

Research needs for future internal combustion engines

Dawn K. Manley, Andrew McIlroy, and Craig A. Taatjes

The challenges of internal combustion require a broad collection of research discoveries to make the transition from hardware-intensive, experience-based fuel development and engine design to simulation-intensive, science-based design.

Dawn Manley is the manager of the reacting flow research department, Andrew McIlroy is the senior manager for chemical sciences, and Craig Taatjes is a researcher in the combustion chemistry department, all at Sandia National Laboratories' Combustion Research Facility in Livermore, California.

Combustion drives the developed world's economy. Transportation is second only to industrial use as the largest consumer of energy in the US and accounts for about 60% of our nation's use of petroleum—an amount equivalent to all of the oil the country imports. The numbers are staggering: Some 10 000 gallons of petroleum are burned in the US each second of every day. Although new energy sources are being developed and renewable fuels are emerging to replace crude oil, improvements in the efficiency of internal combustion engines hold the promise of increasing our energy security and mitigating climate change.

The environmental consequences and health hazards posed from urban smog and other combustion byproducts led to US regulation in the late 1970s designed to limit the emission of nitrogen oxides (NO_x), hydrocarbons, and other pollutants from internal combustion engines. Controlling those emissions while maintaining high efficiency is a continuing challenge. In the last decade, a combination of improved combustion technologies and exhaust after-treatments has nearly eliminated those emissions from gasoline spark-ignited engines. Emissions from the more efficient compression-ignited diesel engines have proven more difficult to control. For example, catalytic converters are not practical for diesel engines because residual oxygen in the exhaust poisons the catalysts. For a review of internal-combustion basics, see the box on page 48.

Standards continue to tighten, with new diesel emissions regulations taking effect in 2010. For consumers to continue benefiting from the high efficiency of diesel engines, meeting those new regulations is critical.

A path forward

The monolithic nature of transportation energy use—liquid fuels used in internal combustion engines—means that unlike in industrial energy use, a relatively small number of technologies and fuel sources need to be considered. New fuel sources include biologically derived fuels such as ethanol and biodiesel, and fossil-fuel sources such as oil sands, predominantly from Alberta, Canada, and oil shale from the western US. All those hydrocarbons produce fuels

that are chemically different from traditional gasoline and diesel. But they also offer the potential to considerably reduce our dependence on foreign oil, as all except the Canadian oil sands can be produced domestically. Moreover, the use of bio-derived fuels also has the potential to reduce carbon dioxide emissions, although not without other complications such as problematic NO_x emissions from biodiesel combustion and the possibility of global food-supply shortages.

In 2006 the Department of Energy's Office of Basic Energy Sciences held a workshop entitled "Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels." The workshop brought together more than 80 participants from academia, industry, and national laboratories in the US and Europe, with expertise spanning physics, chemistry, modeling, and engine and turbine design. The workshop report is available at http://www.sc.doe.gov/bes/reports/files/CTF_rpt.pdf.

Participants identified a single, overarching grand challenge for 21st-century combustion science: the development of a validated, predictive, multiscale combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines used for transportation. The aircraft industry offers a compelling example. It has already embraced computational modeling in its design and optimization stages of airframe production and has greatly reduced the need for expensive testing. That capability is likely to enhance engine performance, shorten development cycles, and lower development costs.

The grand challenge emphasizes a *validated* modeling capability—the determination that the model captures the essential physical phenomena with adequate fidelity. That's a tall order in the case of an internal combustion engine, whose range of relevant length scales spans nine orders of magnitude, from a few angstroms, at which atoms and molecules bond, to several centimeters, the size of cylinders; the range of time scales is commensurately broad.

At each scale, phenomena are measured using different instruments, are simulated using diverse modeling approaches, and are understood conceptually with varying levels of insight. A multiscale framework that can encompass all

A primer on internal combustion

Spark ignition and diesel are the two most common engine types, but they have vastly different combustion control mechanisms. In a typical gasoline engine, a premixed stoichiometric fuel-air mixture is compressed and ignited by a spark at an optimal time relative to the piston stroke. The reaction propagates through the mixture as a wave, its speed determined by the rate at which heat and combustion radicals (short-lived, highly reactive molecules) diffuse into the gas ahead of the mixture. Turbulent eddies in the reactant mixture greatly increase the rate at which the mixing occurs, and hence the rate at which the flame propagates and energy is released. As depicted in panel a of the figure the outward-going hot flame (red) travels in front of the burned gas (blue).

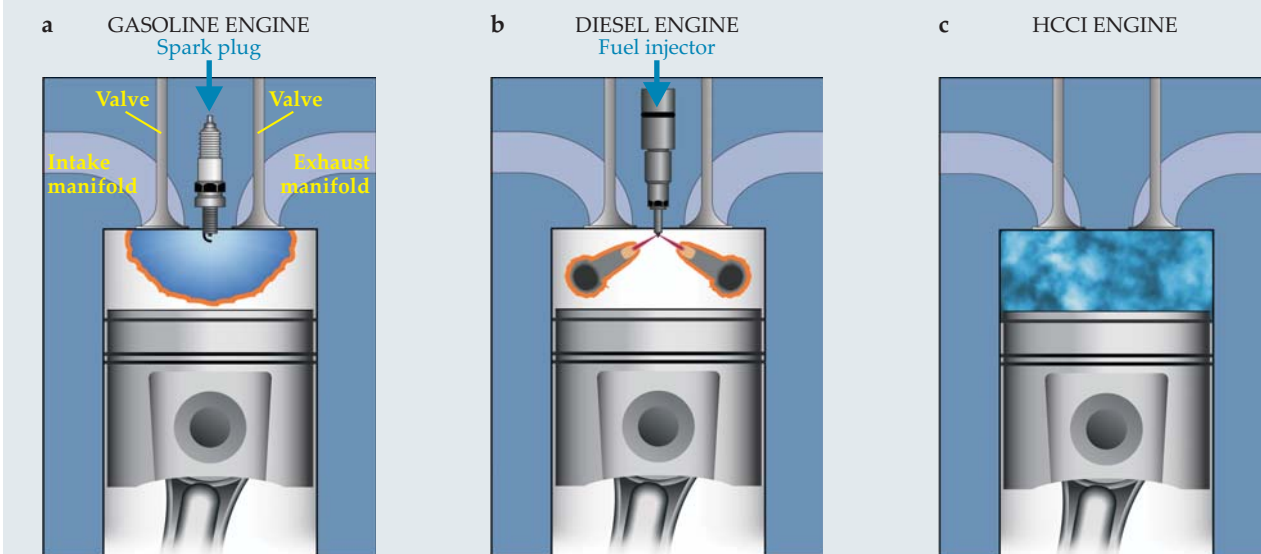
The high temperature (above 2000 K) of the stoichiometric combustion leads to the formation of nitrogen oxides (typically NO and NO₂), which are largely removed by the three-way catalytic after-treatment in all spark-ignition engines manufactured since 1980. The power output is controlled by restricting the amount of air drawn into the engine, commonly called throttling, and injecting correspondingly less fuel. Overall, throttling and the low compression ratio of a spark-ignited engine result in significantly less fuel efficiency than a diesel engine.

Diesel engines are compression ignited with timing controlled by the injection of liquid fuel into an air- and exhaust-filled cylinder. The chemical reaction occurs at the interface where the fuel and air meet; the reaction rate and the amount of heat released are determined by the rate at which fuel and air diffuse to the interface. In a diesel engine, the fuel and air have little time to mix before combust, and although the overall mixture has an excess of oxygen, a range of fuel-air mixtures exist during combustion starts. Combustion of fuel-rich

regions produces soot (pictured as the two black blobs in panel b), and stoichiometric regions burned at high temperatures—as high as 2600 K in diesel engines—produce nitrogen oxides. Panel b illustrates the fuel entering the cylinder as two narrow liquid streams (red) from the fuel injector that then break up into droplets.

Although highly advanced, both types of engine still operate well below their thermodynamic limit of efficiency. With suitable technology, spark-ignited gasoline engines could, in principle, be made 50% more efficient than ones currently produced, and diesel engine efficiency could be improved by 25% or more. Novel ways to increase efficiency and lower emissions are based on general strategies classified as low-temperature combustion. LTC employs reaction mixtures that are at or below traditionally accepted lean limits of combustion. The low fuel concentrations effectively mitigate soot formation, and the low combustion temperatures (below 1900 K) eliminate the nitrogen oxides.

Homogeneous charge-compression ignition (HCCI) engines exploit a particularly promising LTC strategy in which fuel and air are premixed, as pictured in panel c, and then compressed to the point of spontaneous ignition. The difficulty is that their ignition timing depends on fuel chemistry and mixture preparation, not on an active control mechanism such as the spark in gasoline engines or the fuel injection in diesel engines. The high compression ratios and cylinder pressures combined with that more complex control mechanism is likely to make HCCI engines more difficult to engineer than current gasoline and diesel engines. Increased cost of manufacturing will need to be balanced against reduced fuel use. In principle, the HCCI engines would produce the low emissions of a gasoline engine yet run with the efficiency of a diesel.



the data, models, and concepts and that accurately predicts both microscopic and macroscopic phenomena is currently unavailable. It will require seminal discoveries in chemistry, fluid mechanics, materials science, and applied mathematics. Strategically coordinated advances in experiment, theory, modeling and simulation, algorithm development, data informatics, and distributed petascale computing can, researchers hope, enable those discoveries (see the article by

Douglass Post and Lawrence Votta in PHYSICS TODAY, January 2005, page 35).

All chemistry is local

Effective combustion of hydrocarbon fuel maximizes the energy released as chemical bonds in the fuel are broken and stronger bonds with oxygen are formed. At the same time, it minimizes formation and release of unwanted emissions

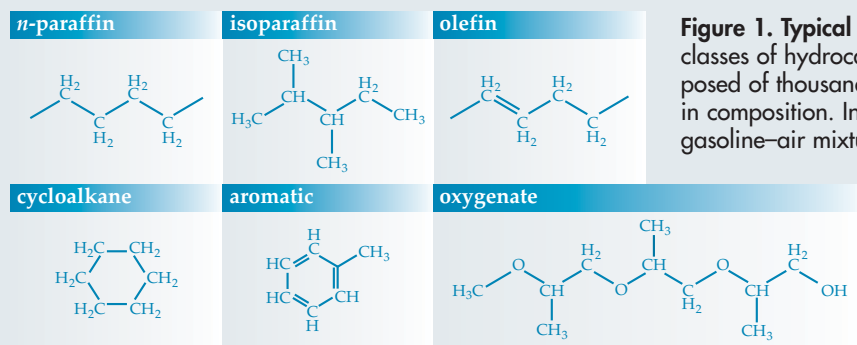


Figure 1. Typical fuel molecules in each of six major classes of hydrocarbons. Transportation fuels are composed of thousands of chemicals and can vary greatly in composition. In spark-ignition engines, compressed gasoline-air mixtures may ignite before the spark; alternatively, after the spark propagation of the flame may change to a detonation wave. Both cases result in engine knock, a pinging sound caused by the impact of shock waves on the cylinder walls. Highly branched compounds, such as isoparaffins, and cycloalkanes burn with little knock,

whereas straight-chain hydrocarbons accelerate ignition and cause knock. In addition, aromatics and isoparaffins increase soot during combustion, whereas oxygenates can reduce carbon monoxide and soot.

such as NO_x and soot. The chemical conversion of fuel and oxidant to products occurs principally through a complex set of free-radical chemical chain reactions. Ideally, one would measure the reaction rate and product distribution as a function of temperature and pressure for each contributing reaction. In practice, that's not possible due to the sheer number of reactions, the broad temperature and pressure range of combustion, and the lack of sufficient experimental control to study so many reactions individually.

A successful strategy will likely be to experimentally characterize prototype fuel-molecule reactivity in detail and then demand that reaction-rate theory reproduce the experimental findings throughout the operating regimes of combustion. Robust, validated chemical theory could then be used to compute kinetic and mechanistic data for unmeasured reactions. For both existing and evolving fuel streams, however, hundreds of chemical species and many thousands of reaction steps contribute to combustion. Manually accounting for all those contributing reactions is clearly an impossible task, and computer-based systems that automate calculation and error estimation of the chemical details become crucial. Indeed, those chemical details dictate the rates of combustion, pollutant emissions, and the ignition behavior of the engine under compression.

Unfortunately, the level of complexity that a predictive combustion model should address is greater still. Fuel-air mixtures are rarely homogeneous and usually contain both liquid and gas phases; ignition occurs in localized regions and proceeds outward; and turbulence, transport, and radiative properties depend on the energy-releasing chemistry. For example, microscopic reaction chemistry in an engine affects the development of macroscopic turbulent flow, and the change in temperature due to the altered flow dramatically affects the reaction rates. Similarly, thermal radiation is a dominant mode of heat transfer in diesel engines because the cylinders contain high levels of soot. At the higher pressures envisioned for many new engine concepts, gas-phase spectral radiation properties and turbulence-radiation interactions will attain great significance.

In addition to higher pressures—up to a factor of 10 greater than the 25 atmospheres of a conventional gasoline engine—combustion processes in next-generation engines will likely be characterized by lower temperatures (below 1900 K). As discussed in the box, low-temperature conditions minimize NO_x formation. Those conditions are achieved by running lean using excess air or by diluting the fuel-air mixture with inert gas, such as exhaust, composed principally of nitrogen, water, and carbon dioxide. Lean conditions have

the added benefit of reducing soot. With lower peak combustion temperatures, though, higher pressures are required to maintain engine power.

Unexplored thermodynamic environments combined with new physical and chemical fuel properties result in complex interactions that are not understood even at a fundamental level. Intermolecular and intramolecular energy transfer affect the local reactive environment. At high pressure, the mean free path becomes extremely short, and qualitatively new reaction intermediates, intermolecular collision events, and diffusion processes affect the chemical behavior during combustion. Further, evolving fuel streams will contain a greater range of hydrocarbon classes—oxygenates, naphthenes (a type of cycloalkane), and olefins among them, as pictured in figure 1—than fuels from current sources. Key aspects of the combustion kinetics of those compounds are unknown even at atmospheric pressure, and in the case of alcohols, esters, and ethers from biofuels, the more polar nature of the fuel also affects physical properties such as evaporation, viscosity, lubricity, heat transfer, and corrosivity.

Researchers must also model the first steps of the combustion process—the mixing and spray dynamics. To account for the wide range of physical and chemical properties of new fuels, current empirical spray models must be replaced by a fundamental first-principles understanding of how a liquid spray disperses, vaporizes, and mixes with air. New insight into the evolution of the spray is likely to come not just from a deeper understanding of fluid mechanics and the chemical reactivity of matter in different phases but also from innovative experimental probes of the turbulent spray at high pressures. The hope is that technical advances could lead to what's termed adaptive combustion, in which, for example, smart fuel injectors adjust to changing fuel characteristics and engine load conditions.

Yet another complication is the surface chemistry that occurs in cylinders, in catalytic converters, and during the formation and burnout of soot, which critically affects current diesel- and jet-engine performance. At higher pressures, lower temperatures, and leaner conditions than those typical of today's engines, an opportunity exists to lessen soot emissions if we gain the scientific insight required to characterize in-cylinder soot formation and destruction processes. One can envision advances in deposition techniques, for instance, to coat cylinder walls with oxidation catalysts to reduce unburned hydrocarbon emissions and control the transfer of heat between combusting gas and engine surfaces.

The grand challenge is to generate predictive, computa-

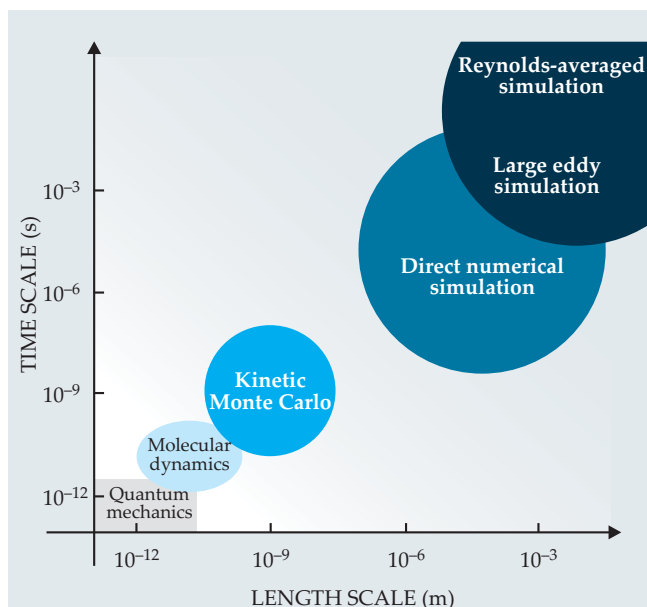


Figure 2. A wide range of approaches are used to simulate combustion. Quantum mechanical treatments describe interatomic processes for a small number of atoms. Molecular dynamics and kinetic Monte Carlo methods describe intermolecular processes for a population of atoms and molecules. Continuum mechanics approaches, such as direct numerical simulation, large eddy simulation, and Reynolds-averaged Navier–Stokes simulations, describe chemical and physical processes at macroscopic scales.

tional models of combustion. Accomplishing that goal requires a broad research program that integrates experiment, theory, and simulation. Unfortunately, researchers lack both the detailed understanding needed to even define the optimized set of validation experiments for advanced combustion strategies and the diagnostic tools required to perform them. Those tools need to be developed for all scales, from individual molecular reactions to combustion chambers. The hope is that researchers may then complete the move from empirical, hardware-intensive fuel and engine design to simulation-intensive design.

Modeling frontiers

One approach to studying real fuels, which may contain thousands of compounds, is to mimic their behavior using surrogate mixtures. The mixtures are created using far fewer compounds, which are easier to implement in a simulation but still contain many of the functional groups found in a real fuel.¹ The possibility of defining optimal fuel characteristics can guide researchers to evaluate the impact of different groups of compounds in a fuel. For example, aromatics and isoparaffins increase soot, *n*-paraffins accelerate ignition, and oxygenates reduce soot under diesel-like conditions.

Physical and combustion properties of the surrogate fuel could then be thoroughly measured for a wide range of temperatures, pressures, and combustors. With fewer fuel components, surrogates provide a simpler basis for developing and testing models of their properties in practical devices. And their simple compositions make them ideal for controlled experiments. In principle, variability in the makeup of a future fuel can be modeled by changing the amount of each

type of compound. For example, biodiesel blend surrogates can be represented by increased levels of a sample methyl ester, while a surrogate for oil-sand fuels would contain higher levels of a cyclic paraffin component. Strategies for predicting nitrogen oxide and sulfur oxide emissions may require other suitable surrogate reaction pathways. The technique of creating and using surrogate mixtures is in early stages of development but promises to accelerate our understanding of evolving fuels.

A predictive model requires a set of chemical reactions to describe the relevant combustion processes. But the corresponding reaction-rate coefficients are unknown for many of the thousands of reactions that occur.² Recent advances in theoretical chemical kinetics provide methods to accurately predict chemical-reaction kinetics from first principles.³ The present implementations of those methods are laborious, often rely on a researcher's chemical intuition, and thus far have been applied principally to alkanes and the simplest aromatic species at high temperatures. Little is known for more complex molecules.

Transport phenomena in engines and gas turbines further complicate combustion chemistry. At the microscopic scale, the changes in fuel composition affect reaction rates; at the macroscopic scale, changes in bulk liquid properties affect fuel injection and evaporation. Yet it remains impossible, even on the world's largest computers, to model phenomena in full detail simultaneously over the nine orders of magnitude that span the spatial scales. One strategy is to develop high-fidelity modeling and simulation tools for segments of the scale range and apply those tools in a practical framework that connects the different segments. That approach may provide a description of the details of molecular kinetics and the macroscopic turbulent mixing that together affect the overall performance.

Figure 2 illustrates a range of approaches that have been applied to combustion simulations. Multiscale modeling capabilities are needed both for scientific discovery and for design and optimization of advanced, efficient, clean engines.⁴ Direct numerical simulation (DNS), for example, is a high-resolution approach that directly solves the fundamental continuum-mechanics equations for chemically reacting flows at the smallest scales and can accurately describe the detailed chemical kinetics and transport phenomena for canonical flows. It can also provide fundamental physical and chemical insight into fine-grained turbulent-chemistry interactions occurring in novel combustion strategies.⁵

Another powerful engineering approach, large eddy simulation (LES), is based on a direct treatment of the large-scale dynamics and physical modeling of the small-scale variations. It can simulate the chemistry and physical processes in an engine cylinder down to the smallest reactive and diffusive scales of turbulence, while including a detailed description of the chemical kinetics of a fuel.⁶ LES can also be used to develop novel engine combustion strategies and as a next-generation engine-development and optimization tool. Even using approaches such as DNS and LES, though, multiscale modeling will require further development to become routinely applicable to real devices.

One difficulty is the numerical challenge of coupling disparate models that operate over different temporal and spatial regimes to create a comprehensive system model. Rigorous error-control procedures have not been developed for many of the submodels relevant to fuel chemistry and engine performance. Each submodel is based on a series of assumptions and approximations that, in turn, have been based on limited tests. As a consequence, researchers do not know

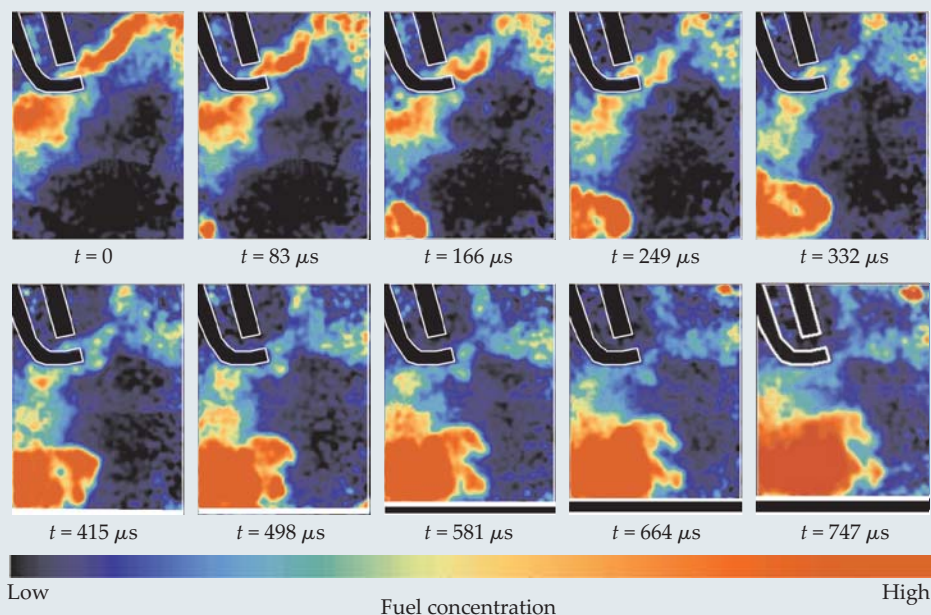


Figure 3. Strong spatial and temporal variations in the distribution of fuel are apparent in this sequence of images of a direct-injection gasoline engine as the fuel vapor passes the spark plug (top left) at time $t = 0$ and mixes with in-cylinder air before ignition occurs. These snapshots are just a few of the 12 000 images per second taken by laser-induced fluorescence of a tracer molecule in the fuel. (Courtesy of Volker Sick; see ref. 17.)

what accuracy to expect in predictions of the performance of new engines and fuels. A better understanding of the multi-scale coupling would allow them to design experiments focused on validating and verifying the models across the scales. A systematic overall approach is needed to create a virtual engine-development framework in which combustion strategies can be simulated in conditions that currently might not appear feasible.

Verification by experiment

Many advanced engine technologies rely on fuel chemistry to time the ignition event. The close relationship of ignition chemistry to engine development requires investigation of thermodynamic properties of new fuels and knowledge of reaction kinetics under conditions that approximate those of new engine designs. The already hostile experimental environment of an internal combustion engine is made more challenging by the higher operating pressures and more dilute mixtures in many of the emerging combustion strategies such as homogeneous charge-compression ignition, described in the box.

Increased pressure broadens spectral features and quenches the fluorescence, which makes many traditional optical diagnostics difficult. New species-specific detection methods are needed for the complex, often multiphase, high-pressure, high-temperature environments that occur in combustion devices. Development of such methods represents a formidable experimental challenge.

Historically, kinetic models of combustion chemistry have largely been developed by comparing experimental measurements with modeling predictions for controllable, representative systems such as low-pressure flames, high-pressure shock tubes (devices that produce a shock wave energetic enough to trigger a reaction), and flow reactors.⁷ Extension of that strategy to measure kinetics relevant to the combustion of nontraditional fuels in new types of engines will require innovation in both reactor design and detection methods.

With modern mass spectrometric and optical spectro-

scopic detection techniques, gas-phase kinetics^{8,9} and thermodynamics measurements¹⁰ of exquisite sensitivity can be carried out on both radical-molecule and radical-radical reactions. For relatively low pressures, kinetics studies are widely performed in reactor cells known as flow tubes at temperature ranges relevant to autoignition—roughly 700 K to 1000 K—and in shock tubes at higher combustion temperatures.¹¹ But those methods become more difficult as the molecular species become larger and as the pressure increases.

A central challenge for investigating the combustion chemistry of future fuels is to devise sensitive gas-phase methods to detect the key large molecular radicals of those fuels at the high temperatures and pressures of novel engine designs. Mass spectrometry is applicable at low pressure. Less intrusive *in situ* methods such as x-ray spectroscopy, broadband excitation, and multiplex spectroscopies using frequency combs might be adapted for harsh combustion environments. Furthermore, the challenge of taking measurements at high pressures and temperatures may be met by innovative cell design.

New diagnostic tools

Designing new engine concepts will require quantitative and sensitive diagnostic tools capable of delivering species-specific, spatially and temporally resolved measurements under engine-relevant conditions. Hot, sooting gases affect the performance of conventional probes and sensors. Moreover, the introduction of probes into a flame may disturb the system and bias the measurement. And conventional sensors may not be fast enough to follow the dynamics of combustion. Optical methods get around those problems. A case in point, figure 3 illustrates a series of high-repetition-rate laser-induced fluorescence images of fuel mixing with air in a cylinder.

Chemical-specific imaging probes become more challenging, however, for applications at high pressures and temperatures. Furthermore, the photophysics of target molecules in the fuel, needed for quantitative interpretation of the measured signals, is not yet understood at the high pressure and temperature conditions of interest for laser-based



Figure 4. Imaging the liquid core in an atomizing spray. (a) The structure of the leading edge of an impinging spray (entering from the upper right) is instantaneously captured using single-shot short-pulsed x-ray phase-contrast imaging with 300-ns resolution. The complex structure of the dense spray arises because of turbulence in the flow. The large balloonlike structure results from the initial ejection of static liquid trapped in the flow cavity, commonly called the sac volume. (Adapted from ref. 18.) (b) The near field of an atomizing diesel fuel spray is captured in this ballistic image taken with high spatial (25 μm) and temporal (3 ps)

resolution; gated detection records only the ultrafast laser photons that pass through the spray without scattering. The image shows voids—possibly caused by cavitation inside the nozzle—and shear-induced periodicity in the complex structure at the edges of the liquid core (outlined in blue). (Adapted from ref. 15.)

and chemiluminescence investigations.¹² Alternative fuels involve new chemical species not found in appreciable amounts when burning traditional hydrocarbon fuels. Measurement techniques will need to be developed for molecules that currently cannot be measured but are identified through simulations as important for novel combustion concepts.

The complexity of combustion systems naturally lends itself to multiplexed detection and analysis tools, such as Fourier-transform spectroscopy and time-of-flight mass spectrometry. And, indeed, those techniques have been applied to time-resolved multiple-species detection in laboratory reactors and in simple combustion systems. They detect many species, but typically only at a single point in space. The hope is to experimentally map the concentration of many species—various fuel components, radicals, pollutants, and other products—in time and space. The current state of the art, depicted in figure 3, maps only the time evolution of a tracer species in the fuel. Understanding the chemistry underlying that evolution in real devices is currently out of reach and will require multiple other measurements recorded at the same time, new methods of analysis, and computationally efficient three-dimensional reconstruction algorithms.¹³ X-ray synchrotron or free-electron laser sources and techniques, such as nonlinear spectroscopy and multiplexed frequency comb-based spectroscopy,¹⁴ may prove useful.

Perhaps the greatest experimental challenge is to capture the full complexity of the turbulent and multiphase reacting flow of an igniting jet of evaporating liquid fuel. To investigate so multifaceted a problem as spray combustion, researchers must resolve the chemical and physical properties of the fuel in its liquid and vapor phases. Some researchers envision powerful imaging capabilities that could simultaneously capture the evolution of the droplet sizes at submicron and submicrosecond resolution. Achieving that goal, however, calls for diagnostics that exploit new methods—the ballistic imaging of the structure of the liquid jet and acceleration of the liquid–gas interface,¹⁵ for instance—and a spectral range from the IR to the THz. To span that range, researchers may use techniques such as magnetic resonance, x-ray absorption, optical microscopy, and light scattering.¹⁶

Figure 4 illustrates two of those techniques, x-ray phase-contrast imaging and ballistic imaging, which can reveal structure in the liquid core of a dense spray.

Chemically sensitive spectroscopies, combined with scattering measurements, could follow the size and composition history of a single droplet in a turbulent multiphase flow. The methods could also follow the evolution of the spray all the way to gas-phase mixing phenomena at high pressure. At the spatial and temporal resolution envisioned, the chemical specificity in both gas and condensed phases would give truly unprecedented information about heterogeneous and interfacial chemistry and dynamics. The measurement of real devices with those methods would provide an exquisitely demanding test for increasingly sophisticated theoretical models.

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