Chemistry Simulation Drives Clean Technology Progress

Scott Drennan, P.E.
Reaction Design

Here's how to determine when to use computational fluid dynamics (CFD) to simulate the detailed chemistry of reacting flows for combustion and chemical processes.

Over the last two decades, significant advances have been made in the area of detailed chemistry and its impact on clean combustion system design, providing fuel and engine developers with new tools to achieve clean designs. This knowledge also provides new opportunities for the development of more-efficient and cleaner chemical processes.

It has long been recognized that an understanding of the detailed chemistry associated with combustion processes is needed for accurate simulation of combustion behavior. One interesting trend is that fuel manufacturers are working with combustion system designers to optimize fuel and equipment designs for efficiency, emissions and performance. The widespread desire to use alternative fuels has increased the need for accurate and fast chemistry simulation.

Computational fluid dynamics (CFD) has become an industry-standard tool for accurate simulation of heat transfer and gas and fluid flow. However, even with today's advanced parallel-processing computers, it is impossible to incorporate the full-reaction mechanisms — which have hundreds of species and thousands of individual chemical reactions — into the simulation. The simulation of combustion (and other chemical reactions) requires resolution of complex geometry, turbulent flow patterns, heat transfer and complex chemistry. While CFD provides a platform to simulate reacting flows in complex geometries, it cannot accommodate fuel-chemistry mechanisms more complicated than a few steps and maintain model stability and a reasonable solution time.

This article discusses the current state-of-the-art in simulating the detailed chemistry of reacting flows for combustion and chemical processes. The strengths and limitations of CFD for detailed chemistry simulation, as well as the process of constructing a detailed mechanism, conducting experimental validation, and reducing the mechanism for use in CFD are also presented. Finally, a discussion of new technologies

MODEL FUELS FOR CLEAN-COMBUSTION DESIGN

The traditional technique of simulating petroleum and alternative fuels using empirically derived chemistry parameters does not accurately simulate the formation of trace species. It also has not provided accurate simulation of chemical reaction performance over a wide range of conditions that are required for use in design and optimization. Thus, the recent development of accurate surrogate fuel models for use in chemical kinetics simulations has been a critical step toward enabling computer-aided engine and fuel design.

With this more-precise computer-aided simulation using detailed chemistry information, the automotive industry has been able to accurately predict complex, chemically driven phenomena, such as engine knock. This level of understanding of the mechanisms in chemical and fuel processing has made it possible to accurately simulate combustion performance, allowing engine designers to avoid costly engine testing and to improve the speed-to-market of new designs. Yet the remaining challenge has been providing the combination of fuel mechanisms and simulation software tools that can quickly compute results and can be efficiently used for design.

Traditionally, fuel manufacturers produced fuels that met specifications of bulk parameters, such as heating value, viscosity, density and volatility, and engine designers developed engines without significant interaction with fuel designers. As a result, the bulk specifications to which the fuel was designed were not sufficient to completely describe the chemical behavior of the fuel when it was burned in the engine or the combustion performance inside of the engine.

Engine and fuel manufacturers are now collaborating in unprecedented ways, for example, through organizations such as the Model Fuels Consortium (MFC; www.modelfuelsconsortium.com), to develop advanced tools for combustion analysis. Fuel designers are developing new fuels and new manufacturing processes, and are interested in how these fuels perform in engines. Until the development of the detailed chemical mechanisms and tools by the MFC, the fuel designer had to rely on engine testing by the engine design companies for information about the impacts of fuel components and manufacturing techniques on real engines.

Through the MFC, a chemical simulation tool based on the industry standard CHEMKIN software was developed to predict important engine design factors, such as ignition delay, flame speed, knock, octane and cetane number, without relying on engine tests. This has allowed fuel designers to improve fuel production efficiency while maintaining satisfactory performance in the engine. This positive interaction between fuel and engine designers has resulted in an optimization of the well-to-wheel cost of providing new fuel blends and alternative fuels.

and advancements that will be required in the near future to help achieve clean chemical engineering design is given.

The role of detailed chemistry

Combustion is the process of converting a hydrocarbon fuel to water vapor and carbon dioxide through a series of chemical reactions, which are highly dependent on the operating conditions, turbulence levels and concentrations of chemical constituents present in the combustor, reactor or process. It is possible to reduce the many steps of the detailed reaction mechanism to a single reaction, or a set of severely reduced reactions, but in doing so, information on the path of key steps in the overall transformation are lost. These steps include reactions that control the formation of pollutant species such as NO_x, SO_x, CO and unburned hydrocarbons (UHCs). Thus, a reduced-chemistry CFD simulation is unable to accurately represent the impacts of trace species of pollutants on the overall process.

Research over the last 30 years has significantly increased fuel developers' understanding of the detailed steps involved in the reaction of fuel to form combustion products, as well as the impact that various fuel compounds have on combustion. The development of a detailed mechanism involves creating a complete list of the chemical species present and reactions occurring during combustion.

Development and reduction of a reaction mechanism

The creation of a fuel mechanism involves researching all the possible chemical steps that could be involved during the combustion of the fuel, and then validating those steps against experimental data. The result is a "master" mechanism that is valid for that specific fuel under specific operating conditions.

A mechanism developed for combustion at atmospheric pressure, such as in furnaces and boilers, will not be appropriate for high-pressure and high-temperature combustion, such as in gas turbines. Therefore, the operating conditions of interest are important in developing a master mechanism.

Master mechanisms can consist of thousands of reactions and hundreds of chemical species. For example, master mechanisms for gasoline developed recently by the Model Fuels Consortium consist of more than 8,000 reactions and 1,000 species. This level of detail in the master mechanism allows the simulation of trace chemical species, such as pollutants like NO_x, CO and UHCs. While such detail is required, it makes the master mechanism too large for effective use in CFD. Reduction tech-

niques are, therefore, employed to decrease the size and complexity of the mechanism.

A master mechanism (or detailed kinetic mechanism) is a collection of elementary reaction steps with appropriate rate constants that together describe a chemical process. Elementary reaction forms involve free radicals and are extremely useful in understanding the underlying chemistry of the combustion process, especially in describing the effects of fuel mixtures and operating condition ranges.

Literature on combustion kinetics spans three decades and serves as a good resource for kinetic data for many hydrocarbon fuels. Combustion science has advanced to the point where master detailed mechanisms can be developed for many fuels and processes (such as oxidation and pyrolysis), but unfortunately such mechanisms may not be available in adequate detail or accuracy without rigorous validation through experiments.

Development of a new master mechanism requires an understanding of the principles of chemical kinetics in order to generate elementary reaction steps and assign their rate constants. Elementary reactions can be classified into various categories, and rules of thumb can be used to estimate reaction rate parameters. To determine the rate constants for some complex and important reactions, experimental data on fundamental kinetics must be generated. Advances in computational chemistry also allow the use of high-level quantum mechanical calculations to accurately estimate thermodynamic properties as well as rate constants.

Fundamental flame experiments are used to validate the master mechanism. These experiments include laminar flame speed, ignition and extinction limits, and species concentration profiles in premixed and non-premixed flames.

Once the master mechanism has been determined, engineers can develop model fuels — *i.e.*, blends of specific pure components, such as heptanes, isooctane, dodecane, etc., that have the same combustion behavior as the real fuel. These model fuels can then be used with confidence in chemistry simulation models to predict complex combustion behavior.

Almost all mechanism-reduction processes follow a similar approach, in which a fully detailed chemistry model is first employed in a reduced-geometry or idealized-flow simulation for a targeted condition or set of conditions. Skeletal mechanisms are developed by eliminating chemical reactions and species related to performance parameters that are not of interest to the application. For example, if the formation of soot is not of concern, then the reactions that generate soot can be deleted without loss of accuracy.

Additional mechanism reductions can be accomplished by eliminating other reactions (or combined reactions) with specific simulation parameters of interest and with a specified level of acceptable error. Ultimately, the reduced or skeletal mechanism can be used in simulations with either reduced simulation time or improved simulation convergence. Of course, the use of reduced mechanisms increases the amount of error associated with the simulation.

Information extracted from the results of these simulations, such as sensitivity coefficients or rates of production of various species, are then used to determine the importance of different reactions and species to the model predictions. Once a reduced chemistry model is created, it can be verified against the full (or master) mechanism by running the same simulation with the reduced chemistry and comparing the results of interest. The verified, reduced-chemistry model can then be used with some confidence in a CFD simulation, provided that the range of conditions represented during the reduction is sufficient to cover the range that will be encountered in the CFD simulation.

Equivalent reactor networks for detailed chemistry simulation

The use of equivalent reactor networks (ERNs) represents an exciting new technique to enable the application of detailed chemistry for the design of clean combustion systems. An ERN is created by representing a complex reacting-flow system as a series of idealized reactors linked in a way that represents the system as a whole. A benefit of using ERNs is that full detailed chemical-kinetic mechanisms can be quickly applied to the reaction network because the details of the complex geometry and flow field have been simplified.

Zero-dimensional and one-dimensional kinetic modeling has been practiced for more than 30 years to allow the use of detailed chemical mechanisms in simulation. In such reduced-order simulation, the combustor or reactor is devolved into a simplified representation of the complex geometry and operating conditions. Regions in the combustor can be represented as a perfectly stirred reactor (PSR) or plug-flow reactor (PFR). A complete representation of the complex combustor flow field can be obtained by linking the various PSR and PFR reactors into a network with the appropriate downstream and recirculating flowrates.

Once the ERN is created through a careful devolution of the combustor flow field, the detailed reaction mechanism can serve as input to simulation software to develop an understanding of chemical behavior and performance. A well-constructed ERN will allow rapid and accurate application of full, detailed fuel mechanisms for predictions of combustion performance factors, such as emis-

sions and flame stability. The idealized reactors mimic the complexity of the geometry and flow field, yet in a manner that allows rapid simulation of detailed chemistry. The ERN approach can be used to study master mechanisms for different types of fuel, and to evaluate the impacts of various fuels on important combustion parameters, such as flame speed, ignition delay, and the formation of such pollutants as NO_x, CO, SO_x, and soot (UHCs).

It is critical that the ERN is a true representation of the actual combustor or chemical reactor flow field in order for the simulation to be accurate and valuable in the design process. This requires detailed evaluation by expert personnel during the creation of the ERN, which takes time and is not practical during the design process.

So, a trade-off exists between accuracy in the geometry and accuracy in the fuel chemistry. A new software simulation technique is needed to allow detailed chemistry to be employed with CFD in order to produce accurate modeling of flows and accurate combustion simulation. Vendors need tools that seamlessly link CFD and the ERNs to provide rapid application of detailed chemistry in modern chemical reacting system design.

Just as the use of ERNs gives combustion system designers the ability to effectively incorporate simulation into the design workflow and accurately predict emissions and other parameters, the use of ERNs allows reactor designers to predict chemical process parameters.

Soot formation and particle creation

ERNs are an efficient platform on which to perform simulations of soot and particle behavior using the detailed chemical reaction mechanism. The simulation of soot formation in a reactor can be extended to reactor networks, allowing for more complete and accurate representation of the complex geometry of the combustor or reactor. The use of ERNs and soot particle prediction capabilities allows the process designer to refine the combustor or reactor design for improved performance, either by eliminating soot production or enhancing it to achieve a specific number, density and size distribution of the soot particles.

There are both good and bad types of soot. Usually, soot formation is seen as bad and something that should be avoided. However, there are several critical areas where soot formation is either the goal of the process itself or greatly helps in achieving production goals. Some processes, such as methane reforming for ammonia production, are fouled by soot formed during the chemical reaction process. In contrast, soot can be very helpful in enhancing radiation heat transfer in process and refinery heaters as well as in burners that are tuned to achieve a specific heat-transfer profile.

The understanding of soot formation mechanisms has allowed process designers to define short-lived species that act as soot precursors. Compounds such as polycyclic aromatic hydrocarbons (PAHs) are known to be responsible for the inception of soot formation at certain operating conditions. However, simplistic or global chemical mechanisms do not provide information regarding the levels of PAHs, and the detailed process chemistry is required to perform simulations that accurately track the inception, growth and destruction of soot particles.

When a PAH is present at flame temperatures without oxygen, it creates a soot particle that grows in mass as a result of gaseous reactions on the surface of the particle. As the soot particle moves through the flame and oxygen is added (still at a high temperature), the soot particle becomes smaller as a result of surface oxidation reactions. Various fuel/air mixing strategies can be employed to minimize the formation of the soot precursor PAH and ultimately lead to cleaner combustion systems.

The titanium dioxide and carbon black industries are built on the creation of particles — in much the same way as soot particles are formed. Titanium dioxide is the particle that gives white materials, such as paint and plastic, their bright white color. Carbon black is used in a variety of applications to produce deep black tones, such as printer toner and asphalt. While these particulate products are created in vastly different ways, their production depends on detailed chemical reactions and operating conditions that control the size, distribution and shape of the particles. Understanding how to simulate the detailed chemistry and its interaction with fluid dynamics is critical in learning how to design more-efficient manufacturing techniques that produce higher-quality products.

In closing

The lessons learned from the development and application of a detailed understanding of the chemical kinetics of combustion can be readily applied to chemical processing applica-

tions. Just as the use of ERNs gives combustion system designers the ability to effectively incorporate simulation into the design workflow and accurately predict emissions and other parameters, the use of ERNs allows reactor designers to predict chemical process parameters, products and byproducts.

The progress being made in the development of master mechanisms and reduced-chemistry reaction mechanisms will drive wider acceptance and integration of simulation in the design of reacting-flow systems. Projects such as the MFC have provided fuel and engine manufacturers the science and tools they need to incorporate more chemistry into their simulation methods, allowing them to meet rapid development schedules and the need for accuracy.

Future work is needed to develop more accurate particulate chemistry, such as that involving the formation of soot in combustion devices. New emissions regulations are targeting not only the mass emissions of soot, but also the size distribution of those soot particles. The development of accurate soot-particle chemistry knowledge and simulation tools is critical to the further advancement of clean chemistry or combustion technologies. CEP

BENEFITS OF CFD WITH ACCURATE CHEMISTRY

A key benefit of CFD is its ability to simulate the fluid mixing and heat transfer processes in a reactor system. Often, reactors are designed without an understanding of how to optimize the chemical process or fluid mixing that occurs within the device. The result is equipment that may be much larger than required or less-than-optimal process efficiency or yield.

CFD can also be used to reduce emissions when it is used with accurate chemistry mechanisms. Low-emissions designs for process heaters and incineration equipment often require complex fuel/air mixing strategies. CFD is ideal for this type of analysis and optimization.

SCOTT DRENNAN, P.E., is the director of applications engineering for Reaction Design (6440 Lusk Blvd., Suite D-205, San Diego, CA 92121; Phone: (858) 550-1920; E-mail: sdrennan@reactiondesign.com), the provider of CHEMKIN — software that solves chemical kinetics. He has experience in low emissions combustion technology development and R&D management at COEN Burner Co. and the Electric Power Research Institute. He has an MS in mechanical engineering from the Univ. of California at Irvine with an emphasis on low-NO_x combustion and liquid fuel atomization for gas turbine combustors.