrations, from the small hydrocarbons to the aromatic species. This comparison was made for an equivalence ratio of 2.2 and a 1620 K plug-flow region.
Figure 4. Comparison of gas-phase species predicted (lines) with those measured (symbols) in the MIT experiments.

Figure 5. Comparison of soot mass concentration as a function of PFR residence time for the original and the revised (including PAH condensation) mechanisms.
For the soot formation mechanism, we compared the effects of including only the acetylene-based HACA growth mechanism and the effects of also including the condensation of pyrene on the soot-particle surface as an additional growth path. Figure 5 demonstrates that the condensation path provides a significant contribution to the particle growth under these conditions and dramatically improves agreement with the experimental measurements.

Further work is underway to test and expand the reaction mechanisms for soot nucleation, growth, and oxidation, under a broader range of combustion conditions and fuels, using the particle-tracking capability.

6 CONCLUSIONS

Reduced-geometry or idealized-flow modules are an important auxiliary tool to CFD when investigating chemically reacting flows. Even as computers get faster, the mechanistic data required to elucidate chemistry phenomena continues to grow at a similar pace. Thus for the foreseeable future there will be a need for reduced-geometry models that include more chemistry detail. These models are used as direct approximations of actual flow conditions, in generating look-up tables for CFD, and as part of equivalent reactor networks. For this reason, it is essential that we continue to advance the chemistry models and to expand the ways in which detailed chemistry information can be integrated with practical CFD simulation. This work demonstrates an advanced treatment of particle-size distribution tracking, which incorporates detailed gas-phase chemistry for particle-precursor formation, nucleation phenomena, and mass-conserving growth of particles by coagulation, deposition, and PAH condensation. Implementation in CHEMKIN allows scrutiny of the assumptions regarding dominant reactions for particle growth and facilitates hypothesizing of alternative reaction paths. The use of surface-kinetics formulations also allows researchers to more easily apply results from the surface-science literature in the areas of material growth and oxidation.

REFERENCES


[32] Anantharaman, B.; Green, W. H.; McRae, G. J., Modification of Coverage Dependent Functionality in Surface CHEMKIN.