

The Internal Combustion Modeling Considers All Factors

Increasing fuel efficiency in automotive engines while simultaneously reducing their exhaust emissions is a challenge. Modeling the combustion process is essential to meeting that challenge.

THE internal combustion engine—in particular the fuel that powers it—has been a powerful motivator for government decision-making and foreign policy in this century. Countries have been invaded and wars fought over petroleum. Germany lost World War II in part because it ran out of gasoline. Given the concerns over worldwide oil reserves and greenhouse gases, it is not surprising that considerable research is devoted to increasing the efficiency of the internal combustion engine, especially for the automobile, a major consumer of petroleum and source of carbon dioxide emissions.

But increasing efficiency, so that less fuel is used to produce the same amount of energy, is not a simple engineering task. Greater efficiency reduces carbon dioxide emissions but increases regulated exhaust emissions in the form of oxides of nitrogen (NO_x), which are a major source of photochemical smog. If the combustion process is modified to reduce NO_x emissions, these systems then emit large

Engine at Work

amounts of particulate matter and carbon monoxide.

In spark-ignited engines, which most automobiles today use, another problem arises when efficiency is increased. With an increase in the compression ratio comes a tendency for the engine to knock or ping unless the fuel includes an additive like tetraethyllead or MTBE (methyl tertiary-butyl ether).

This interplay of efficiency and emissions—and to a lesser extent engine knock—is at the heart of almost all research today on the automotive engine and on other practical combustion systems such as gas turbines, industrial burners, boilers, and so on. Fixing engine knock with a fuel additive is easy. But recall that leaded fuel was a major air pollutant, and MTBE is currently polluting groundwater. Reducing exhaust emissions is equally challenging.

Trial-and-error research on the combustion engine produced results for many years, including the first solution to the problem of engine knock. However, by the middle 1970s, computers had advanced sufficiently for use in detailed, full-system modeling, a cheaper and more effective way to explore combustion problems.

A challenge for modeling automotive fuels is the enormous variation in their chemical makeup. On a day-to-day basis, refineries mix and match the hundreds of components in the fuel they produce to meet certain mandated specifications. But there are broad tolerances in those specifications, which largely dictate only that the fuel will make an engine run and that it meet a particular octane (antiknock) or cetane (diesel-ignition) rating. This variability is what makes modeling so challenging and so important. Modeling makes it

possible to predict with confidence the effect of each of the ingredients on the overall fuel mixture.

At Livermore, modeling of the combustion process was an offshoot of nuclear weapons research. According to Livermore physicist Charlie Westbrook, an internationally recognized authority on combustion and combustion modeling, “Modeling the combustion process really isn’t very different from modeling what happens in a nuclear weapon. Instead of looking at the reactions of protons and neutrons in a weapon, we started looking at what was happening to hydrocarbon and oxygen molecules under combustion conditions.”

Livermore’s computational capabilities have always been among the best in the world. Add to that Livermore’s multidisciplinary staff and you have a powerful modeling team. Charlie Westbrook today leads the Chemistry and Chemical Engineering Division in the Chemistry and Materials Science Directorate, but for years he was in the trenches leading much of Livermore’s combustion modeling work. Working with computer experts, engineers, and others, his team produced some revolutionary results. That tradition continues today in work on a novel engine design, a new method for reducing NO_x emissions from diesel engines, and reformulated diesel fuels.

Early Results

Livermore brought its talents to three major cooperative research groups formed in the middle 1970s by the Department of Energy with Ford Motor Company, General Motors Corporation, and Unocal. Other participants in these groups included universities, private industrial firms, and the Los Alamos

and Sandia national laboratories. While working in collaborations that lasted for almost 20 years, group members won about one-third of the Horning Memorial Awards given by the Society for Automotive Engineering for the best paper on engine–fuel relationships presented at the society’s annual meeting.

One major project of the research groups modeled flame quenching at engine walls. In the cylinder of an automobile engine, a flame ignited by a spark propagates through an air–fuel mixture and toward the cylinder walls and piston. Before this project began, engine researchers everywhere were certain that a major source of unburned hydrocarbon emissions was the extinguishing of the flame as it approaches the relatively cold walls of the cylinder. They thought the process left behind a thin layer of unreacted fuel.

Modeling results seemed to support that traditional view until near the end

of the ignition process, when data indicated that fuel trapped in the cold boundary layer at the wall begins to diffuse back out toward the high-temperature region where it is rapidly consumed. Later research confirmed that unreacted fuel in the piston ring crevices is actually the primary source of unburned hydrocarbon emissions.

Equally revealing was a chemical kinetic study of fuel additives for engine knock in spark ignition engines, for which Westbrook and William Pitz, also of Livermore, received the Horning Award in 1991.¹ Knocking occurs when the flame from the spark plug does not consume the gases in the piston chamber fast enough. The remaining “end gases” spontaneously combust, sending a damaging shock wave across the chamber.

Engines operate most efficiently at the highest compression ratios, but that is precisely where knocking occurs. Engine knock therefore sets an upper limit to the compression ratio at which a spark-ignited internal combustion engine can operate. Suppressing knock permits engines to operate at higher compression ratios and thus to achieve higher fuel efficiency and lower carbon dioxide emissions.

In the 1920s, years before air pollution became a major issue, trial-and-error research produced an effective solution for engine knock that was used for decades: the additive tetraethyllead. Since leaded fuel was eliminated in the 1970s, other additives have been used that work in a variety of ways.

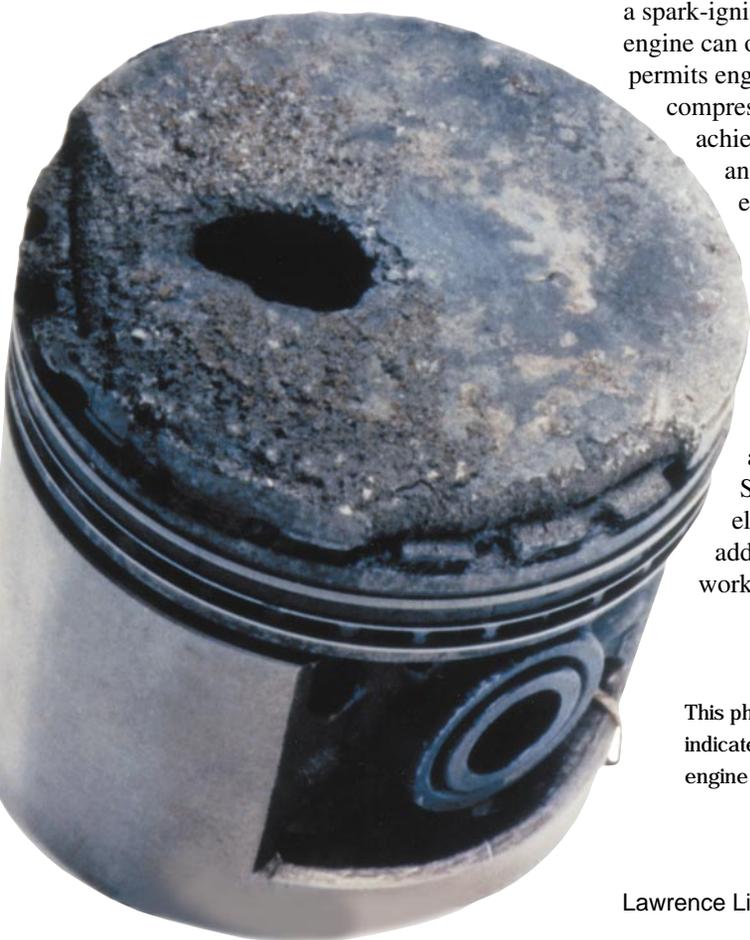
Today, MTBE is the oil refiners’ additive of choice for suppressing knock. But MTBE leaking from underground storage tanks has been found to be contaminating groundwater (see *S&TR*, April 1999, pp. 21–23).

Westbrook and Pitz’s award-winning paper was the culmination of a long-term study of the fundamental chemical factors that control knocking. Earlier work had resulted in models for different families of elementary reactions with varying dependencies on temperature, pressure, and fuel–air concentrations. Working up from simple to complex molecules, from single-component fuels to fuel mixtures, the research team simulated the ignition of fuels with a variety of ignition characteristics. They also examined an array of proknock and antiknock additives, including MTBE. The goal of this work was to provide chemical engineers with the ability to predict the knock behavior of arbitrary mixtures of hydrocarbons and additives.

Sleuthing Chemical Reactions

Livermore developed the chemical kinetics model known as HCT, for hydrodynamics, chemistry, and transport, for use in all of this early work. Because of limited computer capabilities early on, modeling of hydrocarbon oxidation and ignition could consider fuel molecules containing only one or two carbon atoms. But those simple models served as the basis for mechanistic studies of larger fuel molecules, which are made up of many smaller ones. The extensive research on engine knock, for example, would not have been possible without those smaller building blocks.

Mechanisms for hydrocarbon fuel reactions range from relatively simple to extremely complex. As shown in the table to the right, hydrogen–air combustion produces just 7 species, involving about 20 chemical reactions. Reactions involving cetane produce



This photo of a badly damaged piston indicates the effects of long-term engine knock.

1,200 species and are much more time-consuming to model. Each species requires a differential equation to explain its behavior in any reaction. Fortunately, with recent strides in advanced parallel computing, large, complex kinetics problems may be handled comparatively easily.

The HCT code permits the use of a variety of boundary and initial conditions for reactive systems, depending on the needs of the particular system being examined. Over the years, the code has been used to study the combustion properties of many hydrocarbons, including methane and other paraffin fuels; natural gas; alcohols such as methanol and ethanol; oxygenated fuels, including dimethyl ether and MTBE; aromatics such as benzene, toluene, and naphthalene; as well as blends of automotive fuels for particular octane ratings. HCT has also been applied to studies of various exhaust emission species such as NO_x , metals, and chlorinated, brominated, and fluorinated species.

A more recent application of the HCT model has taken it far from the automotive industry. With HCT, researchers at Livermore are studying the kinetics of chemical warfare nerve agents to learn more about their

reactions and how they evolve over time so that protection against them can be improved.

An Engine for the Future

Today, a version of HCT is proving indispensable for research on an innovative engine concept known as Homogeneous Charge Compression Ignition (HCCI). Combining features from both spark-ignition and diesel engines, the HCCI engine is promising the high efficiency of a diesel engine with virtually no NO_x or particulate emissions. The engine can operate using a variety of fuels. Given this mix of attributes, it is not surprising that considerable research is going on around the world on the HCCI engine. Much of Livermore's research on it has been done in conjunction with a major industrial partner.

In the HCCI engine, fuel is homogeneously premixed with air, as in a spark-ignited engine, but with a high proportion of air to fuel. When the piston reaches its highest point, this lean fuel autoignites (spontaneously combusts) from compression heating, as in a diesel engine. But remember that autoignition is what causes knock in a spark-ignited engine. Knock is undesirable in spark-ignited engines because it enhances heat

transfer within the cylinder and may burn or damage the piston. But in an HCCI engine, with its high air-to-fuel ratio, knock does not damage the engine because the presence of excess air keeps the maximum temperature of the burned gases relatively low. When the danger of engine damage is eliminated, autoignition becomes a desirable mode of operation.

Engineer Ray Smith began working on HCCI at Livermore in the mid-1990s. He realized early on that understanding chemical kinetics was the key to controlling HCCI combustion. This realization, combined with Livermore's access to detailed chemical kinetics codes such as HCT, quickly made the Livermore team a leader in HCCI analysis at a time when others did only experimental work.

In 1996, the Livermore team modified HCT by incorporating models required for engine analysis, such as an engine heat-transfer model, a turbocharger model, and a model for exhaust gas recirculation. This version then analytically predicted for the first time the regions of best operation for HCCI engines running on methane and natural gas.

More recently, the Livermore team, now led by Salvador Aceves-Saborio, has developed a comprehensive model for predicting HCCI combustion, linking HCT with a fluid mechanics code to calculate the effect of temperature distribution on HCCI combustion. This methodology not only predicts experimental pressure traces with great accuracy but also has produced the first prediction of hydrocarbon and carbon monoxide emissions, including where those emissions originate within the cylinder. All of this information is important for determining a course of action for emissions control in HCCI engines.

Livermore is now working with mechanical engineers at the University of California at Berkeley to verify the modeling results experimentally. A

Chemical Kinetic Model

Large database contains:

- Thermodynamic properties of species
- Reaction rate parameters

Reaction mechanisms grow with molecular complexity:

Fuel	H ₂ (hydrogen)	CH ₄ (methane)	C ₃ H ₈ (propane)	C ₆ H ₁₄ (hexane)	C ₁₆ H ₃₄ (cetane)
Number of species	7	30	100	450	1,200
Number of reactions	25	200	400	1,500	7,000

More complex fuels make much greater demands on computing time during modeling. Until improvements were made in advanced parallel computing, only simple fuel molecules could be modeled.

single-cylinder HCCI engine has been operating at the Berkeley campus and producing data since April 1999. A four-cylinder diesel engine has recently been modified as an HCCI engine. Thus far, modeling data and experimental results tally very well.

Autoignition must occur almost exactly at the point where the piston reaches its maximum height within the cylinder. Timing of autoignition is thus critical, but the HCCI engine gives up two timing control mechanisms: The start of ignition is not directly controlled by an external event such as the beginning of injection in the standard diesel or the sparking of the spark plug; and the heat release rate is not controlled by either the rate and duration of the fuel-injection process, as in the diesel engine, or by the turbulent flame propagation time, as in the spark-ignited engine.

Detailed modeling of engines using a homogeneous charge of various fuels has shown that by knowing the precise conditions (fuel species, temperature, and density) at the start of compression, the beginning of combustion can be accurately predicted. But knowing in theory the initial conditions and controlling the timing are two different things.

Aceves-Saborio says, "The control problem is what keeps the HCCI out of the auto showroom, and we are studying

various options." One is to inject recirculated exhaust gases into the fuel-air mixture to raise the fuel temperature quickly. Another option is to use small amounts of dimethyl ether to enhance ignition slightly. Aceves-Saborio notes, "Most of our future work will be directed at engine control. It will be a challenge."

Cleaning Up Diesel Emissions

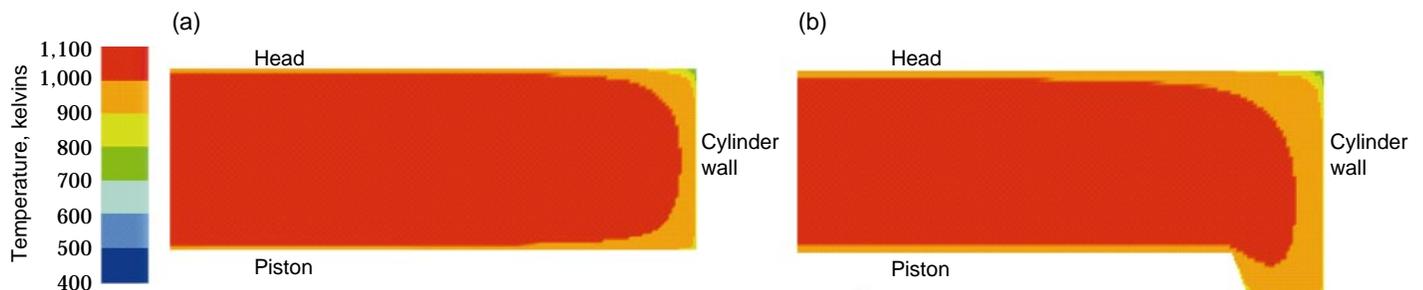
The catalytic converters used today in spark-ignited gasoline automobiles are responsible for major reductions in tailpipe emissions of carbon monoxide, hydrocarbons, and NO_x . But that kind of catalysis does not work well on diesel engines, which operate on lean fuel-to-air mixtures. Exhausts from these engines contain an excessive amount of oxygen that inhibits the chemical reduction of NO_x to nitrogen (N_2), rendering catalytic converters useless for NO_x removal.

Lean-burn engines such as the diesel are the focus of most engine research today because they offer fuel economy unmatched by any other commercially viable engine. But they must run cleaner and produce fewer emissions if they are to gain more widespread use. While diesel engines can rather easily be optimized to reduce either NO_x or particulate matter, cutting one usually causes an increase in the other. With a new process developed at Livermore, it

appears that both emissions can be reduced. The engine can be optimized for low particulate matter and high NO_x , and Livermore's technique then reduces the NO_x to harmless molecules such as N_2 .

Building on Livermore's years of experience in plasma physics, a team led by physicist Bernie Penetrante has developed a process to reduce NO_x in lean-burn engine exhausts. Known as Plasma-Assisted Catalytic Reduction (PACR), the process combines a nonthermal plasma with a catalyst. One application of this process involves a nonthermal plasma produced by short pulses of high voltage on a metal wire inside a metal cylinder (see schematic on p. 9 at top right). The plasma serves to oxidize the nitric oxide (NO) and hydrocarbons to nitrogen dioxide (NO_2) and partially oxidized hydrocarbon products, respectively. These plasma-conversion products are then reduced over a catalyst to nitrogen, carbon dioxide, and water.

The PACR process would not be where it is today without modeling early on to determine what the plasma can and cannot do. Generation of the plasma, by itself, does not guarantee a means for efficient oxidation of NO to NO_2 , which is necessary for enhancing the reduction of NO_x to N_2 over the catalyst. Lean-burn engine exhausts contain large amounts of water vapor in



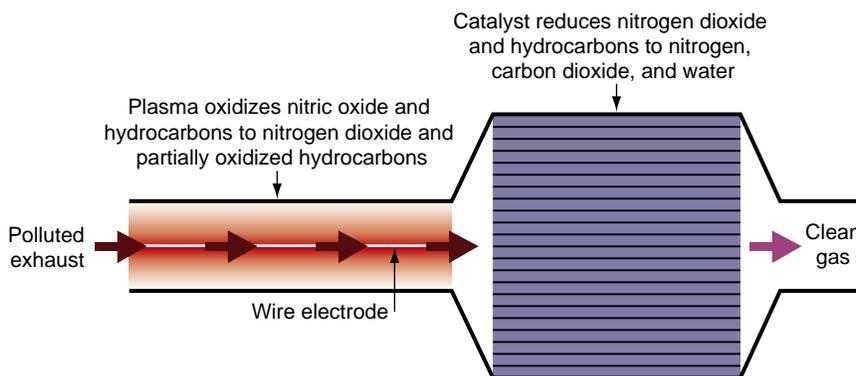
Temperature distributions before combustion in two possible Homogeneous Charge Compression Ignition (HCCI) combustion chamber designs, (a) and (b). Chamber design (a) produces significantly lower hydrocarbon emissions because it has a smaller "cold" crevice near the cylinder wall.

addition to oxygen, prompting the plasma not only to oxidize NO to NO₂ but also to oxidize NO₂ to nitric acid. Livermore's models are guiding the development of the PACR process, in which the plasma oxidizes NO to NO₂ without further producing acids.

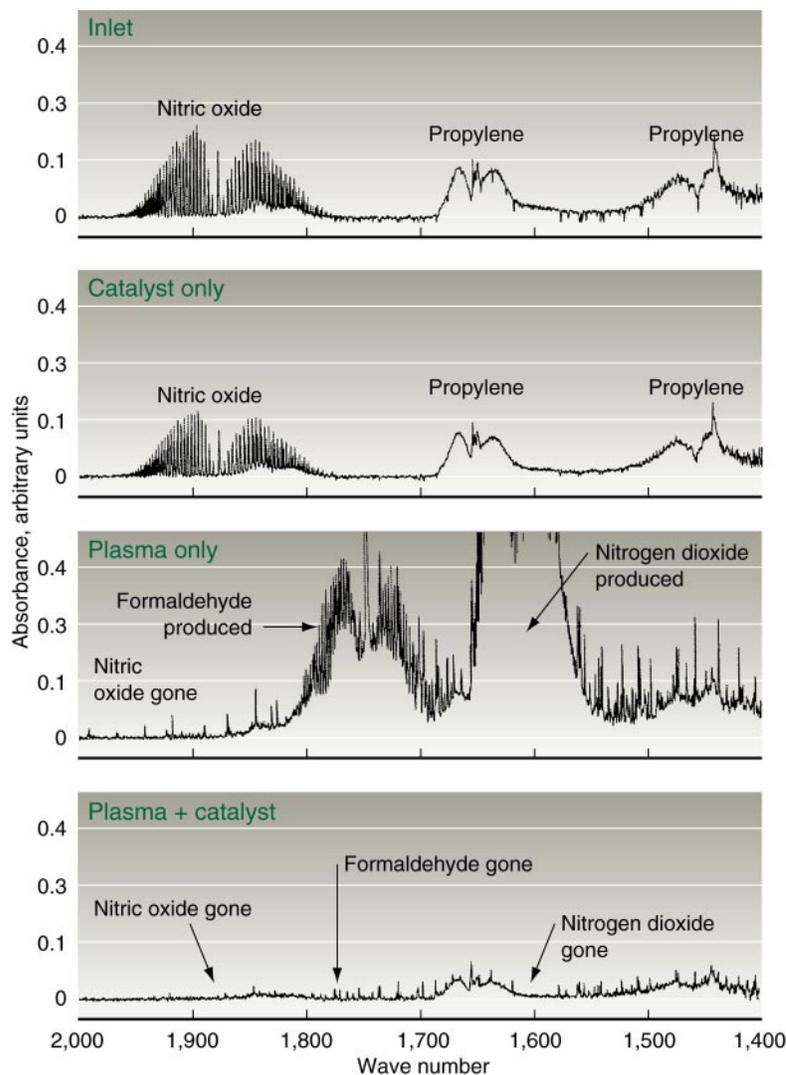
Use of the plasma also avoids a problem that confounds most proposed diesel catalysis systems. The current state-of-the-art catalysis method uses platinum or another precious metal to convert NO_x to N₂ in diesel engines. But diesel fuels have a fairly high sulfur content. Catalysis with precious metals tends to oxidize sulfur dioxide (SO₂) to sulfur trioxide (SO₃), which then fouls the catalyst and produces particulates. Using low-sulfur fuels might avoid this problem, but the PACR process gets around it altogether without precious metals or low-sulfur fuel. By simulating the activity of the exhaust gases in the plasma, the team learned that the presence of unburned hydrocarbons makes the plasma "tolerant" of SO₂. The unburned hydrocarbons scavenge the reactive free radicals that would otherwise oxidize SO₂, thus allowing the plasma to be very selective.

Thus far, the team has developed a bench-scale prototype of the system. With it, they have successfully run tests on a portion of the exhaust from a diesel engine and on controlled laboratory gases that simulate exhaust mixtures.

Spectrographic analysis of exhaust emissions demonstrates the benefit of plasma-assisted catalytic reduction. Plasma plus catalysis almost completely eliminates emissions from diesel engines.



A schematic of the plasma-assisted catalytic reduction system. A nonthermal plasma is produced by short pulses of high voltage on a metal wire inside a metal cylinder.



The team has recently scaled up the system to handle the full exhaust flow from car and truck engines.

A New Look at Diesel Fuel

California's Air Resources Board and the U.S. Environmental Protection Agency are proposing regulations for substantially reducing emissions of NO_x and particulate matter. These regulations will pose a major challenge for diesel engines, which currently produce significant amounts of both types of emissions. Working with several engine companies, a Livermore team has been using the HCT code to simulate ignition and particulate production in advanced diesel engines running on oxygenated fuels.

In particular, they are looking at how fuel molecular structure influences emissions. Several alternative fuels—such as dimethyl ether and dimethoxy methane—have been suggested to reduce soot and NO_x in diesel engine operations. These fuels contain no carbon-to-carbon bonds and produce little or no soot, and, like other fuels containing oxygen atoms such as alcohols and ethers, they reduce NO_x emissions by lowering flame temperatures. Charlie Westbrook is leading the modeling effort to more fully understand how these fuels react and how to exploit their beneficial properties.

Environmental scientist Dave Layton and his team are contributing to this work in a novel fashion by preparing life-cycle analyses of the various fuels and additives under consideration. Looking beyond how the fuels will operate in an engine, they are examining the full effects of the fuels from their production through subsequent distribution, storage, and use.

Westbrook notes, "This kind of life-cycle analysis was not done for MTBE. Engineers knew it would suppress

knock and reduce carbon dioxide, and at the time, that seemed to be enough. We now know that a more thorough investigation is needed before new fuels and additives are introduced."

Layton, Westbrook, and others at Livermore have proposed to the Department of Energy that a Consortium for Fuels Assessment be established at Livermore to perform life-cycle analyses of new fuels and additives. The goal is to learn as early as possible what the full ramifications of a new additive or fuel will be and to evaluate any necessary mitigation measures.

The Work Ahead

Given our peripatetic lifestyles, it is clear that automobiles powered by the internal combustion engine are with us to stay, at least until some better mode of transportation comes along. For most consumers, the car's flexibility and relatively low cost outweigh its deleterious effects on petroleum reserves and the environment.

But it is no accident that the U.S. Department of Energy and other organizations are focusing most of their research on diesel and HCCI engines. These fuel-efficient engines promise to

make oil supplies last longer. Once autoignition in the HCCI engine is effectively controlled, it may well be the engine we use until the fuel cell becomes an economic option. Developing fuels that burn cleaner and affect the environment less will improve the overall picture even more.

Modeling engine processes is key to this research. Livermore researchers have already made major contributions and show no sign of stopping any time soon.

—Katie Walter

Key Words: Combustion modeling, diesel fuels, HCT code, Homogeneous Charge Compression Ignition (HCCI), internal combustion engine, Plasma-Assisted Catalytic Reduction (PACR).

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Reference

1. Charles K. Westbrook, William J. Pitz, and William R. Leppard, "The Autoignition Chemistry of Paraffinic Fuels and Pro-Knock and Anti-Knock Additives: A Detailed Chemical Kinetic Study," paper no. 912314, Proceedings of the SAE International Fuels and Lubricants Meeting and Exposition, Toronto, Canada, October 7–10, 1991.

About the Scientist



CHARLES K. WESTBROOK received a B.S. in physics from Harvey Mudd College and a Ph.D. in applied science and engineering from the University of California at Davis. He joined Lawrence Livermore in 1968 in the Physics Directorate, where he served as division leader of the Computational Physics and Applied Physics Divisions. He recently became division leader of the Chemistry and Chemical Engineering Division in the Chemistry and Materials Science Directorate. His honors include the 1991 Horning Memorial Award from the Society of Automotive Engineers for the best paper of the year on engine–fuel relationships and the 1992 Thomas Midgley Award from the American Chemical Society for outstanding contributions in the field of chemistry related to the automotive industry. Westbrook has authored approximately 250 refereed publications on combustion, chemical kinetics, and physics.