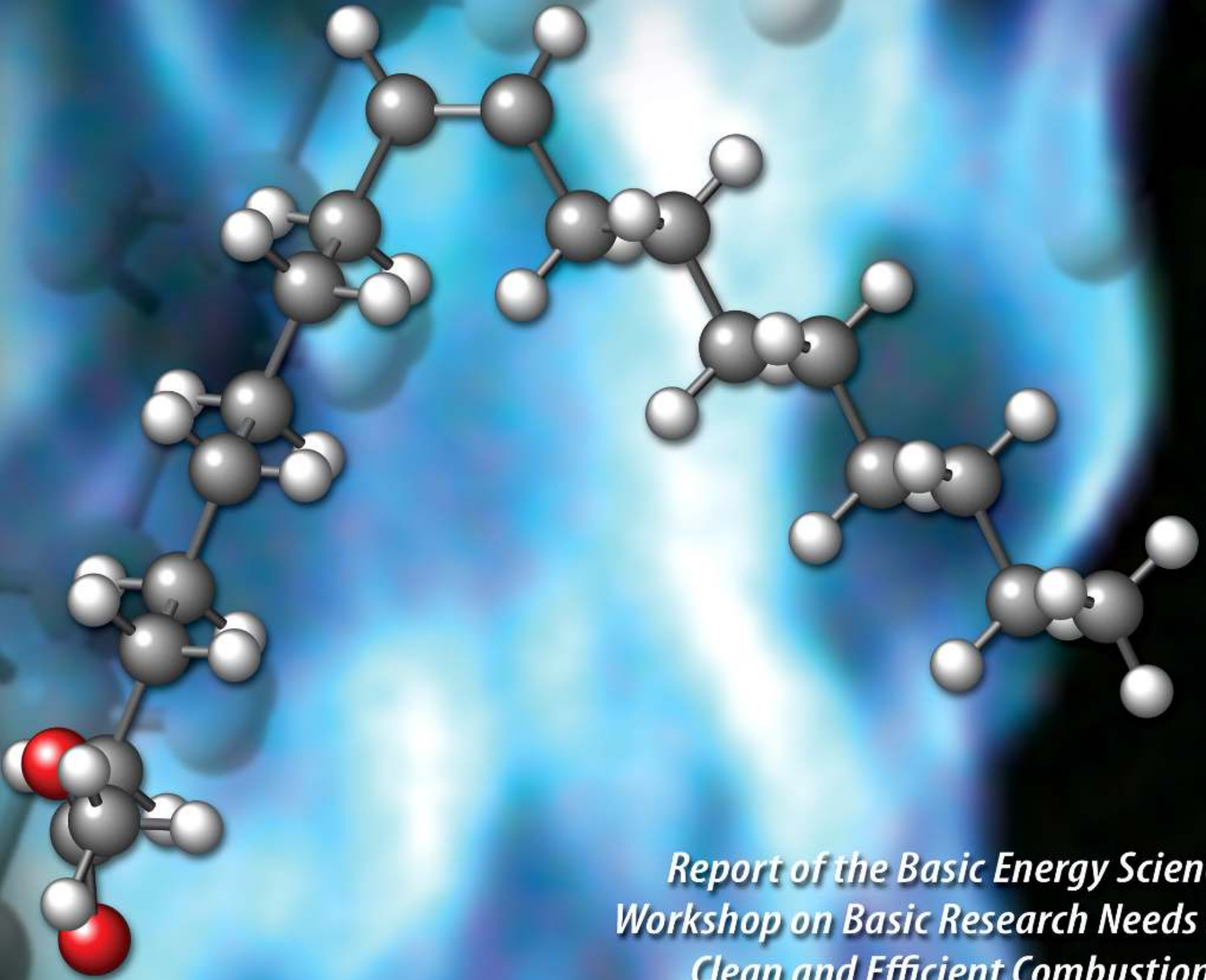
Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels



Report of the Basic Energy Sciences Workshop on Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels

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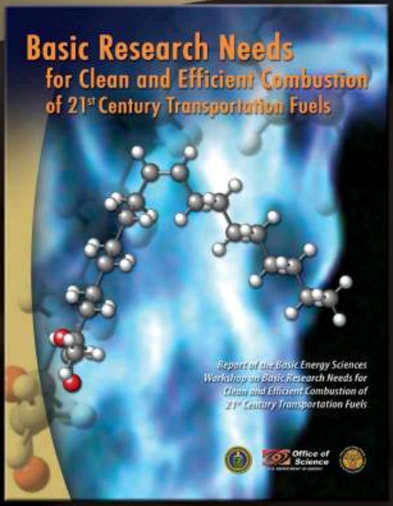
Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels

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On the Cover:

Transportation fuels for the 21st century will be derived from a wide range of sources from oil sands to biofuels. Here, a prototypical biodiesel, oleic acid methyl ester, burns in a clean blue flame. Biodiesels offer a potential hedge against global warming and may contribute to US energy security by enhancing renewable domestic feedstocks. The esters of biodiesel present new chemistry challenges through the inclusion of heteroatoms, the oxygen atoms shown in red among the grey carbon and white hydrogen atoms.

The wide range of potential 21st century transportation fuel sources poses many challenges. Complex reaction mechanisms will need to be developed more quickly and for species whose chemistry is poorly understood. Compounding these challenges is a simultaneous shift to new engine technologies that rely on unexplored pressure and fuel/air mixture regimes.

BASIC RESEARCH NEEDS FOR CLEAN AND EFFICIENT COMBUSTION OF 21st CENTURY TRANSPORTATION FUELS

Report of the Basic Energy Sciences Workshop
on
Clean and Efficient Combustion of 21st Century Transportation Fuels

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CONTENTS

NOTATION

ACRONYMS AND ABBREVIATIONS

4D	four dimensional
ASC	Advanced Simulation and Computing
BES	Basic Energy Science
BP	British Petroleum
C_1-C_4	hydrocarbons
C_3H_3	propargyl radical
C_7H_{16}	n-heptane
C_8H_{18}	iso-octane
CA	Crank Angle
CBCS	cyber-based combustion science
CCRD	Cross-Cutting Research Direction
CCS	Cross-Cutting Science
CFD	computational fluid dynamics
CH	carbon hydrogen
CH_4	methane
CMCS	Collaboratory for Multi-scale Chemical Science
CN	cetane number
CO	carbon monoxide
CO_2	carbon dioxide
COSMO	Consortium for Small Scale Modeling
COSMO-RS	a novel *a priori* predictive method for fluid phase dynamics
CTL	coal to liquid
DNS	direct numerical simulation
DOE	Department of Energy
E	Energy
EERE	Energy Efficiency and Renewable Energy
EGR	exhaust gas recirculation
EIA	Energy Information Administration
EPA	Environmental Protection Agency
ES	expert system
EU	European Union
FCVT	FreedomCAR and Vehicle Technologies (DOE)
FT	Fischer-Tropsch
GC	grand challenge
GDI	gasoline direct injection
GT	gas turbine
GTL	gas to liquid
H_2	hydrogen
H_2O_2	hydrogen peroxide
HC	hydrocarbon
HCCI	homogeneous charge compression ignition
HEI	Health Effects Institute
HFRR	high frequency reciprocating rig
HPC	high performance computing
IC	internal combustion
ICE	internal combustion engine
ICP	In situ conversion process
IR	infrared
ISO	International Organization for Standardization
ITR	Information Technology Research Program (NSF)
LD50	LD stands for "Lethal Dose". LD50 is the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals. Measured in mL/kg.
LDA	laser Doppler anemometry
LES	large-eddy simulation
LIF	laser-induced fluorescence
LII	laser-induced incandescence
LTC	low temperature combustion
MC	Monte Carlo
MD	molecular dynamics
MON	motored octane number
MTBE	methyl tertiary-butyl ether
N_2	nitrogen

NASA	National Aeronautics and Space Administration
NMR	nuclear magnetic resonance
NNSA	National Nuclear Security Administration
NO_x	nitrogen oxides
nPAH	nitrated polycyclic aromatic hydrocarbon
NREL	National Renewable Energy Laboratory
NSF	National Science Foundation
O_2	oxygen
OEDC	Organization for Economic Development and Cooperation
OPEC	Organization of the Petroleum Exporting Countries
PAH	polycyclic aromatic hydrocarbon
PDA	phase Doppler anemometry
PES	potential energy surface
PIV	particle imaging velocimetry
PLIF	Mie/Rayleigh/planar laser induced fluoresence
PRD	priority research direction
PrIMe	process informatics model
QM/MM	quantum mechanics/molecular mechanics
R	alkyl radical
R&D	research and development
RANS	Reynolds-averaged Navier-Stokes simulation
RAS	Reynolds-averaged simulation
RFS	renewable fuels standard
RMG	Reliability Management Group
RO_2	alkylperoxy radical
RON	research octane number
RQL	rich-quench-lean
SACI	spark-assisted compression ignition
SciDAC	scientific discovery through advanced computing (USDOE, Office of Science)
SI	spark ignition
SO_x	sulfur oxides
SUV	sports utility vehicle
TDC	top dead center
TNF	turbulent non-premixed flame
TS	transition state
TST	transition state theory
USIA	United States Information Agency
UV	ultraviolet
VUV	vacuum ultraviolet
WSD	wear scar diameter

UNITS OF MEASURE

Å	angstrom
bbl	barrel
BTU	British thermal unit, equal to 1 055.05585 joules
cm	centimeter
CAD	Crank Angle Degrees
ºC	degree Celsius
E	energy
J	angular momentum
J/deg.CA	joules per degree crank angle
K	Kelvin
mL/kg	milliliter per kilogram (measurement of LD50)
nm	nanometer
Quad	quadrillion BTUs
THz	terahertz

EXECUTIVE SUMMARY

EXECUTIVE SUMMARY

From the invention of the wheel, advances in transportation have increased the mobility of human kind, enhancing the quality of life and altering our very perception of time and distance. Early carts and wagons driven by human or animal power allowed the movement of people and goods in quantities previously thought impossible. With the rise of steam power, propeller driven ships and railroad locomotives shrank the world as never before. Ocean crossings were no longer at the whim of the winds, and continental crossings went from grand adventures to routine, scheduled outings. The commercialization of the internal combustion engine at the turn of the twentieth century brought about a new, and very personal, revolution in transportation, particularly in the United States. Automobiles created an unbelievable freedom of movement: A single person could travel to any point in the country in a matter of days, on a schedule of his or her own choosing. Suburbs were built on the promise of cheap, reliable, personal transportation. American industry grew to depend on internal combustion engines to produce and transport goods, and farmers increased yields and efficiency by employing farm machinery. Airplanes, powered by internal combustion engines, shrank the world to the point where a trip between almost any two points on the globe is now measured not in days or months, but in hours.

Transportation is the second largest consumer of energy in the United States, accounting for nearly 60% of our nation's use of petroleum, an amount equivalent to all of the oil imported into the U.S. The numbers are staggering—the transport of people and goods within the U.S. burns almost one million gallons of petroleum each minute of the day. Our Founding Fathers may not have foreseen freedom of movement as an inalienable right, but Americans now view it as such.

Knowledge is power, a maxim that is literally true for combustion. In our global, just-in-time economy, American competitiveness and innovation require an affordable, diverse, stable, and environmentally acceptable energy supply. Currently 85% of our nation's energy comes from hydrocarbon sources, including natural gas, petroleum, and coal; 97% of transportation energy derives from petroleum, essentially all from combustion in gasoline engines (65%), diesel engines (20%), and jet turbines (12%). The monolithic nature of transportation technologies offers the opportunity for improvements in efficiency of 25-50% through strategic technical investment in advanced fuel/engine concepts and devices. This investment is not a matter of choice, but, an economic, geopolitical, and environmental necessity. The reality is that the internal combustion engine will remain the primary driver of transport for the next 30-50 years, whether or not one believes that the peak in oil is past or imminent, or that hydrogen-fueled and electric vehicles will power transport in the future, or that geopolitical tensions will ease through international cooperation. Rational evaluation of U.S. energy security must include careful examination of how we achieve optimally efficient and clean combustion of precious transportation fuels in the 21st century.

The Basic Energy Sciences Workshop on Clean and Efficient Combustion of 21st Century Transportation Fuels

Our historic dependence on light, sweet crude oil for our transportation fuels will draw to a close over the coming decades as finite resources are exhausted. New fuel sources, with differing characteristics, are emerging to displace crude oil. As these new fuel streams enter the market, a series of new engine technologies are also under development, promising improved efficiency and cleaner combustion. To date, however, a coordinated strategic effort to match future fuels with evolving engines is lacking.

To provide the scientific foundation to enable technology breakthroughs in transportation fuel utilization, the Office of Basic Energy Sciences (BES) in the U.S. Department of Energy (DOE) convened the Workshop on Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels from October 30 to November 1, 2006. This report is a summary of that Workshop. It reflects the collective output of the Workshop participants, which included over 80 leading scientists and engineers representing academia, industry, and national laboratories in the United States and Europe. Researchers specializing in basic science and technological applications were well represented, producing a stimulating and engaging forum. Workshop planning and execution involved advance coordination with DOE Office of Energy Efficiency and Renewable Energy, FreedomCAR and Vehicle Technologies, which manages applied research and development of transportation technologies.

Priority research directions were identified by three panels, each made up of a subset of the Workshop attendees and interested observers. The first two panels were differentiated by their focus on engines or fuels and were similar in their strategy of working backward from technology drivers to scientific research needs. The first panel focused on novel combustion, as embodied in promising new engine technologies. The second panel focused on fuel utilization, inspired by the unique (and largely unknown) challenges of the emerging fuel streams entering the market. The third panel explored crosscutting science themes and identified general gaps in our scientific understanding of 21st century fuel combustion. Subsequent to the Workshop, co-chairs and panel leads distilled the collective output to produce eight distinct, targeted research areas that advance one overarching grand challenge: to develop a validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications.

Fuels and Engines

Transportation fuels for automobile, truck and aircraft engines are currently produced by refining petroleum-based sweet crude oil, from which gasoline diesel fuel and jet fuel are each made with specific physical and chemical characteristics dictated by the type of engine in which they are to be burned. Standardized fuel properties and restricted engine operating domains couple to provide reliable performance. As new fuels derived from oil sands, oil shale, coal, and bio-feedstocks emerge as replacements for light, sweet crude oil, both uncertainties and strategic opportunities arise. Rather than pursue energy-intensive refining of these qualitatively different emerging fuels to match current fuel formulations, we must strive to achieve a “dual revolution” by interdependently advancing both fuel and engine technologies. Spark-ignited gasoline engines equipped with catalytic after-treatment operate cleanly but well below optimal efficiency due to low compression ratios and throttle-plate losses used to control air intake. Diesel engines operate more efficiently at higher compression ratios but sample broad realms of fuel/air ratio, thereby producing soot and NO_x for which burnout and/or removal can prove problematic. A number of new engine technologies are attempting to overcome these efficiency and emissions compromises. Direct injection gasoline engines operate without throttle plates, increasing efficiency, while retaining the use of a catalytic converter. Ultra-lean, high-pressure, low-temperature diesel combustion seeks to avoid the conditions that form pollutants, while maintaining very high efficiency. A new form of combustion, homogeneous charge compression ignition (HCCI) seeks to combine the best of diesel and gasoline engines. HCCI employs a premixed fuel-air charge that is ignited by compression, with the ignition timing controlled by in-cylinder fuel chemistry. Each of these advanced combustion strategies must permit and even exploit fuel flexibility as the 21st century fuel stream matures. The opportunity presented by new fuel sources and advanced engine concepts offers such an overwhelming design and operation parameter space that only those technologies that build upon a predictive science capability will likely mature to a product within a useful timeframe.

Research Directions

The Workshop identified a single, overarching grand challenge: *The development of a validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications*. A broad array of discovery research and scientific inquiry that integrates experiment, theory, modeling and simulation will be required. This predictive capability, if attained, will change fundamentally the process for fuels research and engine development by establishing a scientific understanding of sufficient depth and flexibility to facilitate realistic simulation of fuel combustion in existing and proposed engines. Similar understanding in aeronautics has produced the beautiful and efficient complex curves of modern aircraft wings. These designs could never have been realized through cut-and-try engineering, but rather rely on the prediction and optimization of complex air flows. An analogous experimentally validated, predictive capability for combustion is a daunting challenge for numerous reasons: (1) spatial scales of importance range from the dimensions of the atom up to that of an engine piston; (2) the combustion chemistry of 21st century fuels is astonishingly complex with hundreds of different fuel molecules and many thousands of possible reactions contributing to the oxidative release of energy stored in chemical bonds—chemical details also dictate emissions profiles, engine knock conditions and, for HCCI, ignition timing; (3) evolving engine designs will operate under dilute conditions at very high pressures and compression ratios—we possess neither sufficient concepts nor experimental tools to address these new operating conditions; (4) turbulence, transport, and radiative phenomena have a profound impact on local chemistry in most combustion media but are poorly understood and extremely challenging to characterize; (5) even assuming optimistic growth in computing power for existing and envisioned architectures, combustion phenomena are and will remain too complex to simulate in their complete detail, and methods that condense information and accurately propagate uncertainties across length and time scales will be required to optimize fuel/engine design and operation. Eight priority research directions, each of which focuses on crucial elements of the overarching grand challenge, are cited by the workshop participants as most critical to the path forward.

In addition to the unifying grand challenge and specific priority research directions, the Workshop produced a keen sense of urgency and opportunity for the development of revolutionary combustion technology for transportation based upon fundamental combustion science. Internal combustion engines are often viewed as mature technology, developed in an Edisonian fashion over a hundred years. The participants at the Workshop were unanimous in their view that only through the achievable goal of truly predictive combustion science will the engines of the 21st century realize unparalleled efficiency and cleanliness in the challenging environment of changing fuel streams.

INTRODUCTION

INTRODUCTION - MOTIVATION AND OPPORTUNITIES

Energy Needs

Our nation requires a secure, economical, and environmentally acceptable energy supply to uphold our standard of living, ensure our national security, and maintain our economic competitiveness. Currently 85% of our nation's energy comes from hydrocarbon sources including natural gas, petroleum, and coal. America's total energy use as of 2005 was split among transportation (28%), industrial use (32%), residential use (22%), and commercial use (18%). While total energy consumption has increased, this distribution has remained fairly constant over the last 50 years, as shown in Figure 1, with the greatest increase in the transportation sector. Transportation accounts for one of the largest uses of energy; indeed when electric power is factored out, transportation is the largest single user of energy. For transportation, 97% of transportation energy derives from petroleum. Of total petroleum consumption, 44% is used for gasoline, 14% for diesel, and 8% for aviation fuel. The fraction of petroleum imported into the U.S., 60%, is roughly equal to that consumed in the ground transportation sector. The transportation sector's dominant role in consumption suggests that efficiency improvements in this sector can have a large impact on the nation's energy use. The monolithic nature of transportation energy use, liquid fuels used in internal combustion engines, means that unlike industrial energy use, a relatively small number of technologies and fuel sources need be considered.

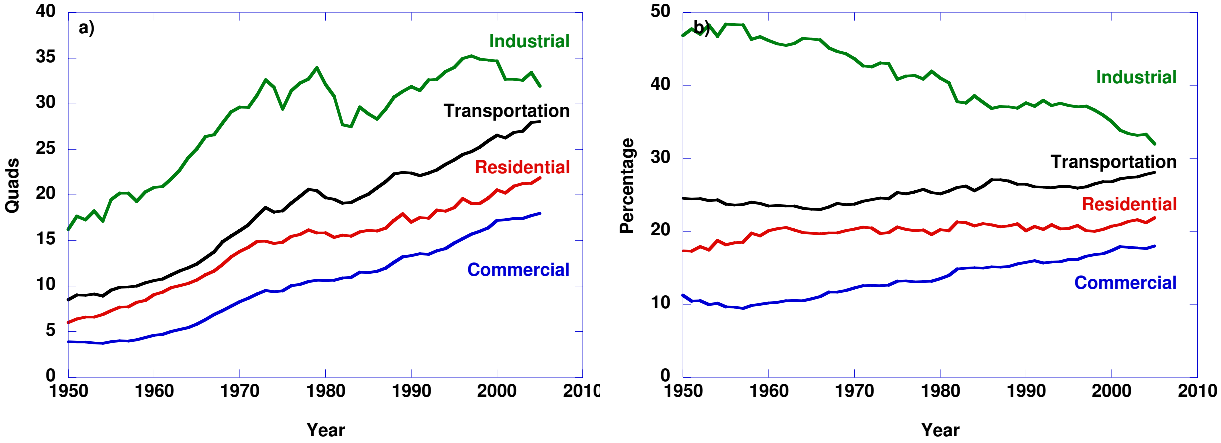


Figure 1. a) Energy consumption by end use in the United States from 1950 to 2005 in quadrillion BTUs (Quads). b) Relative energy use by end use in the United States from 1950 to 2005. Source: Energy Information Administration, Annual Energy Review 2005, Report No. DOE/EIA-0384(2005).

Petroleum plays the central role in the current transportation energy picture and indeed in the world's total use of energy. The total demand for energy is expected to increase steadily throughout the world with particularly large increases in the demands from emerging economies, as shown in Figure 2. Total oil use is projected to grow from 162 Quads in 2003 to 239 Quads in 2030 with 60% of that increase being used in transportation.

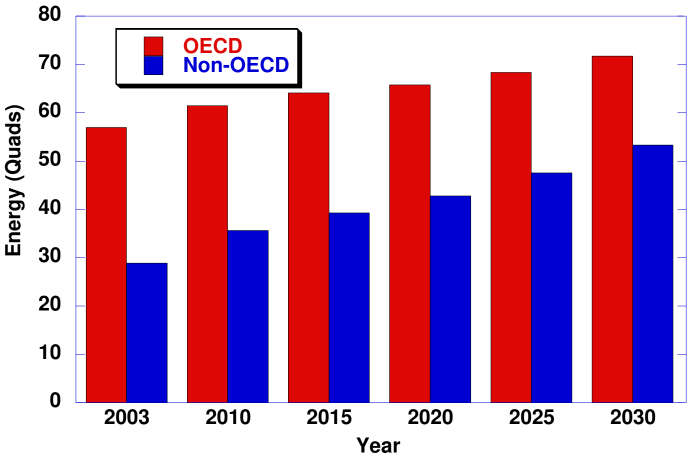


Figure 2. Projected worldwide transportation energy use in Quads from 2003 to 2030. OECD is the Organization for Economic Development and Cooperation. OECD member countries represent the developed world and non-OECD member countries the developing world. Source: Energy Information Administration, Annual Energy Review 2005, Report No. DOE/EIA-0484(2006).

While energy demand is increasing steadily, oil prices have remained relatively stable until recently, as shown in Figure 3. After adjusting for inflation, oil prices have historically stabilized in the range \$20-\$30/barrel with the exception of the 1970's oil crisis and current prices. The peak in the 1970's has largely been attributed to OPEC production restrictions. The current rise in prices does not correspond to artificially limited production. With projections of a steady rise in demand, new sources of liquid hydrocarbon fuels will be needed to maintain energy prices near their historic values.

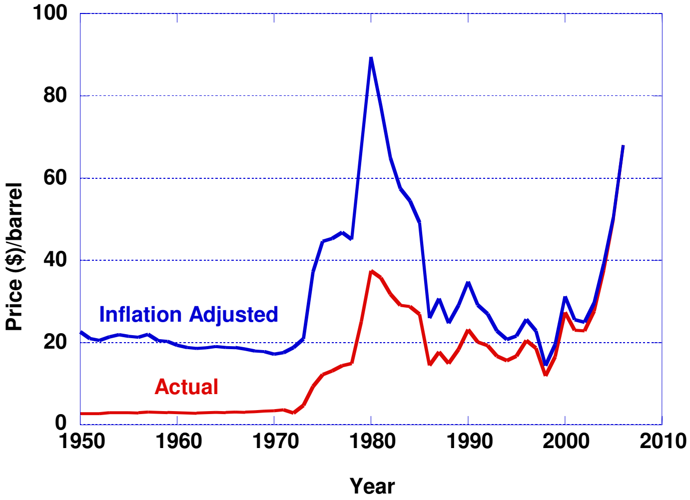


Figure 3. Oil prices 1945 to present in actual dollars and inflation adjusted dollars.

Table 1 lists the largest known oil reserves. At current consumption rates, about 18 billion barrels per year, these reserves would last for approximately 70 years. As noted above, consumption is projected to increase by 50% in the next 20 years. While new reserves are continuing to be added, the rate of new discoveries is declining, as shown in Figure 4. Various estimates with different assumptions have been made regarding the peak of oil production and lifetime of reserves. Although there is disparity in these estimates, oil is certainly a finite resource. Most estimates indicate that the "end of oil", as we now know it, i.e. light sweet crude, will occur in the next 50-100 years.

Other than the oil sands of Canada, the reserves shown in Table 1 lie in countries with complex to unfriendly relations with the U.S. The ever-increasing reliance of the U.S. on energy from such regions is a national security issue. Diversifying our energy sources to include more domestic fuels would enhance U.S. security, generate new industries and jobs, and protect our economy from geopolitical upheaval. Essentially all of the alternative fuel sources can be domestically produced or are found in stable, friendly regions.

Table 1: Largest known oil reserves.

Rank	Country	Proved reserves (billion barrels)
1.	Saudi Arabia	261.9
2.	Canada	178.8[1]
3.	Iran	125.8
4.	Iraq	115.0
5.	Kuwait	101.5
6.	United Arab Emirates	97.8
7.	Venezuela	77.2
8.	Russia	60.0
9.	Libya	39.0
10.	Nigeria	35.3

NOTES: Proved reserves are estimated with reasonable certainty to be recoverable with present technology and prices. 1. Includes 174.5 billion barrels of oil sands reserves.
Source: Oil & Gas Journal, Vol. 102, No. 47 (Dec. 10, 2004). From: U.S. Energy Information Administration. http://www.eia.doe.gov/emeu/international/petroleu.html .

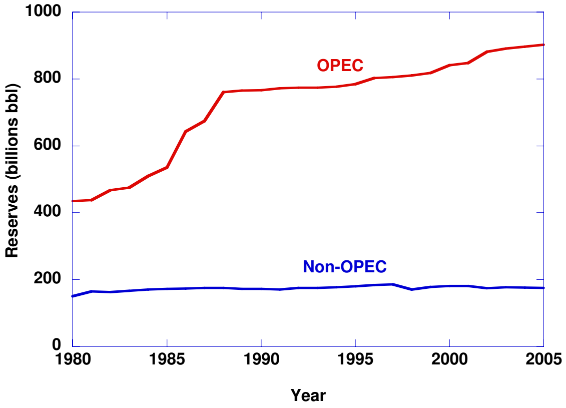


Figure 4. Proved oil reserves 1980-2005, not including Canadian oil sands, from BP Statistical Review of World Energy, June 2006, http://www.bp.com/statisticalreview.

Energy Consequences

Energy use has consequences that extend beyond immediate applications. Environmental impacts can be particularly significant. Urban smog is largely attributed to combustion byproducts. The adverse health effects associated with smog have led to considerable regulation in this country to limit the emissions of NO_x, hydrocarbons, and other pollutants from internal combustion engines. Controlling these emissions while maintaining high efficiency is a challenge for combustion scientists and engine manufacturers. A combination of improved combustion technology and exhaust after treatments has reduced and nearly eliminated these emissions from gasoline spark-ignited engines. Diesel compression ignition engine emissions have proven more difficult to control in part because catalytic aftertreatment systems have not been practical for these engines. Regulations continue to tighten, with new diesel emissions regulations to come into effect in 2010. The high efficiency of diesel engines makes it critical to meet these new regulations.

Increasingly, human activity and in particular anthropogenic emission of CO_2 are linked to global climate change. Recent studies have shown strong correlations between the atmospheric temperature and atmospheric CO_2 and methane concentrations over hundreds of thousands of years, as shown in Figure 5.

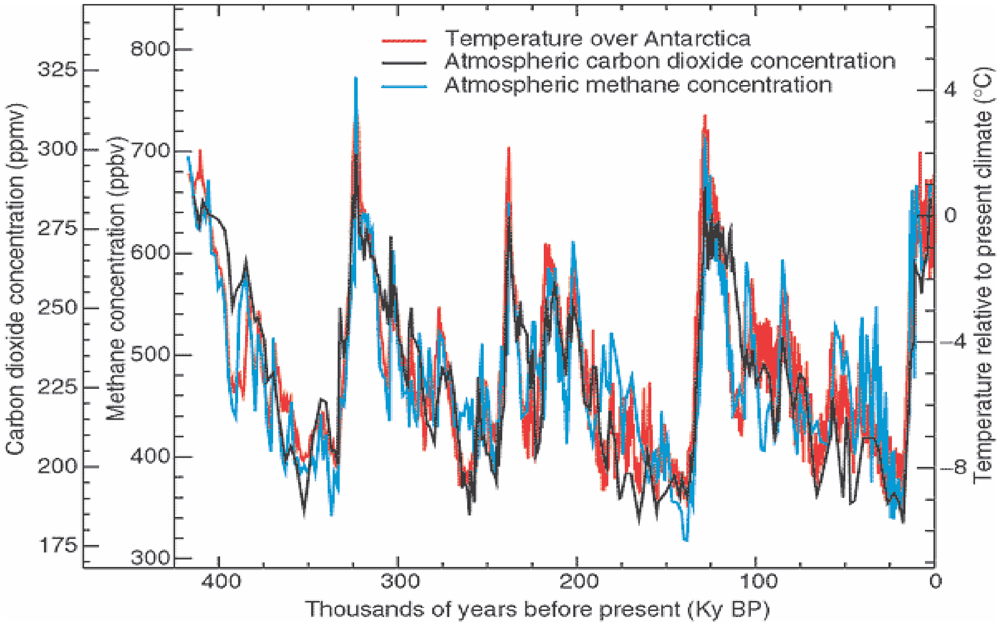


Figure 5. Correlation of atmospheric temperature over Antarctica with carbon dioxide and methane concentrations. Source: Petit J.R., Jouzel J., Raynaud D., Barkov N.I., Barnola J.M., Basile I., Bender M., Chappellaz J., Davis J., Delaygue G., Delmotte M., Kotlyakov V.M., Legrand M., Lipenkov V., Lorius C., Pépin L., Ritz C., Saltzman E., Stievenard M. (1999). "Climate and Atmospheric History of the Past 420,000 years from the Vostok Ice Core, Antarctica". *Nature* **399**: 429-436.

Given this strong correlation and growing evidence that CO_2 is causally related to global warming through the greenhouse effect, the rapid rise in atmospheric CO_2 concentration over the past 50 years is noteworthy. As shown in Figure 6, atmospheric concentrations of CO_2 have risen to over 370 ppm, well above the historical peaks of 300-325 ppm shown in Figure 5 associated with past cycling from periods of warming to ice ages. The long atmospheric lifetime of CO_2 (50-200 years, US EPA) indicates that essentially permanent, significant reductions in anthropogenic CO_2 emissions are required to stabalize CO_2 levels within even a few generations.

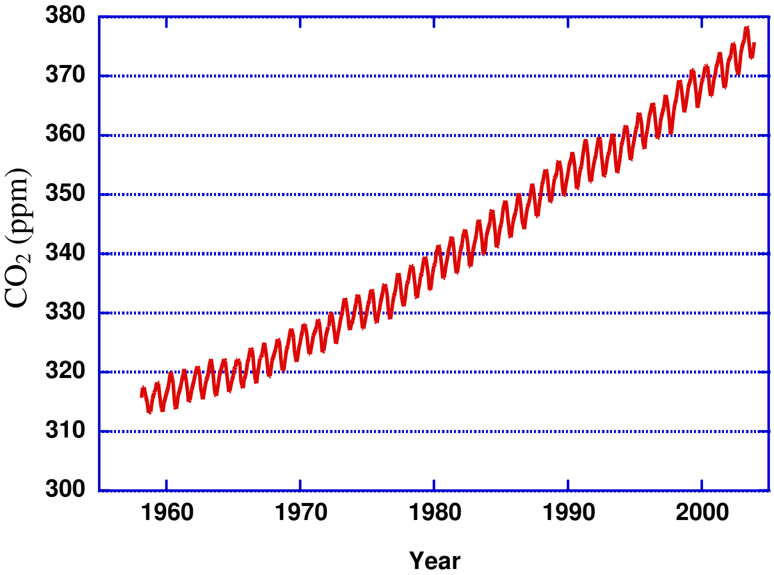


Figure 6. Measured CO_2 concentration for the last 45 years at Mauna Loa, Hawaii. Source: C. D. Keeling and T. P. Whorf, "Atmospheric CO_2 Concentrations - Mauna Loa Observatory, Hawaii, 1958-2002," Numeric Data Package NDP-001, Oak Ridge, TN, Carbon Dioxide Information Analysis Center, Revised August 2003, http://cdiac.esd.ornl.gov/ndps/ndp001.html

Anthropogenic greenhouse gas emissions come primarily from energy production. In 2002, U.S. greenhouse gas emissions were dominated by energy-related CO_2 emissions. These emissions accounted for 82.8% of U.S. greenhouse gas emissions in that year. Combustion accounts for essentially all of this CO_2. Increases in efficiency can reduce these emissions, and switching to renewable fuel sources such as biofuels can further reduce or eliminate the net CO_2 emissions.

While not the focus of this document, energy use is integrally connected to our nation's and the world's economy. The U.S. economy in particular has been driven over the last 50 years by the availability of relatively cheap oil. We take for granted that transportation of goods and people is inexpensive, enabling the dispersion of the population in the U.S. over wide ranges. Our standard of living is based on the ability to move goods over great distances quickly and cheaply. Although there may be great controversy over whether the peak in total oil production is near, there is little doubt that the supply of light, sweet crude, the cheap oil on which our economy is built, will peak in the next few decades. As new, typically more expensive sources of fuel come on line, efforts to produce higher efficiency will help maintain an economically acceptable infrastructure while also mitigating adverse environmental effects.

Path Forward

As combustion technologies move forward into the 21st Century, several challenges lie ahead. Environmental acceptability will play a key role in an evolving regulatory climate. At the same time, reducing the U.S. dependence on foreign oil is likely to continue as a prime driver. These two forces may push in different directions, particularly if carbon management regulation becomes a reality. For example exploiting proven oil shale reserves could reduce the U.S. dependence on foreign oil, but tapping these reserves would not reduce carbon emissions. Other developments hold the promise of addressing both issues simultaneously; for example, increases in efficiency would both reduce emissions and reduce foreign oil consumption.

Two developments in the transportation energy sector offer new challenges and opportunities: (1) utilization of non-traditional fuel sources, and (2) the creation of novel engine technologies. Appendix 1 provides a more extensive review of the state of these two areas. New fuel sources include bio-derived fuels, such as ethanol and biodiesel, and new fossil fuel sources, such as oil sands and oil shale. These new fuel sources offer a number of advantages and challenges. They generally require substantially more processing from feedstock to fuel than traditional oil. They offer the potential to reduce substantially our dependence on foreign oil since all except the Canadian oil sands may be produced domestically. The bio-derived fuels may also reduce emissions of CO_2.

As new engine technologies are developed, this processing becomes an opportunity to optimize the fuel stream for new engines and potentially to develop fuels substantially different from the current gasoline and diesel fuels. Indeed, new fuels may be required for some new engines to function within existing environmental regulations. Together these developments offer the potential for more efficient, cleaner transportation systems that use domestic energy sources.

THE WORKSHOP ON CLEAN AND EFFICIENT COMBUSTION OF 21ST CENTURY TRANSPORTATION FUELS

The U.S. Department of Energy (DOE) Office of Basic Energy Sciences held a Workshop on Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels from October 30 to November 1, 2006, in Arlington, Virginia, to determine and prioritize scientific issues and opportunities that might address the challenges associated with the efficient utilization of new and evolving transportation fuels. This workshop followed the format of earlier BES workshops, including the overarching "Basic Research Needs to Ensure a Secure Energy Future" (October 2002) and topical basic research needs workshops on the hydrogen economy (May 2003), solar energy utilization (April 2005), superconductivity (May 2006), solid-state lighting (May 2006), and advanced nuclear energy sources (July-August 2006).

The workshop brought together over 80 participants, including experts in a range of scientific and engineering disciplines related to fuel chemistry, physics, and utilization (Appendix 2 contains the full list of participants). Participants were drawn from academia, industry, and national laboratories in the U.S. and Europe, with expertise spanning physics, chemistry, modeling, and engine and turbine design. Their charge was to identify basic research needs and opportunities underlying utilization of evolving transportation fuels, with a focus on new or emerging science challenges that have the potential for significant long-term impact on fuel efficiency and emissions. The workshop generated a set of priority research directions (PRDs) aimed at scientific breakthroughs that would enable revolutionary, not evolutionary, progress in fuel utilization. A single, overarching grand challenge (GC) is identified, that of predictive modeling of combustion in realistic devices. Such a capability would fundamentally change the way combustion devices are designed and provide the ability to optimize new combustion systems based on alternative fuels and new combustion strategies in ways that are currently impossible.

The workshop was comprised of three panels that examined the fundamental science challenges associated with evolving transportation fuels. The first panel addressed the utilization of fuels, with a focus on the increasing diversity of fuels and their characteristics. The second panel addressed evolving combustion technologies, with an emphasis on the interplay between fuels and the devices. A third panel represented cross-cutting and out-of-the-box research challenges such as high-pressure kinetics and advanced diagnostic techniques. The chairs of the panels were drawn from universities and national laboratories.

Patricia Dehmer, Director of BES, launched the opening plenary session of the workshop, presenting the charge to participants and the scope. Experts from academia and industry set the stage with plenary talks on the technology and economic drivers for cleaner fuels and combustion devices, the current state of transportation fuels and devices, and perceived scientific challenges associated with evolving fuel sources. James Eberhardt, from DOE’s Office of Energy Efficiency and Renewable Energy, FreedomCAR and Vehicle Technologies Program Office, briefed the participants on the magnitude of the nation’s energy problem with respect to conventional fuel sources, and summarized current efforts in the use and development of evolving fuel sources and engine technologies. The chairs of the workshop panels then outlined specific scientific questions, the answers to which could generate game-changing advances in the use of transportation fuels.

Following the opening plenary session, the participants divided into individual panels that examined evolving fuels, new combustion strategies, and cross-cutting science (see Appendix 3 for the workshop programs). Each of these panels invited experts to analyze the grand challenges and scientific routes to achieve them. The panels then developed a set of high-priority research directions with the potential to produce revolutionary breakthroughs in fuel utilization and technologies for the transportation sector. The panel chairs also gathered emerging cross-cutting research directions (CCRDs) which became candidates for the GC. Selection and development of the final GC occurred at additional workshop-level meetings between the panel chairs and conference chairs. These PRDs, CCRDs, and GC are the major output of the workshop and comprise the bulk of this report.

OUTLINE OF REPORT

This report presents information on several levels. This Introduction describes the motivation and challenge of reducing the nation’s dependence on crude oil while simultaneously describing the potential for improvements in efficiency and emissions for new fuel types and new combustion devices. The reports from the panels give overviews of the scientific basis for each of the panel areas, and describe the research challenges that must be met for evolving fuels to replace current crude oil resources.

The associated PRDs represent the collective ideas of the workshop and are its most specific output. They identify high-priority science with the potential to clear away current technological roadblocks and generate revolutionary progress in bringing new fuels to a point at which they can substantially replace conventional sources. These PRDs and CCRDs are promising routes to achieving the GC.

A brief Conclusion sums up the main body of the report and is followed by three appendices that provide additional information helpful in understanding the workshop and this report. Appendix 1 contains a technology assessment that describes the current state of combustion technologies and fuels used for transportation. It also presents a high-level overview of the various technological gaps associated with evolving fuels. Appendices 2 and 3 list the participants of the workshop, and the workshop plenary and breakout agendas.

REPORTS OF THE PANELS OF BASIC RESEARCH NEEDS FOR CLEAN AND EFFICIENT COMBUSTION OF 21ST CENTURY TRANSPORTATION FUELS

Reports of the Panels of Basic Research Needs for Clean and Efficient Combustion of 21^{st} Century Transportation Fuels

NOVEL COMBUSTION PANEL

CURRENT STATUS

New combustion strategies are under investigation for internal combustion engines (ICEs) for ground transportation [Zhao et al. 1999, 2003] and gas turbines (GT) for air transportation [Ballal and Zelina 2004]. These novel combustion strategies offer the potential for enabling propulsion systems with significantly increased fuel efficiency and dramatically reduced pollutant emissions. Moreover, concurrent with the fuel efficiency improvements, reductions in greenhouse gas emissions (CO_2) responsible for global climate change would occur in direct proportion. Fuel efficiency improvements enabled by advanced combustion technologies of 50% or more for automotive engines (relative to spark-ignition engines dominating the road today in the U.S.) and 25% or more for heavy-duty truck engines (relative to today's diesel truck engines) are possible in the next 10 to 15 years. Substantial efforts are currently under way toward such targets in the U.S. as part the DOE/EERE FreedomCAR and 21st Century Truck programs. For civil aviation gas turbine engines, a 15% reduction in fuel consumption and associated CO_2 emissions, and a 70% reduction in NO_x are envisioned in the next decade through optimization of novel combustion technologies coupled with improvements in temperature tolerant materials (NASA Ultra-Efficient Engine Technology Program). In the long term, development of active control approaches for improving gas turbine performance and reducing emissions hold additional promise. Regulations on CO_2 emissions, such as the new EU CO_2 cap and trade regulation to stabilize civil aviation emissions at 2005 levels just adopted in late 2006, may also result in significantly more aggressive CO_2 reductions and efficiency improvements for engines.

Simultaneous with efforts to increase the fuel efficiency and decrease the environmental impact of engines for transportation, a new, diversified fuel source future is emerging in the marketplace as we move forward into the 21st century. The changing fuel picture is driven by government policy and high oil prices. Bio-derived fuels are already being blended with gasoline and diesel fuel for automotive and heavy-duty ground transportation. For example, ethanol currently accounts for about 3% of the automotive fuel use in the U.S. and is expected to rise significantly. Likewise, biodiesel use in the U.S., while very small, has undergone a 300-fold increase in six years. Fuels derived from oil sands, heavy-crude oils, and Fischer-Tropsch (FT) gas-to-liquid processes are also entering the market in limited, but growing quantities. For civil aviation gas turbines, synthetic FT fuels appear the most viable fuel in the near term. Recent successful flight demonstrations with FT/kerosene fuel blends underscore their potential, though significant additional research is needed. Biodiesel blended with kerosene may also be relevant in the near future for aviation, but challenges, such as thermal stability, still exist. The trend of fuel diversification by blending new fuels with current oil-derived fuels is likely to continue and accelerate, especially with respect to bio-fuels, which have a long-term potential for being carbon-neutral fuel sources. Furthermore, fuels from additional new sources such as oil shale and coal-to-liquids will potentially enter the market in the future, bringing their own fuel characteristics.

While the ultimate fuel path that will emerge in the coming decades is unclear and will depend on many factors, it is certain that dramatic changes have already started and will continue to occur. This changing fuel supply picture, combined with the need to develop high-efficiency, clean engine technologies to reduce fuel use, greenhouse gas emissions, and pollutant emissions, creates significant new uncertainties and unprecedented challenges for engine manufacturers and fuel producers—challenges that did not exist when the fuels were derived solely from easily obtained sweet crude oil. Engine manufacturers will need to develop engines that can accommodate large variations in fuel composition as fuels from diverse feedstocks are blended in increasing quantities with gasoline, diesel and potentially jet fuels, or as completely new fuels emerge. Concurrently, fuel producers will be faced with the challenge of producing fuels that are compatible with emerging high-efficiency engines enabled by novel combustion strategies. Along with the challenges, however, comes an opportunity to optimize fuel and engine technologies for maximum efficiency and minimum environmental impact. The opportunity to incorporate fuel properties into the ICE and GT design approach is intriguing. A collection of bio- and synthetic fuels used either in place of, or blended with conventional hydrocarbon fuels, provides an opportunity to benefit from the best features of each fuel. These fuels may enable novel combustion approaches, and the possible elimination of sulfur may open up other advanced approaches previously thought impossible. Together, the emerging engine and fuel picture offers the potential for dramatically more efficient, cleaner transportation systems that rely to a greater extent on domestic energy sources.

To achieve the “dual revolution” of simultaneously advancing both fuels and engines, fuel producers and engine manufacturers alike will need a comprehensive science foundation on which to develop and build their new fuel production processes and engine designs. This foundation must span a range of knowledge from the most fundamental facets of fuel chemical and physical properties for a wide range of future fuels, to the impact of these properties on all aspects of the performance and emissions of the emerging new high-efficiency, clean engine technologies. It must also include both the knowledge-base and the advanced modeling and simulation tools that embody the information. Such a foundation will help steer the emerging fuel-engine picture toward the most energy-efficient and lowest environmental-impact solution and to reduce the risks associated with large capital investments that will be needed to build future engine and fuel production capabilities. Such a foundation will also help strengthen U.S. competitiveness in the critical transportation technology field.

The most promising directions for novel combustion strategies for high-efficiency, clean ICEs and GTs involve combustion of lean or dilute fuel-air mixtures beyond limits that have been reached to date. In general, the new combustion strategies require operating near poorly understood limits of combustion stability and/or at conditions for which the combustion reaction zone development in IC engines and stabilization in GTs are not understood. A major additional complication to the challenge is the fact that these strategies are typically fuel sensitive. This sensitivity adds great uncertainty given the emerging fuel picture and means that a greatly improved understanding of how fuels will impact the various combustion strategies will be required to enable and optimize efficient, clean transportation propulsion systems for the emerging diversified fuel source future.

Novel combustion strategies for ICEs range from compression-ignition combustion of very dilute fuel-air mixtures, referred to as Low-Temperature Combustion (LTC), to spark-ignited combustion of stratified fuel air-mixtures achieved by injection of gasoline directly into an engine cylinder, referred to as Gasoline Direct Injection (GDI). The LTC option, for gasoline and diesel fuels, offers the highest efficiency and cleanest combustion potential relative to today's spark-ignited automotive engines dominating the road in the U.S today. The GDI option offers about half the efficiency improvement of LTC, but at potentially lower cost and less complexity. GDI's efficiency improvement comes from using the quantity of fuel injected to control engine load (i.e., power output). This form of load control eliminates the substantial "throttling energy losses" associated with load control achieved by restricting the intake air and fuel charge in current spark-ignited engines dominating the road today. LTC options combine the advantages of load control via the quantity of fuel injected with higher, diesel-like compression (or expansion) ratios. In a way, advanced engine development efforts under way have begun to combine advantages of gasoline and diesel engines.

Efforts to advance GT combustors to reduce fuel consumption and emissions are also pushing combustion into regimes where flame stabilization and propagation become very sensitive to disturbances. Staged combustion strategies in GTs with fuel rich combustion zones followed by fuel lean combustion zones (Rich-Quench-Lean [RQL] combustion), move combustion into non-conventional GT combustion regimes that overall provide a good compromise between flame stability and reduced emissions. Further reductions in NO_x emissions are also being pursued via the development of staged-combustion, lean burn GTs that will use Twin Annular Premixed Swirlers (TAPS) [Mongia 2003].

Low Temperature Combustion

LTC enables high-efficiency engine architectures similar to today's diesel engines for ground transportation, but with the potential for dramatically lower pollutant emissions. Higher efficiency is achieved by operating at high compression (expansion) ratios and by using the quantity of fuel injected to control engine load (power output), as in a diesel engine. Compression-ignition combustion of very lean or dilute fuel-air mixtures, which result in combustion temperatures in the 1500K to 2000K temperature range, about 500K below conventional diesel and spark-ignition engine technologies, leads to near zero NO_x formation. In addition, the fuel-air mixtures are tailored via premixing or fuel injection strategy to avoid rich fuel-air mixtures that result in soot formation [Kamimoto and Bae 1988].

Enabling high-efficiency, low NOx and soot emission engines through control of fuel-air mixture ratio and resulting combustion temperatures

Moderate temperatures and reacting fuel-air mixtures rich in fuel typically result in soot formation for most hydrocarbon fuels as illustrated in the schematic. Higher temperature regions and reacting fuel-air mixtures lean in fuel through stoichiometric result in NO_x formation. (A stoichiometric mixture, which is defined to have an equivalence ratio of one, has just enough air and fuel to completely consume both during combustion.) In a traditional Spark-Ignition (SI) engine, the combusting fuel-air mixture is very close to stoichiometric, which results in high temperature conditions and significant NO_x formation. In a traditional Diesel engine, there is little time for fuel and air to mix before combustion, therefore there is a range of fuel-air mixtures when combustion starts. The fuel rich combusting regions in a Diesel form soot while the stoichiometric combusting regions form NO_x. Novel combustion concepts being explored for high-efficiency, low pollutant emission engines are based on strategies for achieving Low-Temperature Combustion (LTC). LTC requires the formation of reacting mixtures in an engine that are dilute enough to not produce the high temperatures that lead to NO_x (thus the reference to low-temperature combustion) and that have well-enough mixed fuel and air to avoid soot formation. It is important to note that the exact combinations of temperature and fuel-air mixture ratio that will lead to best performance and lowest pollutant formation will depend highly on the nature of the fuel, indicating the impact of the evolving diversified fuel source future on LTC needs to be understood.

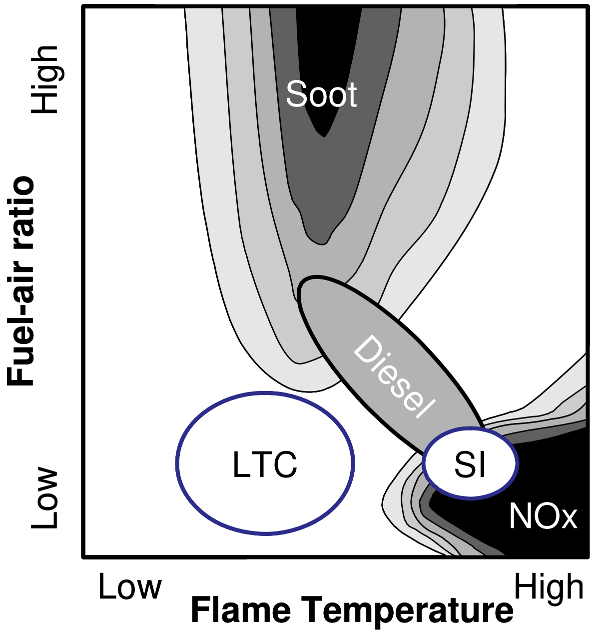
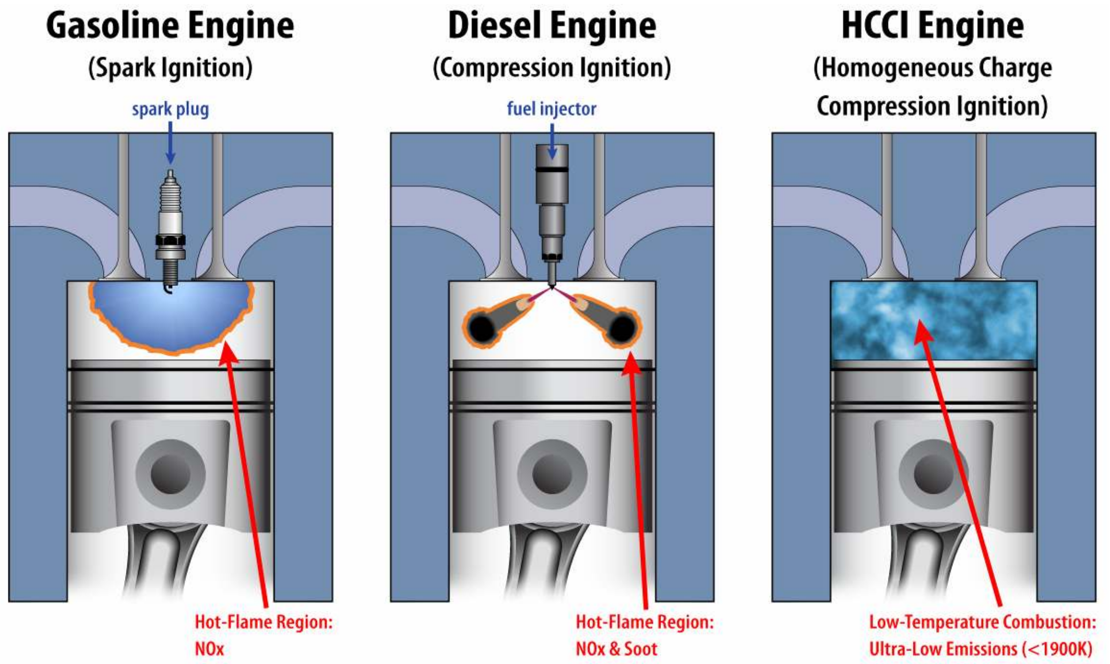


***Figure 1:** Traditional Spark-Ignited (SI) gasoline engines and Diesel engines have to operate at unfavorable combinations of temperature and fuel-air ratios for the formation of NO_x, and in the case of Diesels, soot. Novel low-temperature combustion (LTC) devices aim at creating conditions where the formation of soot and nitrogen oxides is avoided.*

A homogeneous charge compression ignition (HCCI) strategy is the simplest form under which LTC operation can be realized [Najt and Foster 1983]. Ignition of fuel and air completely premixed prior to ignition occurs volumetrically upon compression with combustion proceeding volumetrically at a rate determined largely by temperature-controlled chemical kinetics and temperature non-uniformities in the fuel-air mixture.

Current and future internal combustion engine concepts



In a typical gasoline engine, a premixed fuel-air mixture with just enough air to burn all the fuel injected is compressed and spark-ignited (SI) at a specified, optimal time. The high temperature resulting from the stoichiometric combustion leads to significant NO_x formation. However, the NO_x along with other pollutants formed can largely be removed by the three-way catalyst aftertreatment system on all SI engines on the road today. The power output (load) of an SI engine is controlled by restricting (commonly called throttling) the amount of air drawn into the engine and injecting correspondingly less fuel. Overall, the throttling and low compression ratio of an SI engine result in a significantly less fuel efficient engine than a Diesel engine. In part, the lower efficiencies can be overcome with more recent developments that use direct injection of gasoline into the cylinder to eliminate the throttling losses. This option adds substantial flexibility towards ultra-lean combustion but at the expense of more challenging exhaust gas aftertreatment systems. Direct injection can also be an enabler for HCCI engine technology, a new combustion strategy under investigation that approaches the high fuel efficiency of a Diesel engine while producing very low NO_x and soot emissions – so low there is the potential to meet the 2010 emissions standards without exhaust aftertreatment. As in an SI engine, fuel and air are premixed, however, combustion is started by a compression-ignition process similar to a Diesel engine. Many challenges exist for this promising ultra-clean combustion strategy before use in high-efficiency engines can be achieved. This includes robust methods of controlling the timing of ignition for optimal performance, expanding the useable load range, controlling the engine through transients, and determining the optimal fuel characteristics. Overcoming these challenges, especially in a diversified fuel source future, requires a vastly improved science-base around the fundamentals of fuel ignition, combustion, and emission formation chemistry, and fuel spray and turbulent fuel-air mixing processes, all at the high temperature and pressure conditions relevant to engines.

Another class of LTC operation under development involves compression-ignition of partially mixed fuel and air (a stratified fuel and air mixture) diluted with large quantities of exhaust gas recirculated into the engine intake or retained in-cylinder from the previous cycle (referred to as Exhaust Gas Recirculation or EGR). This stratified-charge, compression-ignition (SCCI) strategy involves directly injecting fuel into the engine cylinder, as in a diesel or GDI engine, but much earlier or later in the engine cycle than in a diesel to achieve enough fuel-air mixing before combustion starts to minimize the formation of soot. The dilution of the fuel-air mixture with EGR results in cooler combustion temperatures avoiding NO_x formation. As with HCCI, SCCI occurs volumetrically upon compression, but in a dilute, stratified mixture. This strategy allows better control of the heat release rate, which is important for achieving best mechanical efficiency and reducing combustion noise. Additionally, concepts are being considered that use spark-assisted compression-ignition (SACI) to combine the advantages of LTC and the robust combustion timing control provided by a spark plug.

LTC CHALLENGES. There are many challenges to implementing LTC and achieving its enormous potential for enabling engine fuel efficiency and clean combustion [Zhao et al. 2003]. Ignition and combustion timing are key issues. Unlike diesel engines, in which combustion starts almost at the instant fuel injection starts, or spark-ignition engines, in which a spark controls ignition timing, LTC engine ignition timing is controlled by fuel-specific ignition chemistry over a relatively long compression period during an engine cycle. This factor makes the timing of ignition and the ensuing combustion rate very sensitive to many parameters, especially fuel ignition chemistry properties. It also means that the emerging diverse fuel picture creates major new challenges because engine performance will be much more dependent on the exact fuel composition that is being used—definitely far more sensitive than for today's engines with today's fuels. Other issues include the limited load range capability for LTC, engine control through load transients, and the lack of a fundamental understanding of how combustion develops and propagates and how pollutant emissions are formed under dilute LTC conditions. Careful tailoring of fuel-air mixture and temperature stratification in-cylinder or control from cycle-to-cycle of in-cylinder conditions have the potential to be used to solve emissions, cycle-to-cycle stability/control, and load range issues. Surface-induced phenomena, like fuel dependent deposit formation, can also have significant influence on combustion due to the altered cylinder surface heat transfer properties and chemical activity. Moreover, many strategies and technologies will require new robust sensing methods for rapid feedback and control of engines.

Mixing of fuel and air in an engine is critical to optimal engine performance

Local mixture composition is the driving parameter for ignition, combustion rate and pollutant formation. Therefore, control and understanding of how fuel, air, and potentially recirculated exhaust gas are mixed is crucial. This is especially important since novel combustion devices, like ultra-lean gas turbines or low temperature combustion engines, are operated close to or even beyond traditionally accessible stable combustion regimes. To guide the exploration of these regimes, numerical simulation of internal combustion engines is rapidly becoming a useful tool for engine design and optimization. However, accurate prediction of flow and mixing processes is the foundation on which these simulations rest. As an example, experiments (Figure 1) show that increasing flow swirl in an automotive low-temperature combustion system can significantly increase the rate of heat release in the late-cycle phase of combustion. It is important to understand in detail what the origin of this effect is to enable engine design improvements. Numerical simulations indicate that the enhanced mixing is due to large-scale turbulent flow structures in the cylinder that transport fuel and air to a common interface (Figure 2). Accurate simulation of both the large-scale flow structures and turbulence generation processes they create is essential if numerical optimization of engines is to succeed.

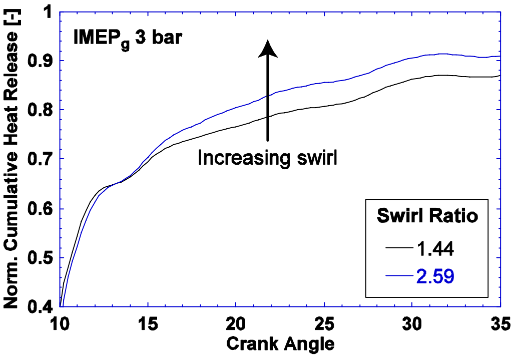


Figure 1

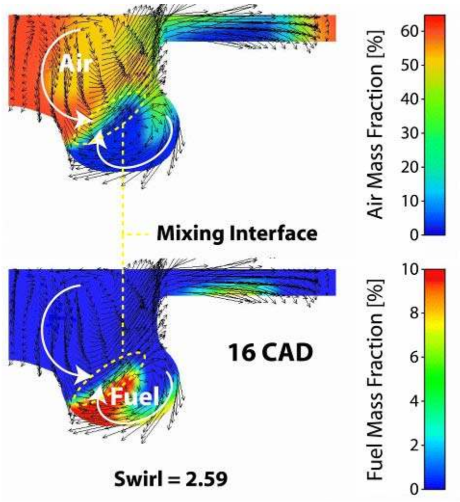


Figure 2

Experimental results courtesy of P.C. Miles, Sandia National Laboratories.

Simulations courtesy R.D. Reitz, University of Wisconsin.

Gasoline Direct Injection

The GDI strategy enables engine architectures similar to today's relatively low-cost gasoline engines, but with the potential for higher efficiency. Higher efficiency is achieved by using the quantity of fuel injected to control engine load (power output), similar to LTC concepts and diesels, as opposed to throttling of the intake air. This unthrottled operation minimizes efficiency losses. Combustion is initiated via spark plug as in a conventional gasoline engine, which allows a robust control of combustion timing, unlike compression-ignited LTC concepts. However, at low output power, the overall fuel-air ratio is so low that combustion would not proceed under homogeneous fuel-air mixture conditions in a GDI engine. Therefore, the fuel cloud must be stratified such that there is plenty of fuel near the spark plug and no fuel near the cylinder walls. This ensures reliable ignition and reduces heat losses to the cylinder walls by keeping combustion away from the walls. Currently, the most promising strategy to produce the required fuel stratification uses spray-guided fuel injection [Drake et al. 2005, 2007]. This direct fuel injection strategy also provides flexibility to fine-tune the fuel-air mixing. Direct injection also allows the flexibility to adjust injection timing and potentially to accommodate changes in fuel properties.

GDI CHALLENGES. Inevitable cycle-to-cycle fluctuations in cylinder flows and the spray formation process can lead to engine misfiring. While rare (~ 1 in 100,000), such misfires are detrimental since unburnt fuel is emitted and the driver's perception of the engine performance is poor. Improved understanding of energy transfer from highly excited spark plasmas into highly stratified mixtures is needed and will critically depend on the nature of the fuel-air mixture at the spark plasma discharge. Fuel-air-EGR mixing, the coupling of turbulence and combustion initiation under stratified mixing conditions also need to be understood and controlled.

Due to locally stoichiometric or even slightly rich conditions, temperatures are higher and NO_x is formed in GDI engines. EGR and/or catalytic converters in the exhaust are needed to control NO_x. The common three-way catalyst used on gasoline engines today does not work for the fuel-lean operation of a GDI engine. As a result, improved understanding of aftertreatment technologies such as lean NO_x traps is needed. This requires the development of significant improvements in our understanding of surface chemistry processes in aftertreatment systems, especially in the oxygen containing exhaust gases of fuel lean engine combustion systems.

Fuel injector development is rapidly progressing; however, there are still problems: some fuel may actually be sprayed onto the piston and cylinder walls and be converted to deposits there; fuel may form soot during rich combustion on the surface; or fuel may be emitted as unburnt hydrocarbons.

Gas Turbines

Staging of fuel-air mixing within gas turbine burners is being pursued to enable the combination of overall lean, low-NO_x (as well as low-soot and low-unburnt hydrocarbon) operation and flame stability. Mostly, this leads to designs with multiple fuel injection positions such as in the Twin Annular Premixed Swirler (TAPS) concept [Mongia 2003]. The design of the combustion chamber must be such that flow conditions are created that hold the flame in place, promote combustion rates by high levels of turbulence, and do not fluctuate too much, so as to keep noise levels low.

Gas turbines

Gas turbines are the heart of modern jets, providing the thrust it takes to lift and fly planes in civilian and military applications. In contrast to reciprocating internal combustion engines that are used in automobiles and trucks, the combustion process in gas turbines is continuous. Fuel is injected into the burners, mixed rapidly with air and the hot exhaust propels the actual turbine. So while some of the complexities that plague reciprocating internal combustion engines are not present in gas turbines, they face their own set of challenges. In particular, operation at very lean (low fuel-air ratio) conditions to reduce the formation of nitrogen oxides puts combustion at the limit where stable combustion can be sustained. In a typical flight pattern, the intake air conditions can change dramatically from dry warm air at ground to sub-zero temperature air at high altitudes including rain, snow and hail. During all conditions, it must be guaranteed that the engine does not fail and performance does not deteriorate. Maintaining combustion stability requires a detailed understanding of the combustion process. This requires an in-depth knowledge of how the nature and quality of the fuel in use affects performance.

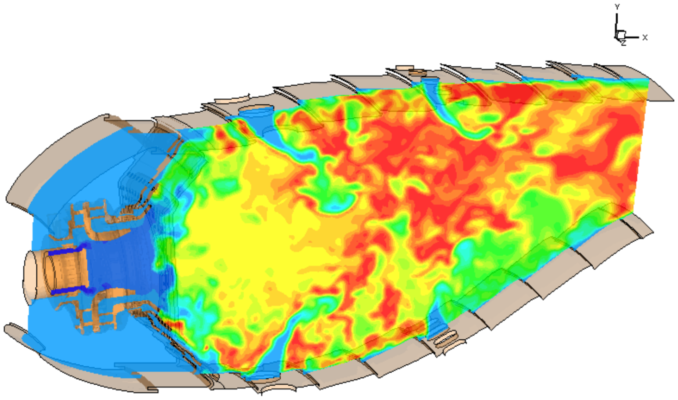
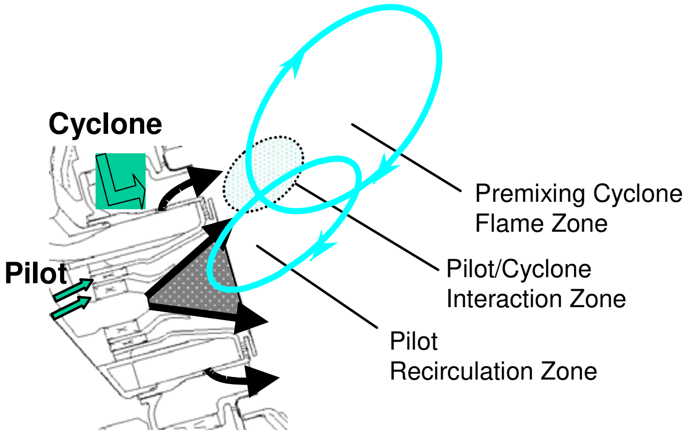


Figure 1: *Cross section through a single burner element. A complete gas turbine houses many of those combustors – all have to work in harmony to ensure the overall stable performance of the entire engine (Image courtesy H. Mongia, GE Aviation).*

Figure 2: *Cross section through a Twin Annular Premixed Swirler (TAPS) burner (Image courtesy H. Mongia, GE Aviation).*



GAS TURBINE CHALLENGES. The key to success with new gas turbine concepts is control over fuel-air mixing properties. The requirement to operate at the lean limit of combustion makes combustion stability very vulnerable to small changes in fuel-air mixture properties. The performance of gas turbines with new fuels, bio-derived or from new fossil sources, that have currently unknown physical and chemical properties will be difficult to predict without further characterization of the fuels properties and their effects. It is also critical to increase the fidelity of simulation-based design tools to expedite and enable the search for globally optimized gas turbine burner systems [Kim et al. 1999]. Purely experimental approaches are too costly and must go hand in hand with simulations.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS

Achieving the significant fuel efficiency improvement and pollutant emissions reduction potential offered by novel combustion strategies, such as HCCI, SCCI, and GDI in ICEs and staged combustion in advanced GTs, such as TAPS, will be challenging, especially in a diversified fuel source future. Issues around adequate range of power output, fuel requirements, proper combustion timing, transient operation, stable operation, engine control, hydrocarbon and carbon monoxide pollutant emissions associated with pushing combustion to the limits of dilute operation must be overcome. Underlying these application challenges are many basic science challenges, opportunities, and research needs surrounding the novel combustion strategies. Among them is the need to develop and integrate multi-scale modeling and simulation tools that can span the multiple orders-of-magnitude (~9) in length and time scales important in the advanced engine combustion technologies. These tools are needed both for scientific discovery and design. Also needed are new diagnostic tools for probing the detailed physical and chemical processes occurring both in the gas-phase and on surfaces at high pressure and temperature conditions, and a detailed understanding of the fundamental combustion/reaction processes involved in the novel highly dilute combustion strategies. Other needs include providing an understanding of fuel film development and combustion on combustion chamber walls, and advancing our understanding of the fundamental surface chemistry which underlies many processes involved in the advanced engine technologies. Additional needs related to fuel combustion chemistry and chemical kinetics, and fuel spray dynamics, are discussed in the Cross-Cutting Science and Fuels Utilization panel reports

Development and Integration of Multi-scale Modeling and Simulation Tools for Discovery and Design

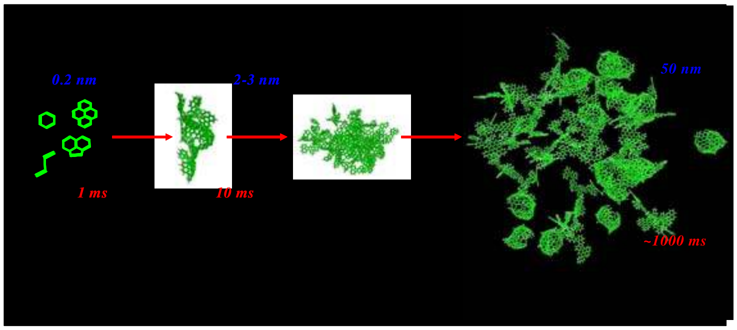
Combustion processes in engines and gas turbines involve relevant physical and chemical phenomena occurring over a vast range of length and time scales ($\sim 10^9$). Since it is impossible to measure or to model all of these phenomena simultaneously over the full range of scales, even on the world's largest computers, we must develop high-fidelity modeling and simulation tools for segments of the scale ranges, and a practical framework for connecting the models to provide a full description from the macroscopic propulsion system scales through to the very detailed microscopic kinetics and turbulent mixing scales. Multi-scale modeling capabilities are needed both for scientific discovery and for design and optimization of advanced high-efficiency, clean engines [Drake and Haworth 2007].

From slow to fast and from small to large: multi-scale problems in combustion

Predictive simulation tools for engine design are required to master the challenge of optimizing the clean and efficient use of future fuels in combination with future engines. Macroscopic features of an engine, as well as the detailed chemistry of new fuels, need to be included in such models. However, a full simulation of all physical and chemical processes that make up combustion in internal combustion engines and gas turbines is particularly difficult because of the range of scales that need to be considered: From individual molecules up to the macroscopic dimension of an engine and from collisions between two molecules to the time it takes to crank the engine through a full cycle

Very detailed models exist that describe phenomena at a particular dimension. For example, the dynamics of molecules at an atomic level, which controls the reaction rates at which molecules react with other molecules, can be computationally predicted with steadily improving accuracy. Large and complex kinetic mechanisms are in use to compute the time history of chemical conversion. Some of the processes involved in combustion are very fast, on a femtosecond timescale, while others require almost seconds to complete. A comprehensive model must be able to solve the corresponding equations simultaneously since most often species are involved in many reactions and therefore it is not always possible to compute the fast reactions separately from the slow ones. This is like trying to follow the time between 60 million years ago (when dinosaurs became extinct) and today in one-second steps while keeping track of what happened during each second.

Similar considerations obtain for spatial scales. Starting at the device level down to the size of atoms, there are coupled processes that link small scales to the large ones. To illustrate the range of scales that are important in combustion processes, one could imagine to cover the distance from the earth to the sun, about 150 million kilometers (92 million miles), in steps of one millimeter (a little more than ~1/32”). Of course, just like with the large difference in the rate at which chemicals react, not all processes are important at all spatial scales. So the challenge becomes how to adequately couple descriptions of processes in subranges of the overall combustion event and how to do this computationally with efficiency and accuracy.



An example of how many time and length scales are involved in the formation of soot particles –which still are too small to be seen individually by the human eye. Molecular Dynamics (MD) methodology has been coupled to Kinetic Monte Carlo simulations to allow the extension of the accessible time scales by orders of magnitude relative to direct MD, while retaining full atomistic detail: from a few carbons to millions of atoms. (Courtesy of Angela Violi, The University of Michigan, 2006).

Addressing this multi-scale challenge is particularly important to successfully understand and predict the effects of alternate fuels. Changes in fuel composition directly affect phenomena at only a few scales (at the microscopic scale, the changes affect reaction rates, while at a much larger scale, changes in bulk liquid properties affect fuel injection/evaporation). But understanding how changes at small scales affect the overall macroscopic performance of proposed new propulsions systems (or, ideally, how both the fuel and the engine changes affect the overall performance of the country's energy system over a lifecycle of several decades) requires very careful coupling across the scales.

The multi-scale challenge has many aspects. High-fidelity device-scale modeling capabilities, such as large-eddy simulation (LES) and direct numerical simulation (DNS), will be required. LES is needed both for developing a scientific understanding of novel engine combustion strategies and as the next generation of engine development and optimization tool. LES can be used to simulate the chemistry and physical processes in an engine cylinder down to the smallest reactive-diffusive scales of turbulence (a 10^5 range of scales), while including a detailed description of the chemical kinetics of a fuel [Oefelein 2006]. DNS tools will be needed to gain fundamental physical and chemical insight into fine-grained turbulent-chemistry interactions occurring in novel combustion strategies [Pantano 2004; Hawkes et al. 2006].

From the viewpoint of applied mathematics and systems engineering, a numerical challenge is to couple disparate models operating over different scale regimes to provide a comprehensive overall system model. Solving this challenge leads to issues of optimization and inverse modeling subject to constraints involving stiff-differential equations. A particularly important but so far largely unaddressed issue is how to impose error control, to achieve predictability. At present many of the submodels relevant to fuel chemistry and engine performance do not have any rigorous error control procedure, and each submodel is based on a series of assumptions and approximations which have been incompletely tested. As a consequence, we do not know what uncertainty to expect in predictions of the performance of new engines and fuels. Better understanding of the multi-scale coupling would allow design of experiments focused on validating and verifying the models for cross-scale coupling; and a much more systematic overall approach is needed to work towards a virtual engine development procedure where combustion strategies can be simulated in regimes that currently might not appear feasible.

Development of New Diagnostic Tools for Discovery

Clean and efficient engine combustion is controlled by interplay of physical mixing and chemical kinetic processes. Significant deficiencies in predictive capabilities of existing models for engine combustion are noted because of limited understanding of these processes. Developing computational models and simulation tools to investigate engine combustion and to design new engine concepts has been hampered by the lack of diagnostic tools for furthering our understanding of the controlling processes under engine-relevant conditions. It is therefore imperative to have new diagnostic techniques suited for the high pressures and temperatures relevant to engines and gas turbines. Diagnostics methods with quantifiable accuracy need to be developed to allow measurements in multi-phase flows of time-resolved, simultaneous, multi-dimensional flow field and scalar distributions. The scalars of interest include temperature, fuel molecules, key intermediate combustion species, pollutant precursors and pollutants like aldehydes, CO and NO_x. Successful implementation of these diagnostics is expected to provide benchmark experimental data of high fidelity for traditional and emerging future fuels that will be used to develop and validate the predictive capability of engine and gas turbine combustion models.

The role of laser diagnostics in combustion research

Detailed measurements of temperature, species concentration, and velocity are needed in combustion studies. However, such measurements are difficult for a number of reasons. First, the hot, sometimes sooting, gases can affect the performance of many conventional measurement probes and sensors, and can even destroy them. Second, the introduction of probes into flames may actually disturb the flame and bias the measurements in an unpredictable way (*e.g.* stick a paper clip into a candle flame and observe the reaction of the flame). Third, conventional sensors might not be fast, sensitive, and selective enough to meet the needs of combustion studies. Fourth, the introduction of probes into gas turbines or engines may not be possible at all because of moving parts or high pressures during the combustion process.

Optical methods and in particular laser-based methods, where the interaction of light with molecules is used as the sensing principle, can be used to overcome many of the limitations of conventional, non-optical measurement techniques. Each chemical species has unique internal energy levels so that when the laser wavelength is matched suitably to such levels, energy exchange processes between the laser beam and the molecules can produce a change in the laser beam or even create new light emission. Such changes or new emissions can be detected and linked with concentrations, temperature, and velocity (Fig.1).

Figure 1: *Schematic illustration of laser induced fluorescence. A photon of wavelength (color)* λ_1 *excites an electron to a higher energy state. When the electron returns to its original state it emits light of wavelength* λ_2*. The emission intensity is linked to temperature and concentration of the molecules. The color of the absorbed and emitted light is specific for each type of molecule, thus finger-printing at a molecular level is enabled.*

Laser diagnostics have become an indispensable tool in combustion research. They allow measurements that provide understanding of the inner physical and chemical processes that control combustion, understanding that is needed to validate and improve computer-based combustion simulations and to assist development-motivated applied research in practical combustion devices. Applications for laser-based diagnostics range from studying the motion of molecules and atoms during chemical reactions all the way to studies in engines and gas turbines (Fig.2).

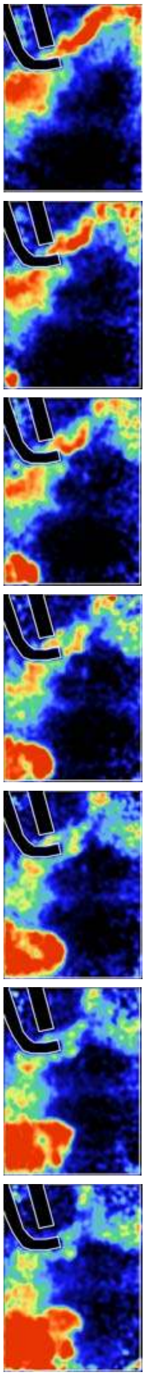


Figure 2: *High-speed laser-induced fluorescence visualizes the fuel cloud that passes the spark plug in a gasoline direct-injection engine at 12,000 images per second, giving access to important time-dependent features. (Images: Smith and Sick, The University of Michigan, 2006)*

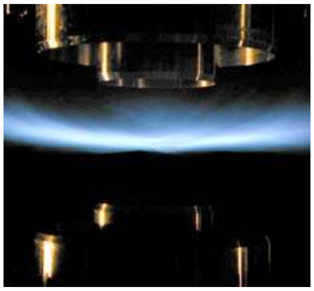
Optical methods, in particular those that are laser-based, are promising candidates to achieve this goal with the potential to resolve processes at small time and length scales. High-repetition rate laser-based imaging techniques of temperature, species, and velocity distributions can address many of the needs but have to be developed for quantitative applications at high pressures and temperatures. It will also be necessary to work on new laser sources that provide tunable laser light at sufficiently high pulse energies for measurements in high pressure environments. Furthermore, the photophysics of target molecules is not understood for high pressure and temperature conditions of interest for laser excited and chemiluminescence investigations but are needed for quantitative interpretation of the measured signals [Koban 2005]. Measurement techniques must be developed for molecules that can currently not be measured but are identified through simulations as important for novel combustion concepts. These techniques could be enabled through new laser sources. Finally, miniaturized, "keyhole" measurement techniques need to be developed that will enable measurements in otherwise inaccessible areas [Sanders 2005].

Fuel injector processes near the nozzle in sprays are also not well understood largely due to a lack of experimental data in this dense spray regime. Common diagnostic techniques do not work in these dense regions due to strong light extinction and scattering, while others, like X-ray absorption [MacPhee 2002], impedance tomography, and ballistic photon [Paciaroni 2004] imaging lack in spatial resolution and/or have poor temporal resolution. Improvements in such techniques are required for making quantitative measurements that will allow progress in understanding and modeling of sprays.

The impact of new diagnostic tools will be broad, ranging from providing data and a first principles understanding needed for validating advanced, detailed computational modeling and simulation tools, to providing improved phenomenological understanding of new combustion devices. New diagnostic tools will also be crucial for discovering novel combustion strategies that might otherwise never be experimentally observed. The first principles understanding and diagnostic tools will be a critical part of developing fuel efficient engines and gas turbines in the emerging diverse fuel source future.

Reaction processes for highly dilute mixtures

Future engine combustion concepts incorporate highly dilute, high-pressure combustion processes that are not well understood [Aoyagi et al. 2006; Hiroshi et al. 2004; Pirault et al. 2005; Zhao et al. 2003]. Developing a clear physical understanding of the dominant physical processes influencing the reaction front structure and propagation will enable development of optimal high-efficiency engines. Expanding fundamental investigations well beyond currently envisaged pressures and composition may allow discovery of combustion regimes and optimal reactant (fuel, diluent, additive) mixtures that can be exploited for efficient, clean utilization of future transportation fuels.



What is a flame? New high-efficiency, low-emission engine concepts are often said to rely on "flameless" combustion. To understand the implications of this statement, it is first necessary to understand the nature of a flame. We have all experienced flames, whether in campfires, candles on a birthday cake, or under the pot on the kitchen range. Nevertheless, most people can only describe a flame in general terms. A flame is "hot," it is usually "attached" to something, and it can be blue or orange. Flames exist in a wide range of shapes and sizes. To a combustion scientist, however, a flame has a more precise definition: it is a spatially-localized, self-sustaining, chemical reaction zone.

Flames are found in two different varieties, premixed and non-premixed. Premixed flames are exactly what the name implies—fuel and oxidant (usually air) are thoroughly mixed together, and the reaction zone propagates through the mixture as a wave. This type of flame is found in spark ignition engines. The speed of the wave through the mixture is 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 can greatly increase the rate at which this diffusion occurs, and hence the rate at which the flame propagates and energy is released. In non-premixed flames, the fuel and oxidizer are spatially-separated, and reaction occurs at a thin interface where they meet. In this case, the rate of chemical reaction and heat release is determined by the rate at which fuel and air diffuse to the interface. Once again, turbulence can greatly enhance this diffusion or mixing rate. This is the type of flame found in the typical diesel truck engine on the road today.

Why do we care if flames exist in engines?

To efficiently extract the thermal energy released by combustion in an engine, the heat release should be complete before significant gas expansion occurs, whether by piston motion in a reciprocating engine or by entering a turbine. For combustion systems employing either premixed and non-premixed flames, engineers tailor turbulent mixing rates, gas temperatures, and composition (diluent) to achieve timely heat release with minimal emissions. Flames will not propagate in highly dilute mixtures, however, and can be extinguished when intense turbulence causes local temperatures to drop excessively. Moreover, energy release rates are limited by either flame propagation speeds or by fuel-oxidant mixing rates. The flameless combustion pursued in novel engine concepts, on the other hand, is characterized by a uniform, simultaneous progress of chemical reaction throughout the reactants. The heat release rate does not depend on flame propagation processes or mixing rates, and can be very rapid. Flameless combustion can also result in a more uniform, lower temperature of the product gases, which can have important advantages when considering pollutant formation and destruction. Understanding the nature of the combustion process, whether it is flame-like or flameless or in transition between the two, is an important first step towards designing high efficiency, clean engines for future transportation fuels.

The focus must be set on obtaining a clear physical understanding and predictive capability of reaction front structure and evolution under highly dilute, high pressure conditions. Fuel mole fractions as low as 0.005 and pressures as high as 500 bar are within the conceptual range of practical engines. Dilute mixtures keep peak combustion temperatures (and hence pollutant formation rates) low, while high pressures minimize energy losses during combustion [Edwards et al. 2006] and restore power density lost via dilution. Under these conditions, the fundamental physical nature of the combustion process is not understood, and observable heat release characteristics often do not correspond either to a conventional flame-like combustion process or to a bulk, homogeneous combustion process.

To develop a science-based understanding of very dilute, high-pressure combustion processes, a balanced application of both computational and experimental tools will be required. Accurate experimental techniques, carefully designed to isolate the influence of specific physical and chemical processes, must be developed and applied to discover the controlling processes. These techniques must possess the necessary spatial and temporal resolution required to resolve the structure and evolution of the reaction zone; and must be sufficiently quantitative to allow the sensitivity of the combustion process to various parameters to be clearly identified as well as to allow for quantitative validation of numerical simulation tools.

Simulation tools and methods must also be developed for accurately predicting the mixture composition, and for faithfully capturing the interaction of flow turbulence with chemical reaction. High-fidelity device-scale modeling tools, such as large-eddy simulation (LES) and direct numerical simulation (DNS), will be required as discussed previously. Chemical kinetic mechanisms and appropriate rate constants applicable at high pressures must be developed—a task that will likely require additional experimental kinetics research support distinct from that described above.

Experimental and numerical tools will be essential for clarifying the nature of the combustion process under dilute, high-pressure conditions and for developing scaling and design rules. The knowledge-base on the novel combustion processes and the simulation tools that embody the information will both be important in the development of advanced ICEs and GTs.

Understanding liquid fuel-films on walls of combustion chambers

Wall films influence performance, emissions, durability, and the basic design of combustion devices spanning a broad range of device sizes. This research direction proposes fundamental research into the chemical and physical properties of future transportation fuels as well as the physical and chemical processes important to film formation, vaporization, surface dynamics, deposit formation, and process control through the influence of films on transport processes and reaction zone structure.

Fuel films can be formed on the interior walls of combustion devices during the fuel injection process. These films occur when fuel sprays penetrate to a wall and deposit fuel on the wall before the fuel can evaporate. Fuel wall films can be important in devices ranging in scale from replacements for batteries powering mobile electronics to engines powering automobiles and light-duty trucks [Pham et al. 2007; Cadou et al. 2003; Ladommatos et al. 2005]. Fuel films are especially possible for the novel combustion strategies employing less volatile fuels in ICEs. The air density in the engine cylinder at the time of fuel injection for LTC strategies is very low, allowing the fuel spray to penetrate all the way to chamber walls and deposit there.

Fuel films can lead directly to noxious emissions from combustion engines and can form deposits causing pre-ignition and deterioration in performance, or they can provide benefits, such as localized cooling of combustion chamber surfaces. High-boiling point, highly polar components associated with transportation fuels derived from new sources can exacerbate problems associated with fuel films and their control. Developing a fundamental understanding of the properties of new transportation fuels, and of the physical and chemical processes influenced by these properties, are keys to the effective use of these fuels.

The fundamental physics and chemistry governing film formation, evolution, and removal processes and the influence of fuel property variations on these processes must be clarified. The principal scientific challenges that must be met fall in both the theoretical and experimental realms. First principles methods are needed to predict the properties of multi-component fuel blends to encompass the large disparity in fuel compositions likely to be encountered in future fuels. Moreover, significant improvements in our understanding and ability to model heterogeneous surface reactions will be needed to clarify fuel film combustion and deposit formation and destruction.

To elucidate the physics of the film formation processes, and to characterize deposits, significant advances must be made in high spatial and temporal resolution diagnostics to probe the near-wall region, as well as diagnostics to perform in-situ characterization of deposit composition and morphology.

The impact of this research on both scientific knowledge and practical technologies will be substantial. In addition to new methods for handling properties and predicting the heterogeneous chemistry of complex fuel mixtures, a wide variety of modeling and diagnostic techniques that can be applied to a broad range of problems will be developed. Moreover, increased knowledge of the physics governing these processes and the ability to accurately model them will directly impact device design.

Surface chemistry for enabling clean, fuel flexible engines

Surface chemistry plays a major role in the performance of many combustion devices, but it remains one of the least-understood aspects. Catalytic converters and related exhaust treatment devices make it possible for high power-density engines to operate with acceptable emission levels. Catalytic combustion, ignition, and reforming make it possible to operate combustion devices at conditions where ordinary flames would be unstable. The formation of soot and other particulates, which critically affect diesel and jet engine performance and human health [HEI 2001], is strongly controlled by surface chemistry, as well as the formation of deposits in combustion devices, which can also impact performance. Surface chemistry is also crucial to the production of alternative fuels and better-performing fuels. As a result, advances in surface chemistry science may enable huge improvements in energy efficiency and emissions control, and reductions in cost in the transportation system.

Basic research is needed to make it possible to understand, predict, and exploit surface chemistry to enable efficient, low-emissions, low-cost transportation. The key need is the development of new tools and concepts that would permit measurement and/or control of surface nanomorphology and chemistry on the length and time scales and under the temperature and pressure conditions relevant for engines. Simultaneous development of suitable computational chemistry methods for modeling these microscopically complex systems would advance the field from its current mostly Edisonian approach to a predictive science. The opportunity presented by new fuel sources and advanced engine concepts offers such an overwhelming design and operation parameter space that only those technologies that build upon a predictive science capability are likely mature to a product within a useful timeframe.

A fundamental surface science challenge is that it is usually difficult-to-impossible to know even the morphology of the surface under the reaction conditions of interest, much less to directly observe the reaction intermediates. In addition, the complexity of these systems makes it difficult to accurately compute the chemistry or to correctly interpret a limited set of observations even for a known structure. There are many methods for measuring and/or calculating the stable species on a clean, flat uniform surface of known composition. But in most real catalysts, the surface morphology is probably not flat, the chemical composition near the surface and the location of the active site are not known, and one can only indirectly determine which reaction intermediates are important.

For engine applications, the situation is even more complicated than usual because of the strong coupling between the gas-phase chemistry/transport and the surface chemistry. Most existing experimental probes for investigating surface chemistry do not work at the high temperatures and pressures relevant in engines.

It is critical that we develop high sensitivity, high spatial resolution, fast experimental methods for measuring the actual surface morphology, composition, and coverage for catalysts of technological interest, under conditions similar to those in engines. This capability would allow us to develop and validate methods for calculating these structures. Methods for reliably predicting the surface structure will add impetus to the development of better methods for calculating reaction rates, and ultimately accurate models for the behavior of the entire system.

Currently, there is a large divide between surface scientists (who make detailed measurements usually on well-characterized uniform flat surfaces) and most catalysis researchers (who make and test new materials), caused by the inability of existing experimental and theoretical techniques to deal with the real-world nanomorphologies. Closing this divide would allow the entire surface chemistry community to be much more effective.

CONCLUSION

Significant advances in internal combustion engine and gas turbine technologies that offer dramatic improvements in fuel efficiency and reductions in pollutant emissions are possible through use of novel dilute combustion strategies. The investigation and development of engines employing novel combustion strategies are in the very early stages. Simultaneously with the efforts to develop more fuel efficient, cleaner engines, a diversified fuel source future is emerging in response to the need for alternatives to conventional oil derived fuels. Emerging fuels include bio-derived fuels that have the potential to become carbon neutral and help mitigate the greenhouse gas emissions implicated in global climate change.

To meet the challenges of developing significantly more fuel efficient engines for transportation in a diverse fuel source future, major advances must be made in the science-base underpinning the utilization of future fuels in high-efficiency engines enabled by novel combustion strategies. These improvements must span a range of knowledge from the most fundamental facets of fuel chemical and physical properties for a wide range of future fuels to the impact of these properties on all aspects of the performance and emissions of the emerging high-efficiency, clean engine technologies.

Critical areas for advancement discussed in the novel combustion panel include: (1) a fundamental understanding of the combustion processes and modes of combustion progression in very dilute fuel-air mixtures at high pressure and temperature conditions relevant to ICEs and GTs; (2) new diagnostic and high-fidelity modeling/simulation tools for discovering and exploring the fundamental chemical and physical processes and their coupling in the novel combustion regimes; (3) a framework for combining the computational tools and methodologies for modeling systems and processes that extend over wide ranges of length and time scales; (4) a first principles understanding and capabilities to measure and predict important surface-controlled or enabled (catalysis) reaction processes; and (5) a comprehensive understanding of fuel-films that can occur on surfaces in engines using novel combustion strategies. Development of this science base will help enable transformative improvement in fuel economy and dramatic reductions in emissions from engines for ground and air transportation when compared with today's engines.

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FUELS UTILIZATION PANEL

CURRENT STATUS

Transportation fuels for automobile, truck and aircraft engines are currently produced by refining petroleum-based sweet crude oil, from which gasoline, diesel fuel and jet fuel each are made with specific physical and chemical characteristics dictated by the type of engine in which they are to be burned. Accordingly, diesel engines burn diesel fuel, spark-ignition (SI) engines burn gasoline, and gas turbines burn jet fuel, and none of these engine types can operate efficiently or at all using the other types of fuels.

As the supply of petroleum-based fuels declines, a number of replacement candidates have been proposed, based on raw materials that are plentiful in North America. These new fuels will be produced from oil sands, oil shale, and coal, as well as from a variety of biomaterials. None of these future transportation fuels is yet in wide use, but relatively small-scale efforts are in progress to identify the best ways to use these fuels from novel sources. In each case, these efforts are focused on modifying the transformed/refined fuel from the oil sands, oil shale, coal or biosources to make the resulting liquid fuel resemble conventional fuel—diesel fuel, gasoline or jet fuel—to the extent that they can simply be combined with current fuels and used in conventional engines. While each of these alternative fuels can be used as the sole fuel for powering modern engines, current plans for each of these novel fuels anticipate that they would be used as minor components of the vehicle fuel, combined with existing petroleum-based gasoline, diesel or jet fuel with the alternative fuel providing 10-20% of the overall mixture.

How do hydrocarbon fuels actually burn?

Progress has been made in recent years towards understanding the fundamental chemistry of combustion of practical transportation fuels, using a wide range of laboratory and engine experiments, chemical theory, and computer simulations of hydrocarbon oxidation [Kohse-Hoinghaus et al., 2005; Miller et al., 2005; Westbrook et al., 2005]. Under ideal conditions, hydrocarbon combustion is the systematic disassembly of complex hydrocarbon molecules into progressively smaller fragments and their subsequent conversion into carbon dioxide and water. The heat release that accompanies these reactions is converted into work by the engine. Pollutant emissions result when combustion is incomplete, and soot is often produced in fuel-rich regions when fuel and air are incompletely mixed before combustion [Richter and Howard, 2000].

The reaction pathways that facilitate combustion are intricate and complex. While it is sometimes convenient to summarize combustion as a single-step overall reaction, as in

$$\text{FUEL} + n_1\, O_2 \rightarrow n_2\, H_2O + n_3\, CO_2 \qquad \text{(R1)}$$

where n_1, n_2 and n_3 depend on the specific fuel being burned, this overall oxidation reaction actually takes place through an immense network of elementary chemical reactions. In the case of a relatively simple fuel such as methane (CH_4), this can involve at least 100 individual chemical species and 250 elementary chemical reactions; and typical transportation fuels such as diesel fuel or gasoline are much more complex than methane and involve proportionately larger chemical systems.

A view of the complexity of hydrocarbon oxidation, in the simplest case of methane, is provided in Figure 1, based on the work of Warnatz (1980).

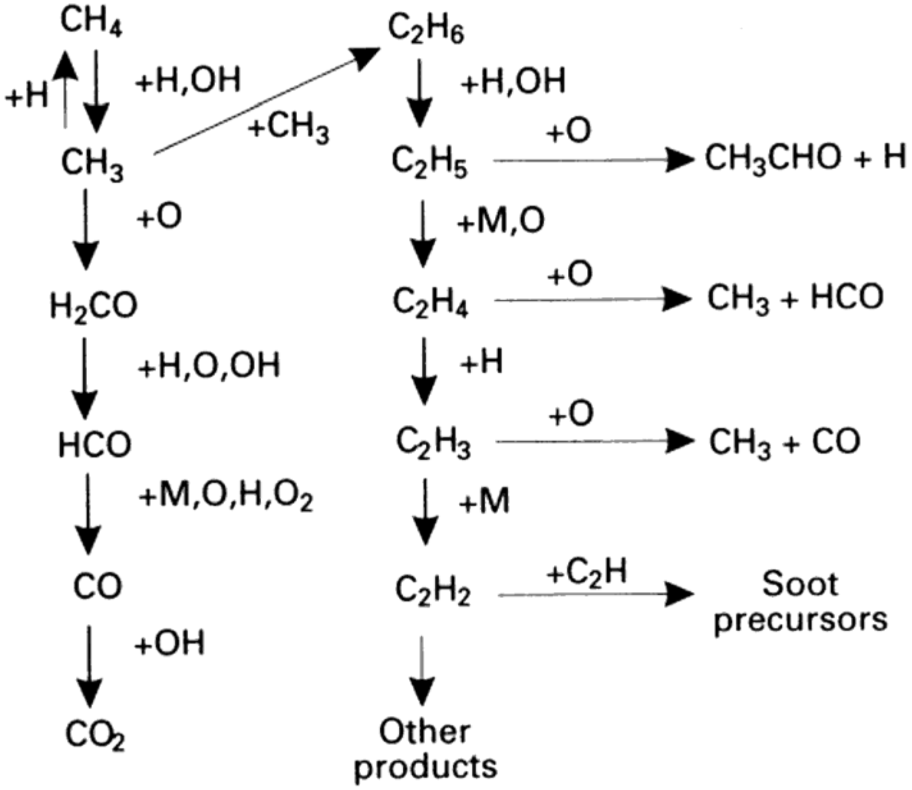

Figure 1. Schematic diagram of reaction pathways in methane oxidation [Warnatz, 1980].

Each arrow in this figure represents many individual chemical reactions, each with a complicated rate as a function of temperature and pressure. Combustion of methane produces considerable amounts of ethane and can even lead to more complex reaction pathways through formation of soot. While combustion of most fuels produces primarily smaller hydrocarbon fragments on the way to CO_2 and H_2O, rich combustion can produce significant amounts of larger hydrocarbon molecules, which further complicates the reaction mechanism. For hydrocarbon fuels as large as n-heptane (C_7H_{16}) and iso-octane (C_8H_{18}), the comparable chemical network can involve as many as 1000 different chemical species and 8000 elementary reactions [Curran et al., 2002].

Complexity of transportation fuels

A number of experimental and computational studies have been carried out to analyze the chemistry of single-component fuels [Simmie, 2003; Westbrook and Dryer, 1984; Griffiths et al., 1993]. Practical transportation fuels, however, are actually very complex, multicomponent mixtures of many individual hydrocarbon and other chemical species. These mixtures are produced in refineries from complex raw materials, combining components to meet legislated physical and chemical targets and produce the different liquid fuels to be used in transportation engines to satisfy domestic demands.

Hundreds or even thousands of distinct hydrocarbon species are present in every gallon of each of these fuels. Their overall structural properties can best be shown by lumping the compositions into a number of fuel "classes", generalized groups of fuel species that have similar structures and chemical properties. One result of such grouping is shown in Figure 2, in which the fuel classes in a typical fuel mixture are n-alkanes, branched alkanes, cycloalkanes, aromatics, and others that include alkenes (olefins) and oxygenates (such as MTBE or ethanol).

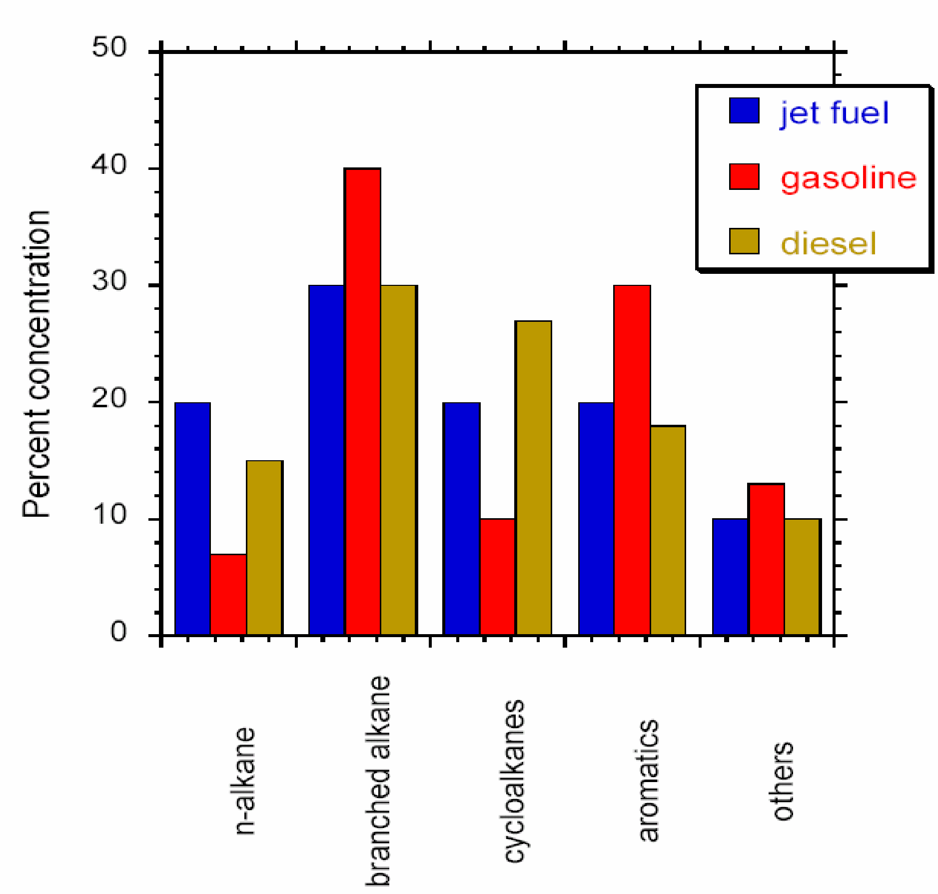

Figure 2. Levels of fuel classes in typical samples of common transportation fuels.

The differences in generalized compositions of fuels for the three types of engines are best understood by remembering how the fuels are burned in different engines. Gasoline is burned in spark-ignition (SI) engines, where fuel/air mixtures are slightly fuel-lean and in which engine knock is a particular concern. Therefore the levels of n-alkanes and cycloalkanes are low and branched alkanes are high because, generally speaking, n-alkanes and cycloalkanes react rapidly and encourage knock, while branched alkanes react more slowly and resist knock. Aromatic hydrocarbons resist ignition and produce high levels of soot, but the spark ignition and lean, premixed conditions in SI combustion avoid these difficulties, so gasoline can accommodate larger fractions of these components.

In contrast, fuel-rich and fuel-lean regions occur in both diesel and jet engines, which encourages the production of soot, so the levels of aromatics and branched alkanes must be reduced to counter this tendency. With no spark to initiate combustion in either diesel or jet engines, the fuel must encourage ignition, which is accomplished by the higher n-alkane and cycloalkane levels.

It is important to remember that all of these transportation fuels are produced from the same sweet crude, petroleum-based oil. Refining separates its components selectively to produce the relative amounts of gasoline, diesel oil and jet fuel that are required by fuel markets. When crude oil is replaced by a different source such as oil sands or coal liquids, the fractions of species in the different molecular classes available to the refinery can be quite different, which can alter the overall composition of the transportation fuels that are then produced. These fuel composition differences then lead to differences in physical properties, combustion performance, and emissions characteristics.

The only proposed new biofuel that seems to be best suited for SI engines is ethanol, a biofuel with a high octane number and resistance to knocking. Fuels from oil sands, oil shale fuels, coal liquids, and most biodiesel fuels are all best suited for blending with existing diesel fuels, because of the dominance of large hydrocarbon molecules in those fuels. These new fuels contain significant levels of aromatic and cyclic paraffin components that make them perform like conventional diesel fuels.

Many of the proposed new alternative fuels contain large molecular species, with increased fractions of compounds such as oxygenates, naphthenes and other types of species, whose physical and chemical properties and combustion kinetics are poorly known. Each type of alternative future fuel has its own unique features or chemical signatures: biomass-derived fuels from celluloses and lignins have high polymeric characteristics; oil sands fuels have unusually high naphthenic content; and oil shale and coal liquid fuels have more aromatic content than conventional petroleum-based transportation fuels. A combination of theoretical, kinetic modeling and experimental studies will be required to develop an accurate understanding of their physical and combustion properties.

Oil Shale – transportation fuels from unconventional sources

The largest deposits of oil shale are in the Green River Formation of Colorado, Utah, and Wyoming, which may contain as much as 1.8 trillion barrels and is one of the highest quality shales in the world. The widely studied Piceance Greek Basin formation in Colorado contains deposits over 500 feet in thickness, located beneath 500 feet of sedimentary rock, while other portions have up to 2,000 feet of overburden. This formation yields more than 25 gallons of shale oil per ton of raw material, translating into nearly 2.5 million barrels per acre. Removing the oil shale efficiently to provide high yields has yet to be fully explored and commercialized, and there are ecological or environmental concerns that remain to be solved.

Raw shale oil is extremely viscous and is difficult to transport, and thermal treatment (on the surface or in situ) is required to produce conventional fuels. Several on-surface retorting technologies have been used at research scales so that bitumen can be partially upgraded and, with mild hydrotreatment, may be adequate to make oil refinery-ready (Figure 1).

Since the early 1980's Shell has been developing the In situ Conversion Process (ICP), consisting of underground heaters drilled into an oil shale deposit. Approximately 15 to 25 holes are drilled per acre to a depth of up to 2000 feet. Electrical resistance heaters are inserted into the holes to raise the surrounding shale deposit to an average temperature of 650°-700°F to release the oil from the shale.

A freeze wall is constructed around the heating grid at a distance of 300 feet from the outermost heaters, which establishes an underground barrier to fluid movement, thus preventing groundwater contamination and the escape of the shale oil. After heating for two to three years, the oil can then be pumped out of the ground.

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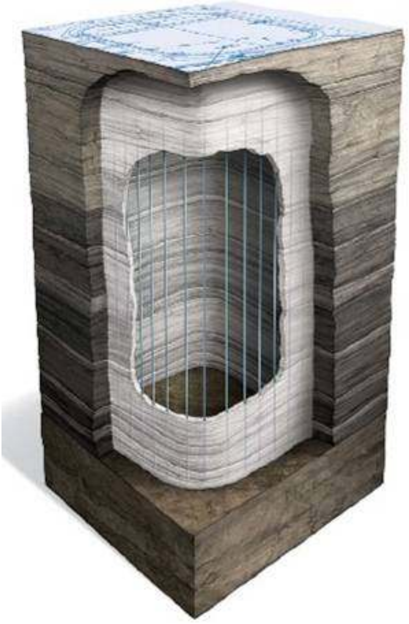


Figure 1. *Schematic of Shell ICP process using freeze wall technology for producing fuel from oil shale.*

The hydrocarbon mixture generated from this procedure is of a high quality and quite different from traditional crude oils, containing much lighter hydrocarbons and almost no heavy ends. The hydrocarbon fractions generated can easily be converted into a variety of finished products, typically 2/3 liquid (30% naphtha, 30% jet fuel, 30% diesel and 10% heavier oil) and 1/3 gas (propane and butane).

Surrogate Fuels

Not only are transportation fuels composed of thousands of individual chemical compounds, but the amounts of each specific component can vary from day to day and from one fuel station to another, making it almost impossible to carry out repeatable experiments with realistic fuels. An important topic of current research is the identification of methods to define representative and reproducible fuel mixtures that can be used to carry out experiments and computer simulations for combustion of real transportation fuels. One approach is to mimic those practical fuels with so-called "surrogate" mixtures, i.e., a suite of a small number of chemical compounds that can reproduce important properties and the performance of realistic, complex fuel mixtures. Physical and combustion properties of the surrogate are then thoroughly evaluated for wide ranges of temperatures, pressures, and combustors, which are then compared to the properties of the real fuel. Because fewer fuel compounds are involved, and because the composition of the surrogate does not change, surrogates provide a cleaner and more reproducible basis for developing and testing models of fuel properties in practical combustors, and for including detailed chemical kinetics in the analyses. An excellent recent example of a surrogate was developed for jet fuel JP-8 by Violi et al. (2002), who used mixtures of 6 - 10 compounds (including iso-octane, methyl cyclohexane, m-xylene, toluene, tetralin and others) to reproduce kinetic properties, including sooting, flame structure and oxidation in flow systems, as well as physical properties such as volatility, boiling curves, and flash point of actual JP-8 fuel. Surrogates can be chosen to reflect unique compositions of any type of fuel. For example, biodiesel fuel surrogates can be represented by increased levels of a methyl ester species, while a surrogate for oil sand fuels would contain higher levels of cyclic paraffin components.

One common approach to construction of surrogates for practical fuels is to take advantage of the same fuel classes already described above and shown in Figure 3.

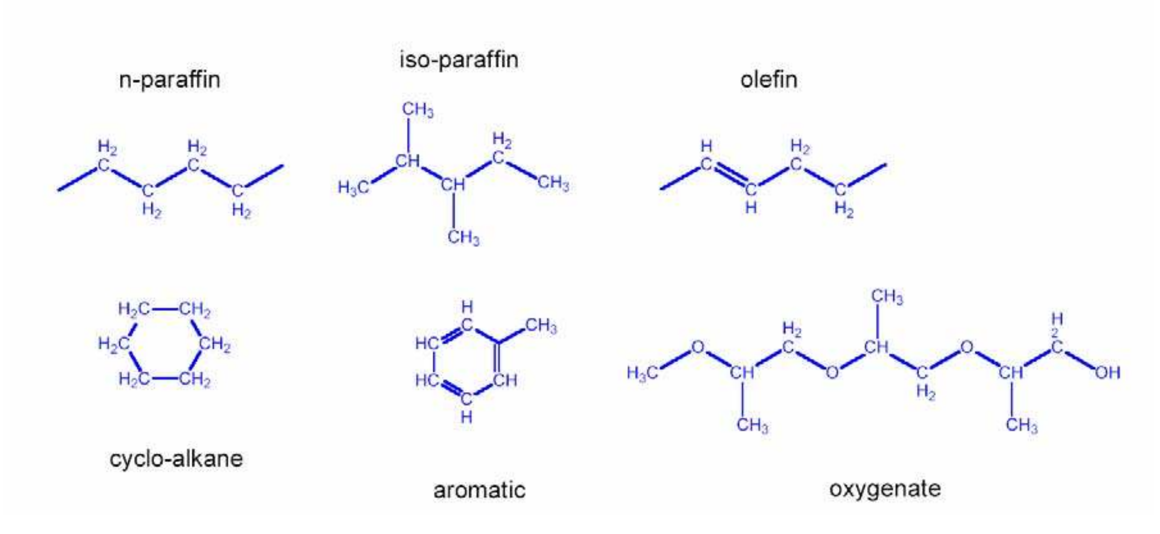


Figure 3. Typical molecules in each of six major classes of hydrocarbons.

The key to this type of surrogate is having one or more representatives of each of these classes with detailed chemical kinetic reaction mechanisms that have been thoroughly validated. Some of the classes, such as the n-paraffins and iso-paraffins, have numerous examples with validated mechanisms, while the cyclo-alkanes and aromatics have only a few. This approach increases in fidelity and value as more representative fuels from each class become available, and it is equally applicable to current and future transportation fuels. For example, a recent study of gasoline ignition under HCCI conditions [Naik et al., 2005] used a surrogate model for gasoline that contained five components, one from each class shown in Figure 3, including n-heptane, iso-octane, 1-pentene, toluene, and methyl cyclohexane. The amounts of each of these components were adjusted to provide a mixture with Motored Octane Number (MON) and Research Octane Number (RON) of 83 and 91, respectively, the same as the experimentally determined values in the gasoline used in their experiments. The technique of creating and using surrogate mixtures for transportation fuels is in very early stages of development [Pitz et al., 2007; Farrell et al., 2007; Edwards et al., 2007], and many further advances and refinements are needed.

Ignition Phenomena

Hydrocarbon ignition of transportation fuels can control combustion systems in a wide variety of ways. In spark-ignition engines, a spark discharge initiates combustion at a predictable time to start flame propagation in the combustion chamber, and undesirable spontaneous ignition of unburned fuel/air in the SI engine chamber can result in engine knock. Compression ignition of fuel-rich mixtures starts the combustion in diesel engines; early ignition, indicated by high CN values of the fuel, and late ignition, with low CN values, produce very different combustion environments and result in much different amounts of NO_x and soot emissions. Products of fuel-rich diesel ignition are ideal building blocks of soot [Dec, 1997; Flynn et al., 1999], and manipulation of the onset of ignition in diesel engines can have a significant impact on the amounts of soot that are produced.

Octane and Cetane Numbers for Hydrocarbon Fuels

Hydrocarbon autoignition in engines is such an important problem that standards have been developed to describe it. In spark-ignition (SI) engines, the key ignition event is the thermal autoignition of the unburned “end gases”, the last portion of the fuel/air mixture to be consumed by the flame that was initiated by the spark discharge. If these end gases are consumed by the flame prior to their ignition, normal operation is observed, but if the end gases ignite spontaneously (due to compressional heating) before they are consumed by the flame, the end gas ignition produces engine knock, which is highly undesirable. The rate of end gas autoignition is measured by the “octane number” (ON), with large values of ON indicating resistance to autoignition and small values indicating rapid autoignition.

In diesel engines, the autoignition of the intake fuel jets is the key event, and it is measured by the “cetane number” (CN) of the fuel. A high CN indicates rapid autoignition, which produces a long premixed burn and shorter diffusion burn, while a low CN results in the opposite results.

Autoignition in the diesel is a very fuel-rich phenomenon, while autoignition in the SI engine occurs at near-stoichiometric conditions. Both phenomena are strongly dependent on the rate of low temperature hydrocarbon oxidation and on the kinetics of alkylperoxy radical isomerization, which is a strong function of fuel molecular size and structure.

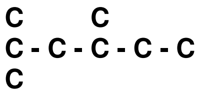
Both processes have established references to describe autoignition. In SI engines, the standards of ON are iso-octane with ON = 100, and n-heptane with ON = 0. For diesel engines, the references are n-hexadecane with CN = 100, and 2,2,4,4,6,8,8-heptamethyl nonane, with CN = 15; use of α-methyl naphthalene as another reference at CN = 0 was discontinued in 1962. These parameters are measured in special test engines, and the ON and CN values of real fuels are determined by comparing ignition rates of the real fuel with ignition of these reference fuels.

The basic chemistry that controls rates of hydrocarbon ignition and is responsible for the differences between slow and rapid ignition in different hydrocarbon molecules is very complex and has only recently become reasonably well understood. The development of chain branching agents via transfer of H atoms within hydrocarbon fuel molecules is the key kinetic step, and the overall process is summarized as “alkylperoxy radical isomerization kinetics”.

n-heptane

C - C - C - C - C - C - C   ON = 0

iso-octane



$$\begin{array}{ccccccccc} C & & & & C & & & & \\ C & - & C & - & C & - & C & - & C \\ C & & & & & & & & \end{array}$$

ON = 100

Reference fuels for octane number in spark-ignition engine combustion

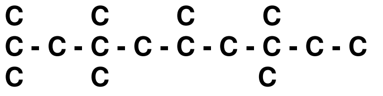
n-hexadecane

CN = 100

C - C - C - C - C - C - C - C - C - C - C - C - C - C - C - C

2,2,4,4,6,8,8-heptamethyl nonane

CN = 15



$$\begin{array}{ccccccccccccccccc} C & & & & C & & & & C & & & & C & & & & \\ C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C \\ C & & & & C & & & & & & & & C & & & & \end{array}$$

Reference fuels for cetane number in diesel combustion

Ignition in Homogeneous Charge Compression Ignition (HCCI) engines is the main event in the combustion cycle and occurs spontaneously, a result of the compression stroke of the piston and the detailed oxidation kinetics of the fuel being employed. Although both diesel and HCCI combustion begin with compression ignition, HCCI avoids the difficulties of soot production by operating under very lean or dilute conditions. HCCI ignition can be manipulated either by varying the fuel composition or by adding ignition promoters or retardants, and a thorough understanding of ignition kinetics is essential to optimizing HCCI combustion.

Basic science has played a significant role in understanding hydrocarbon ignition [Westbrook, 2000], but many fundamental questions still remain. Ignition kinetics are commonly studied experimentally in shock tubes and rapid compression machines. The central issue is identification of the elementary reaction steps that provide chain branching, and kinetics research shows that different sets of reactions provide that chain branching in three different temperature regimes (i.e., high, intermediate and low temperatures), each having its own dependence on equivalence ratio, pressure, temperature, and the molecular size and structure of the fuel. Ignition of complex mixtures of very different chemical species is still poorly understood, and ongoing theoretical studies of energy transfer, reactions of chemically activated complexes, and electronic structure in large molecules are only beginning to contribute to applied combustion problems, e.g. [McCunn et al., 2006].

Low Temperature Combustion

Low temperature kinetics control the onset of ignition in HCCI and diesel engines and knock in spark-ignition engines in a rather subtle way, and these reaction pathways are ultimately responsible for the observed dependence of cetane and octane numbers on fuel molecular structure. The intermediate temperature ignition responsible for each of these phenomena actually begins at about 1000K, when hydrogen peroxide (H_2O_2) decomposes into two OH radicals, followed rapidly by a transition to high temperature chain branching [Westbrook, 2000]. However, kinetic processes unique to the low temperature regime, between about 650K and 800K, can release enough heat to accelerate the time at which a reactive mixture reaches this effective ignition temperature of about 1000K. Experimental, theoretical and kinetic modeling studies, e.g. [Leppard, 1989; Griffiths et al., 1993, 1997; Westbrook et al., 1991], over the past 20 years have examined this phenomenon, and recent work [Carstensen et al., 2005; Taatjes, 2006; Miller and Klippenstein, 2006] has begun to place these kinetic processes on a sound theoretical basis. Recent engine studies [Sjoberg and Dec, 2007a; Sjoberg, Dec and Hwang, 2007b] have shown how these low temperature reactions can be used to accelerate ignition in diesel and HCCI engines. Most of this work, however, has been based on the kinetics of paraffin fuels and on relatively small molecules, and very little is understood about other classes of fuels, including aromatics, cyclic alkanes, and others. Additional questions remain about the impact of elevated pressures and complex mixtures on many of these processes.

A series of reactions is initiated by addition of molecular oxygen to alkyl radicals R to make alkylperoxy RO_2 radicals. These radicals then transfer H atoms within the RO_2 radical to make radicals QOOH with an O-O-H group. Subsequent further addition of another O_2 molecule, followed by another H atom transfer within the radical, lead eventually to production of two OH and other radicals that produce a short-lived and incomplete ignition event. A graphic picture of this regime is shown in the accompanying Figure 4.

Two key steps in this sequence are the internal H atom transfers indicated by the overall reactions

$$RO_2 \rightarrow QOOH \qquad \text{(R2)}$$

and

$$O_2QOOH \rightarrow HO_2Q'{=}O + OH \qquad \text{(R3)}$$

that produce chain branching and rapid reaction at low temperatures. A reasonably general picture, with associated rate expressions, for these steps has been developed [Pollard, 1977; Curran et al., 2002] that can explain many of the available experimental studies in terms of types of C - H bonds, ring strain energies, and degeneracies. Most studies, however, address only n-alkane and iso-alkane reactions. A schematic diagram of one such process is shown in Figure 5a, showing an H atom transfer via a 5-membered transition state ring for a reaction of $RO_2 \rightarrow QOOH$ in a linear alkane molecule.

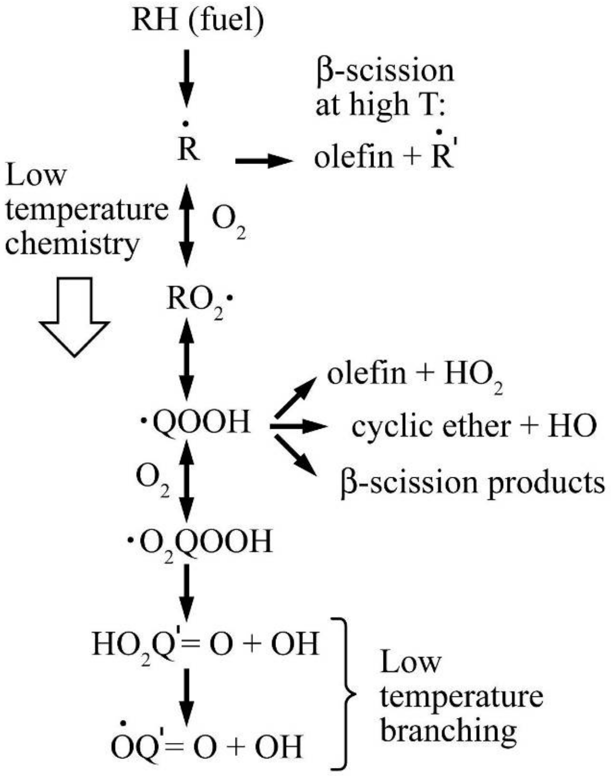


Figure 4. Schematic diagram of alkane oxidation pathways at high and low temperatures, from [Curran et al., 2002].

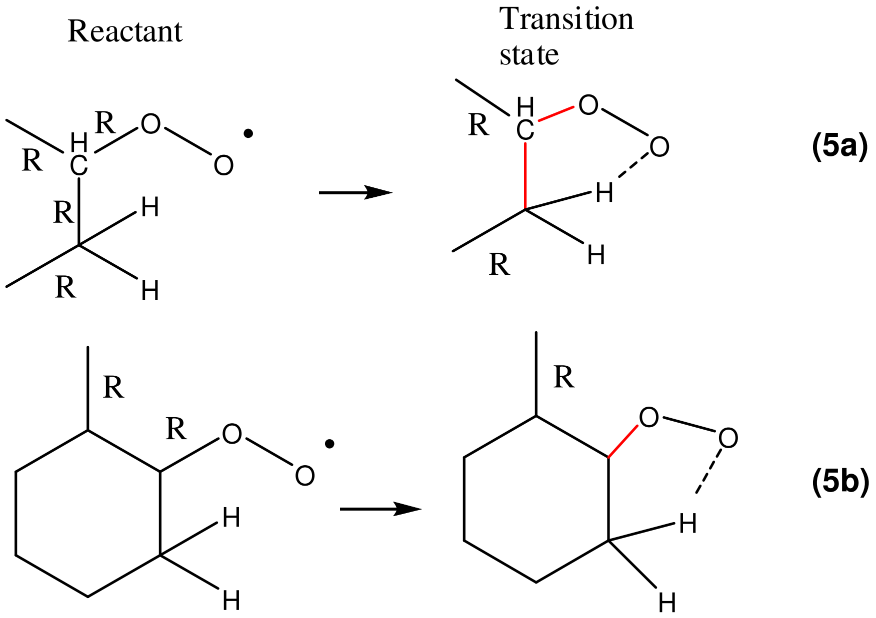


Figure 5. Two similar reactions transferring an H atom from a bond with a carbon atom to the end of a chain of two O atoms. The upper diagram shows the reaction in an alkane fuel molecule, the lower diagram in a cycloalkane molecule. The free rotors in each species are denoted by the letter 'R'; the number of rotors and the change in the number of rotors have important effects on the rates and thermochemistry of such reactions.

However, when the analogous, structurally equivalent process in methyl cyclohexane was studied recently [Pitz et al., 2007], shown in Figure 5b, it was found that the presence of the cycloparaffin ring changed the rate of the $RO_2 \rightarrow QOOH$ reaction significantly. In retrospect, this is not a surprising result, since the cyclic structure influences the electron density in the vicinity of the H atom transfer reaction, but existing methods of estimating the rates of the key processes are inadequate.

The same types of reactions control ignition in many fuels, but the rates of the key processes depend on many structural factors that have not been studied, and a general theory of the key reactions at low temperatures is still elusive.

These low temperature processes are essential in predicting critical parameters for such processes as engine knock, diesel ignition, HCCI ignition, and other practical problems. The basic understanding of these processes is still lacking. Another example in the case of HCCI combustion is discussed below.

Soot production

Most proposed next-generation transportation fuels are anticipated to be alternatives for diesel or jet fuel, and a significant issue with both types of engines is soot production and emissions. Soot is produced in fuel-rich environments where there is insufficient oxygen for hydrocarbon fragments to be completely oxidized. Instead, these small, largely unsaturated hydrocarbon species bond together to produce larger molecules which continue to grow until they become soot. Fuel jets in diesel and jet engines are perfect incubators for soot production because the pure, liquid hydrocarbons that are injected into the combustor do not mix rapidly enough to avoid such fuel-rich regions.

A great deal has been learned in recent years about soot production [Richter and Howard, 2000], and this understanding has been essential in significantly reducing soot emissions over the past decade. These studies have included extensive experimental and kinetic modeling efforts. A number of specific small hydrocarbon species have been identified that are particularly effective in producing soot, including acetylene (C_2H_2), propargyl radicals (C_3H_3), allyl radicals (C_3H_5), and others [Miller et al., 2005]. These small fragments continue to combine, quickly producing small aromatic species, which then grow to build large networks of polycyclic aromatic species, and eventually condense into polymeric species and then particulates as actual soot. This process is shown schematically in Figure 6.

Alternative fuels are a concern because they contain significantly higher levels of aromatic and polycyclic paraffinic hydrocarbon species, all of which produce high levels of the smaller hydrocarbon species that make soot in fuel-rich environments. Thus there is some potential for these fuels to show higher levels of soot production than conventional diesel fuels. Conversely, some alternative fuels, especially in the case of biodiesel fuels, have oxygen atoms within the fuel molecules, and both experimental engine studies [Miyamoto et al., 1998] and kinetic modeling analyses [Westbrook et al., 2006] have shown that oxygen in the fuel produces a significant reduction in soot production relative to conventional diesel fuel. The sooting tendencies of all types of alternative fuels must be examined, and the fundamental fuel properties controlling their sooting behavior must be understood.

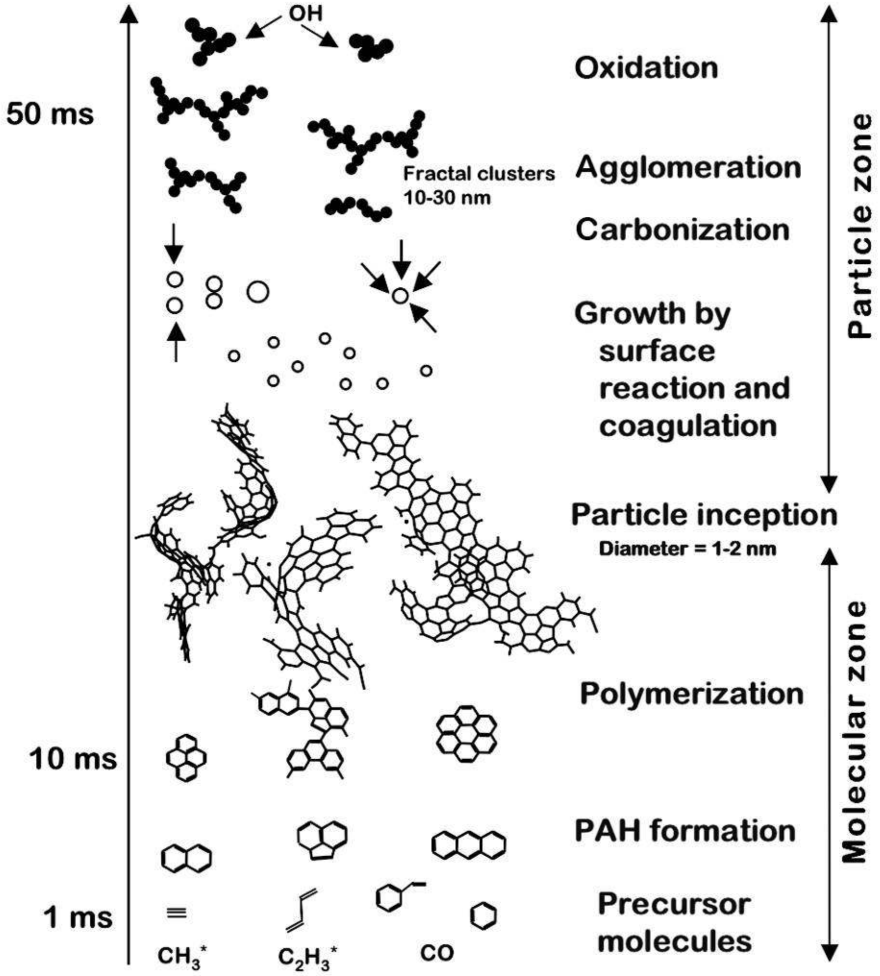


Figure 6. Schematic diagram of soot formation. [Smith (2006)].

HCCI engine combustion

Considerable ongoing attention is being given to the Homogeneous Charge Compression Ignition (HCCI) engine concept [Christensen et al., 1997]. This engine offers the opportunity to achieve high thermodynamic efficiency and sharply or completely eliminate production of soot and oxides of nitrogen (NO_x). It accomplishes the low NO_x emissions by operating at very low product temperatures, which are achieved either by running at very low fuel/air equivalence ratios or with very high inert gas dilutions. A major challenge is that, due to their low product temperatures, HCCI engines also experience large emissions of unburned hydrocarbons and CO, which currently must be reduced via exhaust aftertreatment.

A unique feature of HCCI combustion is that combustion is initiated by thermal autoignition due to rapid compression of a nearly homogeneous fuel/air mixture. This compression ignition is different than in SI engines, where ignition is produced by a spark plug, or in diesel engines, where ignition follows rapidly after fuel injection into very hot, compressed air, close to the end of the piston stroke. The time of ignition in SI and diesel engines is therefore much more predictable than ignition in the HCCI engine. HCCI ignition is also much more dependent on the details of chemical kinetics of the hydrocarbon fuel oxidation than SI or diesel engines.

The most unique feature of HCCI engines, however, is that they have been shown to operate efficiently using natural gas, gasoline or diesel fuel, unlike either SI or diesel engines, both of which require specialized fuels. The fuel tolerance of the HCCI engine is a direct result of the fact that no flame propagation is required, and the only requirement for HCCI combustion is that the fuel ignite at a time close to maximum compression (Top Dead Center, or TDC) of the piston stroke. Virtually any combustible hydrocarbon/air mixture will ignite after being sufficiently compressed, so the primary combustion design challenge is to accommodate the oxidation kinetics of the fuel being employed to ensure ignition at the desired time.

Recent experimental studies of HCCI combustion [Sjöberg and Dec, 2007, 2007b] show how a high ON fuel, iso-octane (ON = 100), and a lower ON fuel (PRF80, with ON = 80) both ignite at the same time in the same engine, as shown in Figure 7. The greatest difference in the performance of the two fuels is that the lower ON fuel has a period of significant heat release early in the engine cycle, prior to the main ignition, while no corresponding early heat release is seen for the iso-octane. This lack of early heat release for iso-octane is a direct result of the much lower rate of low temperature kinetics in iso-octane, which is in turn the result of the molecular structure of iso-octane.

In the accompanying Figure 7, the initial temperature of the iso-octane mixture is 20°C higher than the PRF80 mixture, to compensate for the early heat release of the PRF80 mixture. Other fuel mixtures with different levels of low temperature reactivity can be accommodated with equal flexibility in the same engine by taking into account their relative amounts of low temperature reaction and heat release. Advances in the fundamental chemistry of low temperature kinetics [Westbrook et al., 1991; Pollard, 1977] have made it possible to understand and predict the kinetics of low temperature reaction of different hydrocarbon fuels. Most of these advances, however, have been in the relatively simpler areas of n-paraffin and iso-paraffin fuels, while many fundamental questions remain with respect to the low temperature kinetics of cyclo-paraffins, aromatics, unsaturated and oxygenated hydrocarbon molecules, as well as complex mixtures of different types of fuels. Even the kinetics of simpler n-paraffin and iso-paraffin fuels are incompletely understood, with new elementary reaction pathways still being discovered. Nonlinear interactions between fuels with different ignition behavior are commonly observed, and extensive experimental, theoretical and kinetic modeling studies are essential to examine these effects. Advances in the fundamental understanding of kinetics of ignition of complex fuel mixtures will have a significant impact on the future of HCCI engine development. Additional basic chemistry tools involving features such as electronic structure and energy transfer in systems with large numbers of heavy atoms must be developed in order to resolve the theoretical problems controlling these processes.

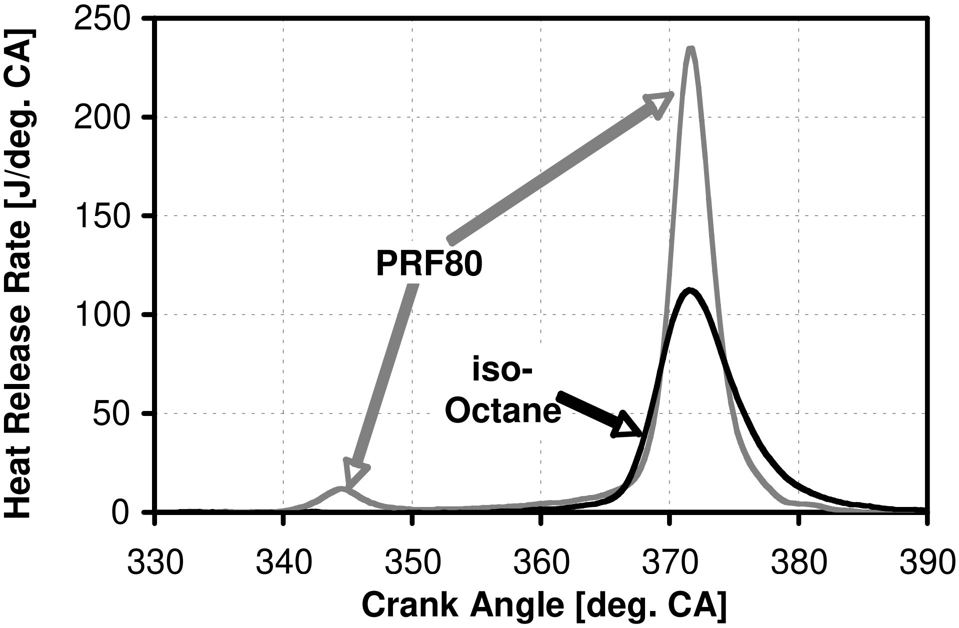


Figure 7. Measured heat-release rates in HCCI engine combustion. [Sjöberg and Dec, 2007a].

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS

Future transportation fuels have many characteristics that are quite different from current practical fuels, including significant differences in composition that may contribute to important differences in combustion behaviors. These compositional details must be thoroughly understood in order to ensure that transportation systems and vehicles will be able to make a good transition from current to new fuels over the coming years. In other ways, the next generation of transportation fuels, using new sources of liquid fuels, are very similar to current fuels in that they consist of complex mixtures of the same classes (see Figures 2 and 3) of hydrocarbons as current fuels. The distinctions lie in the different amounts of components in each fuel class and that, in some cases, specific components in new transportation fuels are somewhat unique. However, many of the tools used to study current fuel chemistry and other properties are the same as those that will be needed to study new fuels. Because the important molecules in the newer fuels are significantly larger than those in gasoline in particular, and diesel fuels to a lesser degree, some other tools will require new advances to examine the new fuels.

Fuel Properties

Most of the fuels being proposed as future transportation fuels are extremely complex mixtures of very large molecules, and fuel characterization is an immediate research need. This is apparent at every stage of conversion of each basic resource from upgrading, refining and to characterization of the eventual liquid fuel. Much of this development is the natural task of the oil refining industry, but considerably more is needed for purposes of basic research. Physical properties of as many as possible of the important components of each fuel must be available to enable physical and chemical modeling activities.

The same needs exist for biodiesel fuels [Graboski and McCormick, 1998], most of which are also mixtures of large oxygenated, largely alkyl ester hydrocarbon molecules whose properties are not well established. Properties of diesel/biodiesel mixtures are very likely to be important for many years, and lack of information on the biodiesel components is a serious limitation. An important basic science element for biofuels is likely to involve genetic modification of the botanical sources for the vegetable oils from which the biodiesel fuels are produced. For example, the major biodiesel fuel source in Europe is the methyl ester produced from rapeseed oil; modern rapeseed oil, Canola oil, is genetically different from rapeseed oil of past decades, which was found to contain oils that were unhealthy for human consumption. Corresponding genetic modifications in vegetable oils to make them more attractive as transportation fuels are extremely likely, as are developments of other sources of biofuels, including molecules secreted by algae and other microorganisms. Characterizations of the physical and chemical characteristics of these rapidly emerging biofuels will require many new processes and techniques.

Biodiesel Fuels

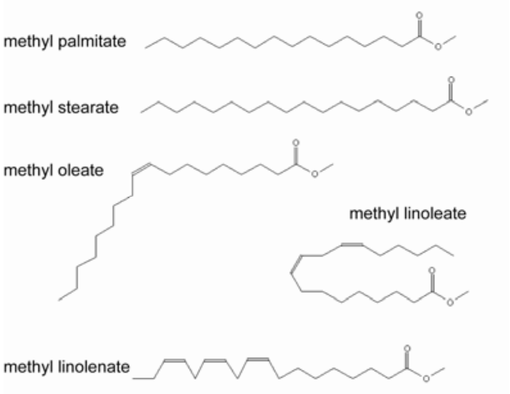
Biodiesel is defined as “fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats”. Biodiesel is typically created by reacting fatty acids from many types of plants, as well as some animal fats, with an alcohol in the presence of a catalyst to produce the desired mono-alkyl esters and glycerin. After reaction, the glycerin, catalyst, and any remaining alcohol or fatty acids are removed from the mixture. The alcohol used is typically methanol (which results in methyl esters as the biodiesel fuel), although ethanol and higher alcohols also have been used. Most biodiesel produced in the U.S. is made from soybean oil, which produces biodiesel fuel consisting of the five methyl esters shown in the accompanying figure. Neat (i.e., 100%) biodiesel can be used, but a blend of between 2% and 20% (by volume) of biodiesel with conventional diesel fuel is preferred to avoid engine-compatibility problems.

Interest in biodiesel fuel use in the U.S. has been growing due to its potential to reduce dependence on imported petroleum, to help mitigate possible negative impacts of global climate change by lowering net CO_2 emissions from the transportation sector, and tax incentives and publicity that have resulted from the efforts of biodiesel advocates.

Biodiesel has a number of other attractive attributes. Engine tests have shown that biodiesel fuel leads to lower emissions of particulate matter, unburned hydrocarbons, and carbon monoxide. Biodiesel typically has improved lubricity and ignition quality relative to diesel fuel, and biodiesel is sulfur-free, so it won’t poison catalytic aftertreatment systems. Furthermore, biodiesel is considered to be a renewable or carbon dioxide-neutral fuel.

Diesel engine emissions of nitrogen oxides (NO_x) increase by approximately 1% for every 10 vol% of biodiesel blended into diesel fuel. Biodiesel also can create problems in cold-weather conditions by plugging fuel filters. Biodiesel is often more susceptible to oxidative and biological instabilities than conventional diesel fuel, though this can be avoided by adding small amounts of stabilizer and biocide. Finally, impurities such as unreacted fatty acids or alcohol, as well as glycerin or catalyst left over from the production process, can accelerate wear or corrosion of engine components.

Many questions remain regarding the properties of biodiesel components in diesel fuels, including both physical and chemical properties, as well as the economic questions of biodiesel fuel production and the potential of biodiesel fuel to impact the transportation fuel market. However, the potential benefits are sufficiently attractive that research must address these issues.



Molecular structures of the five methyl esters that typically comprise soy biodiesel

Since fundamental studies of fuel chemical properties will involve optical measurements, optical properties of components and composite mixtures of these fuels will be essential for many absorption and emissions measurements. While significant advances in laser diagnostics in combustion systems have been made in the past 20 years, steady growth in optical techniques are expected and needed.

Most combustion environments involve high operating pressures, commonly as high as 100 bar for diesel applications, and perhaps as high as 1000 bar in specialized systems in the coming decades. There is a continuing need for experimental facilities that can measure hydrocarbon properties at such elevated pressures. These properties include equation of state parameters, gas phase properties, and liquid properties. Theoretical studies of high pressure phenomena are also seriously lacking. These quantities are needed for current fuels, especially for diesel fuels, and extensions of these studies to properties of next generation hydrocarbon fuels components and mixtures are very important. These are needed for individual component species and for complex mixtures.

Kinetic studies

Kinetic modeling tools are lacking for current transportation fuels due to the lack of detailed mechanisms and reaction pathways for most of the components of these fuels. Most of the research needs for future transportation fuels also apply to current transportation fuels, including diesel and jet fuel and gasoline. It is widely accepted that reaction pathways can be affected dramatically by significant changes in pressure, and reaction pathways for these alternative transportation fuels are not known at extremely high pressures.

Virtually no site-specific elementary reaction rates have been measured for hydrocarbon molecules with more than five or six carbon atoms. In most cases, those rates of H atom abstraction, stable species radical decomposition, radical addition, isomerization, and other reactions are estimated on the basis of reactions with smaller species that have some sort of functional similarity. Most existing experimental kinetic measurements have been made using small species, such as methane, ethane, propane, n-butane and iso-butane for alkanes; ethene, propene and isobutene for olefins; methanol, ethanol, formaldehyde, acetaldehyde, dimethyl ether, and a few others for oxygenates. These data have then been used to estimate the rates of similar reactions for larger species, with confidence limits that are difficult to assess. Direct kinetic studies are needed for large hydrocarbon species of importance to transportation fuels.

Experiments are often used with coupled kinetic modeling and sensitivity analysis to extract rate data for important elementary reactions, frequently involving reactions for which direct kinetic measurements are difficult or impossible to carry out. However, very few such experimental studies have been done for the important components of future or current transportation fuels. Somewhat surprisingly, a fairly extended literature of laboratory experimental chemical kinetic results exists for the gasoline primary reference fuels n-heptane and iso-octane, but the opposite is true of the diesel reference fuels n-hexadecane and 2,2,4,4,6,8,8-heptamethyl nonane, or for species like the former diesel reference fuel α-methyl naphthalene, for all of which very few laboratory experiments have been done; and very little experimental data is available for any polycyclic aromatic or paraffinic molecules in any types of experimental facilities. This is again especially true for experiments in the low temperature regime where many of the most significant differences are observed for different molecular structures. Much more work is needed to expand the experimental databases of kinetic information for the species that are present in future transportation fuels in order to accelerate adaptation of them for practical applications. Advances in chemical theory are also required to describe complex chemical species under extreme conditions of pressure and for species with large numbers of heavy atoms. New theoretical progress and advances in numerical algorithms to exploit corresponding advances in computational capabilities are needed. Software improvements are also needed for chemical system analysis of flames, chemical reactors and many other specific problems; existing modeling tools and their algorithms for simulations of chemically reacting flows are now nearly 30 years old and can be improved significantly.

The need for better characterization and kinetic modeling is even more pressing for transportation fuels themselves. Somewhat surprisingly, this includes gasoline, diesel fuel and jet fuel; very limited experimental literature exists for any of these, much of it very recent and limited to a few shock tube and jet-stirred reactors. Some of these experiments will be difficult because these large, low vapor pressure liquids are difficult to vaporize for gas phase experiments. In many cases, this will require experiments at elevated temperatures in order to overcome the low volatility of the fuel species, and new experimental facilities and techniques will be needed to carry out such experiments.

Very little experimental, theoretical or kinetic modeling information is available at any temperature or pressure for aromatic or simple cyclic paraffin species; the same is true for polycyclic aromatic and paraffinic hydrocarbons, for most of which there is virtually no basic kinetic information. Reaction pathways can change dramatically as pressure (or equivalently, density) increases; new pathways can emerge as increasing pressure begins to inhibit conventional pathways, and this is particularly true for complex isomerization and polymerization reactions of large hydrocarbons and soot precursors. In addition, the heterogeneous processes of gas phase addition to microscopic soot particles and the rates of these processes are almost completely unknown.

Automatic mechanism generation and reduction

Detailed kinetic and other studies are needed for the chemical species that should be used as surrogate components. Since these species are likely to be large molecules themselves, automatic generation of kinetic models for these species will be needed. Automatic reaction mechanism generation tools are currently weakest in the areas of aromatic and cycloparaffinic species, so advances for these fuel classes are needed.

Automatic mechanism generation generally requires “rules” for different classes of reactions, and there are many important classes of reactions for which there is not sufficient understanding of the fundamental processes and critical parameters for rules to be developed. Current capabilities can produce reliable kinetic mechanisms for alkane species and some aromatic species at high temperatures, but there is a need for extending these capabilities to different classes of fuel molecules and to the more complex, low temperature kinetic regime.

The same features apply to automatic mechanism reduction techniques. The major reaction pathways for oxidation of aromatic hydrocarbons are reasonably well established only for the very simplest aromatic species benzene and toluene, and relatively little is known for polycyclic aromatic hydrocarbons that would make it possible to provide reduced or skeletal mechanisms for their combustion.

Surrogate models

Surrogate models for current transportation fuels are limited because models for important components are not available. For example, the primary reference fuels for diesel fuel are n-hexadecane and 2,2,4,4,6,8,8-heptamethyl nonane, and the only kinetic models for either of them are high temperature mechanisms for n-hexadecane [Fournet et al., 2001; Ristori et al., 2001]. N-hexadecane is important in diesel fuel simulations because it provides the low temperature fuel characteristics that play an essential role in simulating diesel ignition and its cetane number, and existing models do not include these reaction pathways.

Due to the complexity of the next generation of transportation fuels, suitable surrogate mixtures are needed to represent them in experimental and modeling research activities. As already noted, the compositions of biodiesel, oil sands, oil shale, and coal oil fuels are each characterized by somewhat different fractions of basic fuel molecule types, and the ability to understand those individual components is essential to be able to describe the overall fuel behavior.

Part of the difficulty is that, perhaps even more so than with conventional gasoline, diesel fuel or jet fuel, future fuels include very large molecules with multiple-ring aromatic and naphthenic ring features, and even single-ring aromatic and paraffinic molecules are at the limit of present modeling and characterization capabilities. Oil sands fuel has a considerably greater naphthenic content than either gasoline or diesel fuel, and the soot-producing tendencies of oil sands diesel fuel are expected to be affected significantly by these non-aromatic multicyclic species; but kinetic studies have only begun very recently on the simplest of such species, such as cyclohexane, methyl cyclohexane, and a few others [Pitz et al., 2007; Silke et al., 2007]. Oil sands, oil shale and coal liquids also contain large amounts of complex multicyclic aromatic compounds, and reaction pathways and kinetic mechanisms for these species are virtually unknown and need a great deal of attention.

CONCLUSION

As supplies of conventional petroleum-based fuels decline, alternative fuel sources will be needed to provide transportation fuels for the remainder of the 21st century. These sources are likely to include fuels produced from oil shale, oil sands, coal, and a wide range of biological sources, including vegetable and animal oils, as well as materials produced from algae and other sources as yet undetermined. A wide range of the properties of these fuels must be known to enable transportation systems to use these fuels in economic and environmentally sensitive ways. Basic science is required to provide this information.

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CROSS CUTTING SCIENCE PANEL

CURRENT STATUS

Conventional internal combustion engines operate in regimes where NO_x and soot are anti-correlated so that reducing one increases the other (e.g. [Heywood, 1988]). Advanced engine designs reduce both pollutants by moving to regimes of lower temperatures, higher pressures, and chemical and/or spark ignition. Conventional fuels come from sweet crude oil, a limited resource largely under foreign control. Non-traditional fuels may be more oxygenated (e.g. biodiesel) and richer in cycloalkanes, highly condensed aromatics, and trace species (e.g. fuels from oil sands). Transitioning to advanced engines and alternative fuels requires basic research in gas phase chemistry, multiphase chemistry and dynamics, and four-dimensional (4D) modeling and simulation.

Gas Phase Chemistry

The fundamental chemistry discussed in this section informs experimental/theoretical studies of more complex, realistic combustion systems.

Gas phase measurements. With modern mass spectrometric and optical spectroscopic detection techniques, gas phase kinetics [Kumaran et al. 1994; Knyazev and Slagle 2002] and thermodynamics [Berkowitz et al. 1994] measurements of unprecedented sensitivity can be carried out on both radical-molecule and radical-radical reactions (see sidebar on high temperature methods for kinetics). For relatively low pressures, kinetics studies are widely carried out in flow tubes in the temperature ranges relevant to autoignition (700 – 1000K) [He et al. 1998a; He et al. 1998b] and in shock tubes at higher combustion temperature [Michael and Lim 1993]. Chemical dynamics of combustion species can be probed by molecular beams with non-thermal energy distributions. Photoionization studies have had a major impact on thermodynamic measurements [Ruscic 2000]. For high pressure conditions, several high pressure shock tube and flow tube instruments have been built [Tranter et al. 2001] that have produced a few key measurements, such as the direct measurement of transient adducts [Tranter et al. 2004] and high pressure limits in recombination reactions.

High-temperature methods for chemical kinetics

Measurement of the fundamental chemical processes involved in combustion requires methods to reach temperatures relevant to combustion while maintaining control over the mixture composition and isolating the reactions under study. There are many techniques that have been developed to accomplish this, and this sidebar discusses the three most common. The simplest is just to heat the reaction cell; this direct approach is usually limited to temperatures below 1000K, although specially designed reactors have been used up to 1900K. Limitations of this method arise from the need for heat resistance of the cell itself, which must be at the process temperature, and from unwanted thermal reactions at the cell walls or during the heating of the gas. Compression heating and shock wave heating overcome some of these obstacles by directly heating the gas, leaving the walls at a lower temperature.

Rapid compression machines, like that shown at the right in Figure 1, heat gases by pushing an initially low pressure gas into a much smaller volume, heating it in the process. These machines are carefully designed to ensure uniform compression and homogeneous heating.

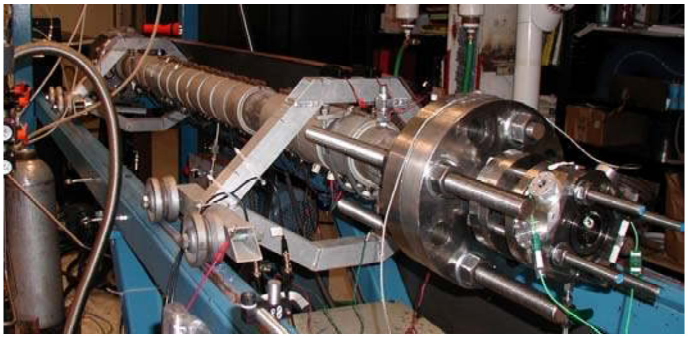


Figure 1. *Rapid compression machine at the University of Michigan (courtesy Prof. Margaret Wooldridge). The reaction mixture initially filling most of the large tube is heated when a shaped piston, driven by a high-pressure gas, compresses the mixture into the small windowed chamber at the far right end.*

Figure 2. *Shock tube at Stanford University (courtesy of Dr. D. Davidson). The silver tube running diagonally across the picture is the shock tube. Laser-based methods measure reaction rates at the far end.*

Almost instantaneous heating is possible with shock tube techniques. As seen in Figure 2, a shock tube is typically a long tube where an inert high-pressure "driver" gas is separated from the low-pressure reactive mixture (the "driven" gas) by a thin diaphragm. When the diaphragm bursts, a shock wave passes through the test gas raising it to reaction temperature. The pressure and temperature behind the shock wave are calculated from the measured speed of the shock wave and gas characteristics. Shock tubes are the most reliable technique for producing very high temperatures (more than 20,000K with explosive-driven shock waves) and pressures from 0.01-1000 bar. These devices are extremely versatile tools for gas kinetics due to the wide range of accessible reaction conditions, lack of wall reactions and the variety of diagnostic techniques available. The rate of reactant loss and product formation can measured in the near instantaneously heated gas behind the shock front.

All of the above methods increase in difficulty as the molecular species become larger and as the pressure increases. Large molecules, especially radicals, can have many isomers in partial equilibrium with each other, high state densities, and more complicated secondary chemistry. Isomerization can compete with vibrational relaxation, and inelastic processes become difficult to define. Optical spectroscopic methods applied to large molecular species at high temperatures are often limited by spectral congestion, overlapping absorptions, quenching, and high rovibrational partition functions. At high pressures (up to 1000 atmospheres are under consideration for advanced engine designs), spectroscopic techniques may encounter boundary layer effects [Michael and Sutherland 1986] and line broadening that affect the interpretation of the signal. Mass spectroscopic techniques involve sampling issues in transitioning from the high pressure gas to the low pressure ionization chamber.

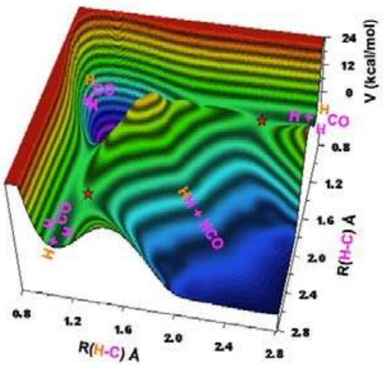
Because of these factors, the most successful measurements are on small species. Improvement in the spectroscopic measurement of combustion intermediates progresses essentially one-molecule-at-a-time as molecular absorption or fluorescence systems are characterized and regions of acceptably low contributions from interfering species are located. Recent development of diode laser-based probes at near-IR and IR wavelengths has facilitated spectroscopic diagnostics for some larger molecules. Several novel techniques appropriate for large molecule detection are being explored that involve X-ray and VUV light sources. Some user facilities offer intense VUV light which can selectively ionize large molecules to allow isomer-specific photoionization detection [Taatjes et al. 2005; Taatjes et al. 2006]. Similarly, spectroscopic techniques have begun to be used that identify chemical species of large molecules by X-ray absorption near atomic resonances [Messer et al. 2005; Muntean et al. 2005]. While these new approaches are encouraging, sensitive and selective measurement of such crucial species as peroxides and peroxy radicals, hydrocarbon, and heteroatom-hydrocarbon radicals remains elusive.

These limitations prevent modern kinetics and thermodynamics laboratory studies of key intermediates in alternative fuels at the high pressures of advanced engine design. For example, the peroxy radicals resulting from the first oxidation steps of fuel molecules are central players in the compression ignition phenomena in many engine designs. The nature of these peroxy radicals and their hydrocarbon radical precursors are not experimentally known, and the chain-branching behavior of resultant peroxy radicals is an open experimental question, despite years of experimental work. For another example, at the highest pressures under consideration, large molecules may experience reactive collisions within unimolecular dissociation lifetimes, leading to gas-phase diffusion-controlled kinetics difficult to characterize with most of today's techniques.

Calculations. Calculations of chemical reactivity are now often directly comparable to combustion measurements. Such simulations typically require calculating both points on the potential energy surface (PES) (see the accompanying sidebar on quantum mechanics to rate constants) and the response of atoms and molecules to those forces. Heats of formation can be calculated to within tenths to several kcal/mol depending on molecule size [Ruscic et al. 2002; Curtiss et al. 1998; Wagner 2002]. Rate coefficients can be calculated with statistical methods to well within a factor of two over large temperatures and pressure ranges [Harding et al. 2005; Pu and Truhlar 2002]. Rate constants involving electronic non-adabatic processes can be calculated to similar accuracy by classical and quantum dynamics methods [Evenhuis et al. 2005], but experience is limited to smaller molecules. Non-statistical reactions and inelastic processes (important in pressure-dependent reaction rates) can be approximately represented by classical trajectories [Lahankar et al. 2006; Skjøth-Rasmussen et al. 2002].

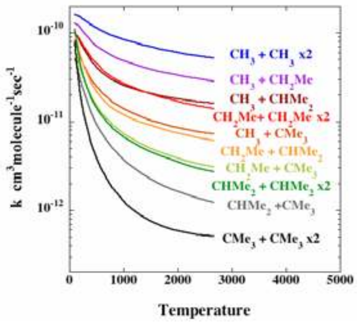
Quantum Mechanics to Rate Constants

Chemical bonds form when atoms share electrons. Reactions form and break bonds and hence calculations of rate constants requires computationally describing electrons. Electrons are too small and fast to be treated by the mechanics of Isaac Newton. Quantum mechanics is required and its application produces a potential energy surface (PES) that describes the forces on atoms. The figure to the left shows the PES for a hydrogen atom (tan color) reacting with formaldehyde (magenta color). There are 9 distances and angles that locate the relevant position of all the atoms for this reaction. That portion of the PES dependent on two C-H distances is displayed (other coordinates are optimized to lower the energy). Like a hiker guided by a contour map, atoms will try to traverse the PES on the path with the lowest energy between reactants and products. Stable reactants and products appear as channels (e.g., H+H_2CO and HH+HCO) or wells (CH_3O) on the PES. The lowest energy path to products HH+HCO goes over a mountain pass on the PES whose highest elevation (called a transition state [TS]) is marked by a star.

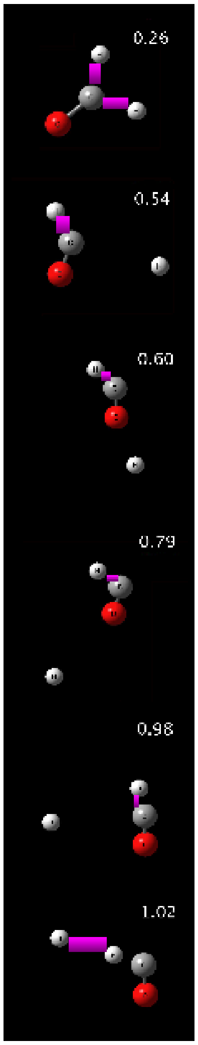


The commonly used approach to calculating reaction rates is a statistical theory called transition state theory (TST). Much like calculating the leak rate of a bucket with a hole in it by comparing the area of the hole with the volume of the bucket, TST calculates the reaction rate as a ratio of the energy-weighted cross-sectional area of the TS to the volume of the reactant channel. TST has been used to predict many combustion rates.

The plot below displays the TST-calculated temperature dependence of the rates of a number of alkyl radical combination reactions. The calculations convincingly demonstrate that the rates slow both with increasing temperature and increasing size of the radicals. Less than half of these rates have ever been successfully measured and none over the entire temperature range needed for combustion modeling.



Although transition state theory has proven to be adequate for many reactions, recently some reactions have been found that bypass the transition state. The frames at the right are an example of a trajectory for the reaction $H_2CO \rightarrow H_2 + CO$ that does not pass through the transition state region for this reaction. At present, accurate treatment of these kinds of reactions requires a more detailed, non-statistical, modeling of the nuclear motion using either classical trajectories or full quantum dynamics.



Some attempts have been made to automate these complex calculations. A computer, given the reactants, produces reliable rates or heats of formation for all species it determines to be relevant. Automatic mechanism generation schemes [Tomlin et al. 1997; Green et al. 2001] employ rate constant and thermodynamics estimators based on empirical rules. Direct kinetics can converge rate constant calculations by optimizing PES point selection [Klippenstein and Harding 1999] but so far only for simple reactions. Heats of formation can be obtained in an "active" way that keeps track of the inherent interdependencies [Ruscic et al. 2004], allowing both quick updates with new knowledge and automated discovery of uncertain bond dissociation energies; but as yet no fully automated method exists to mitigate uncertainties in thermochemical values by calculation.

Beyond obtaining reactivity information, adaptive methods are needed to reduce large kinetics models to the relevant information needed at each grid point in a 4D simulation. While many reduction methods are available [Reagan et al. 2005; Liu and Pope, 2005; Skodje and Davis 2001; Okino and Mavrovouniotis 1998], there is only limited experience with these schemes, little consensus on their applicability, and essentially no information on their error propagation.

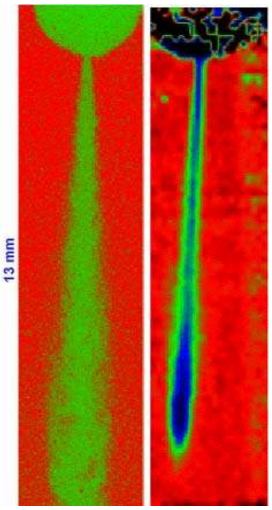
Multiphase chemistry and dynamics

Internal combustion engines generally involve multiple phases, from the liquid fuel that must vaporize and mix with air, to reactions at thin liquid films on cylinder surfaces, to particulate pollutants that form and react in the burned gases. The details of multiphase processes are often poorly understood and empirically modeled.

The turbulent spray that accompanies fuel injection is one of the most important multiphase systems for determining combustion performance, and the dynamics of these sprays depends heavily on the physical and chemical properties of the fuel. The physics of the injection process is presently not computed from first principles but is empirically modeled. Present and newly emerging techniques can image the physical details of spray breakup, e.g., via ballistic imaging [Linne et al. 2006] or X-ray tomography [Cai et al. 2003] of liquid sprays (see sidebar), phase Doppler anemometry (PDA) for the droplets in the downstream region of the spray [Black et al. 1996], laser Doppler anemometry/particle imaging velocimetry (LDA/PIV) for the gas flow [Adrian 1991; Miles and Lempert 1997], and Mie/Rayleigh/planar laser-induced fluorescence (PLIF) imaging of the overall spray [Stojkovic and Sick 2001]. The multiphase chemistry in the secondary stream, where surface-to-volume ratios are high, is still poorly known. Overall burning rates and various other aspects of combustion of isolated droplets have long been studied [Aggarwal 1998] but only with limited (generally gas-phase) speciation. Methods that can probe both phases of the dilute region with chemical specificity remain undeveloped. It is not known if interfacial chemical reactions affect evaporation or subsequent chemistry, especially for blended fuels. The changing chemical composition and kinetics at the liquid/vapor interface have not yet been measured.

X-rays in Combustion Science

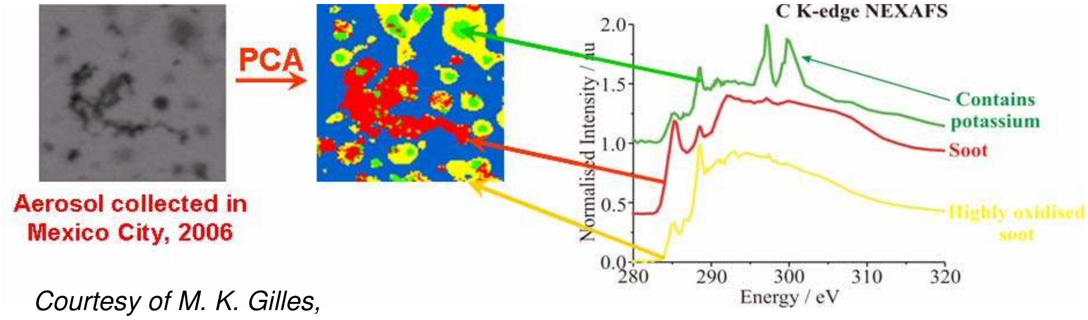
X-rays have substantial advantages over light in other regions of the spectrum for investigating materials. The first advantage is the one that they are most famous for— they travel through things that stop visible light. Media that are opaque or turbid to visible light are often transparent to X-rays. An example of this can be seen to the right, where a liquid fuel spray, generated by a commercial fuel injector, is imaged with visible and X-ray light. Whereas the visible light merely sees a blurry blob because the turbulent flow around the jet scatters the light, the X-ray image penetrates this cloud and shows that the spray has a liquid core that contains most of the injected fuel.



Visible Light **X-Ray Image**

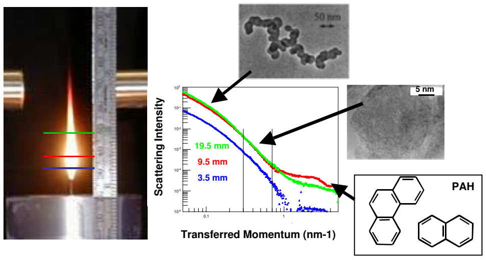
Courtesy of J. Wang, Argonne National Laboratory

Because their wavelength is much smaller than that of visible light, X-rays can distinguish objects on much smaller length scales, making them extremely powerful for imaging applications. Furthermore, characteristic absorptions of X-rays by atoms can directly give information on the nature of chemical bonding. The figure below combines the imaging power of X-rays with the spectroscopic information from the wavelength dependence of the absorption to measure the distribution of chemical species on soot aerosols.



Courtesy of M. K. Gilles, Lawrence Berkeley National Laboratory

X-rays are relatively impervious to extreme conditions and hence can be used to peer directly into flames and combustion devices. At the right, X-rays are scattered at different flame heights. The intensity as a function of angle (related to the label of momentum in the figure) tells the size of soot particles in the flame and their polycyclic aromatic hydrocarbon precursors (PAH).



Courtesy of J. Hessler, Argonne National Laboratory

Coupling the spatial resolution and chemical specificity of X-ray techniques to time-resolved methods is a continuing challenge. Brilliant X-ray sources like the Advanced Photon Source allow images to be taken with short exposure times; short-pulse X-ray sources, like those available from high harmonic generation or from the high-brightness Linac Coherent Light Source under construction at the Stanford Linear Accelerator Center, can bring the time resolution to the scale of atomic motion.

A similar situation exists for probing of particle formation; soot particles are the most prominent of these (generally undesirable) particulates, but other particles are also of concern. (See the accompanying sidebar on soot.) Despite intense studies of soot chemistry, the mechanisms of soot inception, growth, and oxidation remain uncertain. The impacts of metals (from lube oil additives), conditions of high pressure and low temperature in advanced engines, or hetero atoms (oxygen, nitrogen, and sulfur) in alternative fuels are not well known. Inception is the best understood stage of the soot lifecycle, although the roles of the multiple mechanisms for forming the first aromatic ring require further clarification. The growth of multiple rings, the linking of rings into initial particles, the agglomeration of those particles, and then the oxidation of those agglomerates in burnout are poorly characterized. Techniques to study particle formation, e.g., laser [Black et al. 1996] or X-ray scattering [Hessler et al. 2002; Beaucage et al. 2004], have begun to be applied in the high-pressure, reactive environments relevant to combustion pollutants. Sampling and post-analysis of particulates can give size, morphology and composition, and continues to gain in sophistication; but in situ measurement techniques that offer chemical specificity remain largely undeveloped. Moreover, the effects of particle composition and environment on many commonly used detection methods are still poorly understood, but may be critical to their accurate implementation. For example, Laser-Induced Incandescence (LII) is currently used to observe soot formation in the engine, but LII has not been validated at high pressure [Michelsen et al. 2003]. Techniques to characterize and quantify non-heterogeneous solid particles—volatile coatings on nanoparticles, for example—are particularly severely limited.

Soot

Soot is that black substance we can see curling off of candle flames or coming out the exhaust of generally older, poorly functioning cars and trucks. Soot is also a commercial product called carbon black that has a myriad of industrial uses.

Soot is formed in regions of combustors that have high fuel concentrations and relatively little oxygen. Its formation is initiated by reactions of carbon-based fuel molecules produced by partial fuel combustion. These initial reactions produce larger organic molecules containing carbon rings, which are referred to as polycyclic aromatic hydrocarbons (PAHs). Large PAHs associate and condense to form small nascent particles in the size range of 5 nm (see Figure 1). These particles are rich in carbon but relatively deficient in hydrogen.

These incipient particles grow in size to form carbon spheres in the size range of 15-50 nm and aggregate to form larger branched-chain particles of widely varying size (see Figure 2). A typical size for a soot particle produced by a modern conventional diesel engine is ~150 nm, which is too small to be visible to the human eye but small enough to lead to severe respiratory and cardio-vascular illnesses with exposure. Older diesel engines produce much larger soot particles, resulting in billowing black exhaust plumes.

The small size and non-spherical morphology of these particles complicate optical measurement techniques. At higher temperatures soot particles react rapidly with oxygen and under some conditions can be completely oxidized before making it into the exhaust stream.

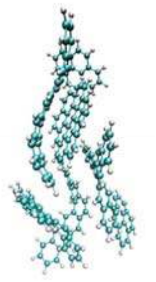


***Figure 1.** Molecular dynamics simulation of PAH clustering reactions underlying soot formation. Image from Shawn M. Kathmann (Pacific Northwest National Laboratory)*

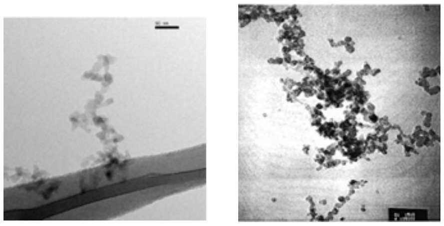


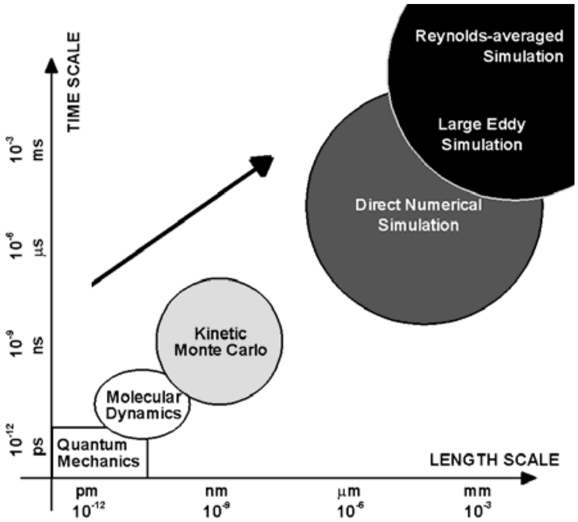
***Figure 2.** Transmission electron microscopy images of a soot aggregates produced in a flame (left) and in a diesel engine (right) [reproduced from (Song et al., 2002, Energy and Fuels 16, 294) with permission].*

Soot simulations are a classic multiscale problem. (See the accompanying sidebar on multiscale simulation methods.) Molecular level modeling of soot has not yet incorporated high level rate constant and thermodynamics calculations, which are difficult for large molecules [Miller et al. 2005]. The transition from bimolecular approaches to gas/surface approaches for soot kinetics calculations has not yet been attempted. However, novel Monte Carlo (MC)/molecular dynamics (MD) calculations with relatively low level representations of forces and rates have been developed to bridge the time scales in soot formation [Violi et al. 2004]. These approaches trace out trajectories of soot particle growth that with appropriate sampling can lead to representations of soot particle shapes and distributions. Modeling of mature soot, including its radiative properties, will require a continuum model that has yet to be attempted.

Multiscale Simulation Methods

The length scales that are relevant in IC engines range from angstroms (10^{-10} m, atomic/molecular processes), to several nanometers (10^{-9} m, soot particles), to several micrometers (10^{-6} m, fuel droplets), to a fraction of a millimeter (10^{-3} m, smallest aerodynamic flow scales), to several centimeters (10^{-2} m, bore diameter), possibly up to meters (the size of the entire device); the range of time scales is commensurately broad. A dynamic range of ~1,000 in length scales is a practical upper limit for current Tera-scale computing. While Peta-scale computing capabilities and algorithmic advances may push this limit up to ~10,000, enormous increases in computing power would be required to fully resolve all scales.

A full computation of engine combustion that is completely resolved at the smallest length/time scales is a task similar to describing the function of your kidneys based on the quantum-mechanical interactions of all the individual atoms: difficult (presently impossible) and not necessarily informative! The knowledge that is needed to describe a particular physical process will often be located at a particular length/time scale. Multiscale approaches are required to model the effects of unresolved scales on larger/longer resolved scales. The challenge of systems with multiple scales is to carry a rigorous description of processes occurring at small/short length/time scales into a (necessarily simplified) model that can be used in calculations that do not resolve these scales. There is naturally some loss of accuracy in this simplification, and one key challenge in multiscale modeling is to quantify and manage the loss of information.



As shown in the figure, the wide range of simulation approaches that are applied to combustion systems includes: quantum mechanics approaches that describe intra-atomic processes for a small number of atoms; Molecular Dynamics (MD) and Kinetic Monte Carlo (KMC) methods that describe inter-molecular processes for a population of atoms and molecules; and continuum-mechanics approaches that describe chemical and physical processes at macro-scales.

Continuum-mechanics approaches may be further categorized based on the range of spatial and temporal scales that are resolved. In direct numerical simulation (DNS), the continuum-mechanics governing equations are solved directly; all relevant continuum scales are resolved. In large eddy simulation (LES), spatially filtered forms of the governing equations are solved; the dynamics of the large scales are captured explicitly while the effects of small scales must be modeled. In Reynolds-averaged simulation (RAS), the probabilistic averaged forms of the governing equations are solved; the effects of any fluctuation about the average must be modeled.

4D Modeling and Simulation

Scientific computing of combustion. Tremendous progress has been made over the past twenty years in the area of computational combustion, including fine-grained (i.e. high-resolution), research-level approaches used to simulate simplified academic configurations, and coarse-grained (i.e. lower-resolution), engineering-level approaches used to simulate complex engineering systems. This progress has triggered in turn profound changes in the way scientific discovery and engineering innovation take place in the combustion field.

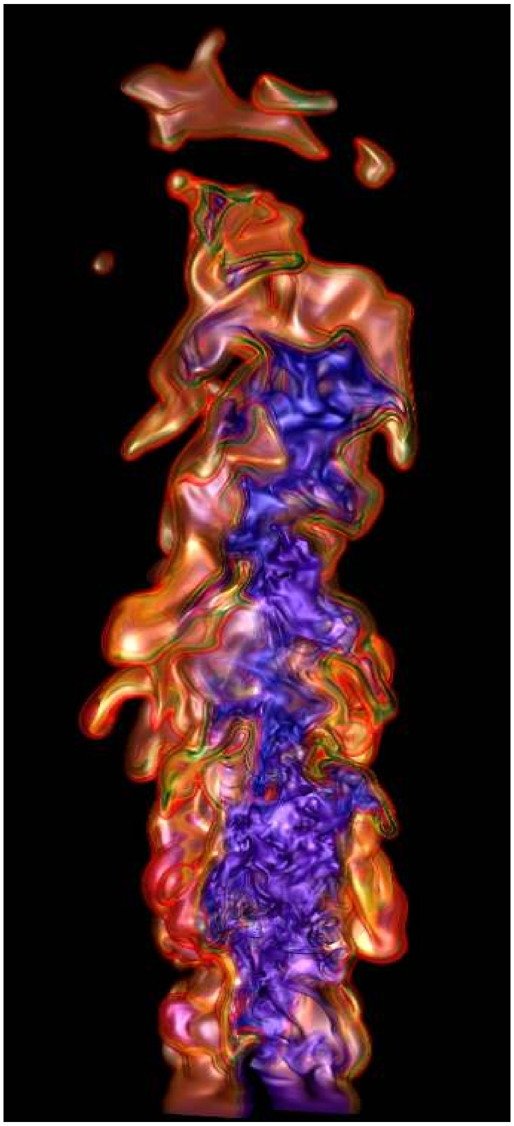
An obvious example that illustrates the depth of these changes is the emergence of computational research as a new scientific approach. This emergence has been driven by progress in hardware technologies (e.g. the high-performance computing—HPC—infrastructure) and software technologies (e.g. developments of numerical methods and algorithms suitable for a first-principles description of chemically reacting flows, i.e. a description based on four-dimensional, continuum-mechanics statements for conservation of mass, momentum and energy). The explosive growth of the HPC infrastructure over the past two decades has been quite remarkable; it currently provides between Tera- (10^{12}) and Peta- (10^{15}) scale computing capabilities (i.e. computational rates between 1 Tera- and 1 Peta-Flops; storage capacity up to 1 Peta-bytes; network bandwidth up to 1 Tera-bits per second) and is expected to exceed the Peta-scale level in the near future.

Examples of computational combustion approaches that have benefited from the sustained growth of the HPC infrastructure include direct numerical simulation (DNS) and large eddy simulation (LES) (see [ASC], [ITR], [SciDAC]). DNS is a high-resolution approach that directly solves the fundamental continuum-mechanics equations for chemically reacting flows, and features high-fidelity descriptions of convective and molecular diffusion transport, coupled with detailed chemical kinetics. (See sidebar on direct numerical simulation.) The DNS approach requires numerical resolution of all relevant physical and chemical scales, both in space and time, and therefore remains limited by computational cost to studies of low-to-moderate turbulence intensities, small-size systems and simple configurations. Despite these limitations, DNS has emerged in the past decade as both the method of choice for fundamental observations of the micro-physics of turbulent combustion, and a much-needed framework to develop and validate the chemical and physical sub-models used in coarser-grained computational approaches [Poinsot et al. 1995; Vervisch and Poinsot 1998; Hawkes et al. 2007; Sankaran et al. 2007].

Direct Numerical Simulation

Direct Numerical Simulation (DNS) is a first-principles description of chemically-reacting flows, i.e. a description based on continuum-mechanics statements for conservation of mass, momentum and energy. DNS provides unique high-fidelity descriptions of turbulent convective transport, molecular diffusion transport and chemical kinetics, in which all relevant physical and chemical scales are resolved, both in space and time. Because of its stringent spatial and temporal resolution requirements, DNS is a computationally intensive approach that requires massively parallel computing power and its domain of application is limited to fundamental studies. With the continual and fast-paced growth in scientific computing hardware and software technologies, DNS is predicted to become the natural companion of detailed experimental laboratory-scale studies of ignition and combustion.

The figure shows a DNS simulation of a typical laboratory combustion configuration corresponding to a (small) turbulent, premixed, methane-air, slot Bunsen flame. The chemical model includes 12 reactive species; the computational domain is decomposed into 200 million cells; and the simulation was performed on 7,000 processors on a Cray XT3 machine at Oak Ridge National Laboratories. The simulation results are used by combustion scientists to gain fundamental insights into the characteristics of the instantaneous flame front in terms of broadening of the preheat zone and surface area wrinkling. This fundamental understanding is applied in turn to test, validate and further develop the chemical and physical sub-models used in engineering-level computational approaches of combustion.



Instantaneous volume rendering of heat release rate (red) and reaction progress variable (blue) in a DNS simulation of a lean turbulent methane-air Bunsen flame (the methane-air flow is from bottom to top). Reproduced with permission from Sankaran, R., E. R. Hawkes, J. H. Chen, T. Lu, and C. K. Law. 2007. Proceedings of the Combustion Institute ***31****, in press.*

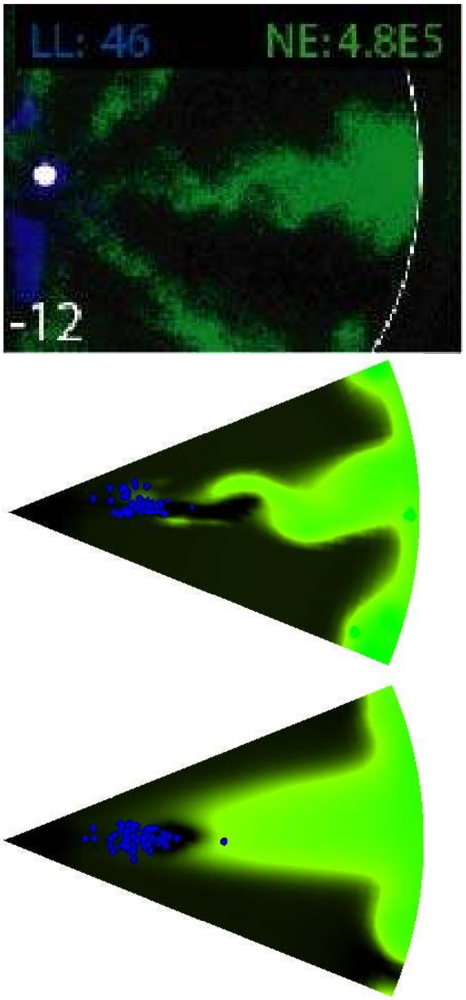
LES is a medium-resolution approach to turbulence simulation based on a direct treatment of the (resolved) large-scale dynamics, and physical modeling of the (unresolved) small-scale variations. (See sidebar on large eddy simulation.) While LES is susceptible to modeling errors and is therefore less accurate than DNS, it corresponds to an effective trade-off between computational cost, performance and accuracy, and features an extended domain of application [Pitsch 2006]. The domain of application of LES ranges from laboratory to practical configurations, and it is worth noting that LES has been recently applied to simulations of Internal Combustion (IC) engines (e.g., Celik et al. 2001; Jhavar and Rutland 2006; Richard et al. 2007].

Large Eddy Simulation

Computer simulations that are targeted for engineering applications require turbulence models. This is especially true for the complex flows that occur inside the cylinders of IC engines. The next generation of turbulence modeling is called Large Eddy Simulation (LES). This name emphasizes the fact that the simulations can capture more of the important large-scale flow features than previous modeling approaches. A generic name for these large-scale features is an “eddy,” which qualitatively describes a swirling motion that is characteristic of turbulent flows. Thus, LES models offer enhanced representations of turbulent eddies and therefore better predictive capabilities. This is illustrated in the accompanying figure.

There are several requirements for LES – faster computers, improved numerical algorithms, and improved physical models. Faster computers are required so that more detail can be incorporated into the simulations. This requirement is progressively overcome with the rapid increase in computer capabilities. The requirement for more accurate, next-generation physical models involves more effort. The purpose of these models is to represent the effects of small eddies – eddies that are too small to be captured in the simulation but still impact the large-scale dynamics.

A key feature of LES models is that they feature low dissipative errors and thereby achieve higher fidelity for the large-scale flow dynamics. Relatively simple LES models have been successfully developed for simple flows. However, for IC engines, with the added complexity of liquid fuel sprays and combustion, the models need to be more sophisticated. This is usually achieved with additional modeling variables and increased complexity.



Snapshot showing combustion around one liquid fuel jet (injection from left to right) in a heavy-duty Diesel engine. The top figure shows the experimental results with the combustion displayed in green and the liquid fuel in blue. The middle figure shows an LES simulation of the same process, and the bottom figure shows a simulation using previous-generation turbulence modeling (RAS). Note that LES captures the wavy structure of the combustion region, while RAS lacks resolution and shows only a smeared region for the combustion.

Engineering computing of combustion. Computational combustion as a new engineering approach followed its development as a scientific approach. Both approaches have been influenced by similar factors, including the following: (1) the growth (i.e. speed-up at an affordable cost) of computer hardware technology; (2) progress made in numerical methods and algorithms (including grid generation methods capable of representing the geometrical complexity of practical systems); and (3) progress made in model descriptions of unresolved physical and chemical, flow and combustion processes (including descriptions of the dynamics of liquid fuel sprays, turbulent flow, turbulent mixing, ignition, combustion and pollutants formation). Computational combustion has now become an established tool in combustion engineering practice, and is considered an important branch in a wider class of simulation tools known as Computational Fluid Dynamics (CFD). In combustion engineering, CFD is primarily used to improve the design and/or reduce the development cost of new systems.

To date, the prevalent approach to treat turbulence in CFD simulations of IC engines remains a lower-level description known as Reynolds-averaged simulation (RAS) [Haworth 2005; Drake and Haworth 2007]. RAS is a coarse-grained approach based on physical modeling of all (large- and small-scale) turbulent flow motions. RAS features an unlimited domain of application; this method, however, is also heavily influenced by modeling errors, requires careful calibration against experimental data, and in the end has limited predictive capability. In contrast, LES (the proposed alternative to RAS) has a much reduced sensitivity to modeling errors, brings valuable information on large-scale flow and combustion dynamics, and has much higher potential as a predictive approach. In addition, RAS in IC engine applications is limited to the calculation of a statistically averaged engine cycle. LES, on the other hand, features a time-resolved formulation suitable to the calculation of individual cycles, and is thereby capable of both producing unprecedented insights into the in-cylinder dynamics, and providing a breakthrough solution to the long-standing problem of differentiating between cycle-to-cycle variations and in-cycle turbulence. A growing consensus in the computational combustion community is that, with the anticipated sustained growth in computer power, LES will soon become the method of choice in CFD simulations of IC engines.

SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS

The Cross Cutting Science Panel challenges in alternative fuels basic research can best be summarized under the following topics: gas phase chemistry; multiphase chemistry and dynamics; and turbulent reactive flows. The last topic represents a more integrated experimental/theoretical effort to characterize combustion systems than is currently available.

Gas Phase Chemistry

Gas phase measurements. The first challenge is to develop sensitive and specific gas-phase detection methods for the key large molecular radicals of alternative fuels and for the high temperatures and pressures of novel engine design. A great scientific opportunity exists to develop “universal” detection methods that can operate under combustion conditions. Mass spectrometry is a “universal” detection method applicable at low pressure. Can novel direct-sampling and ambient-pressure ionization mass spectrometric techniques be developed for kinetics or thermodynamics use? Perhaps in situ methods like X-ray spectroscopy, broadband excitation with spectral cross-correlation, double-resonance tagging methods, and multiplex spectroscopies with frequency combs can be adapted for harsh combustion environments. These methods provide inherently different levels of specificity. Can something short of complete molecular specificity still provide important kinetics or thermodynamics information? The challenge of taking measurements at high pressures and temperatures may be met by innovative cell design. Boundary layer effects could be better understood and quantitatively modeled. Miniaturized, transparent cells might be developed that could sufficiently sustain a well-characterized combustion environment at high pressures.

A related challenge is to develop a detailed and rigorous picture of energy transfer in chemical kinetics, a challenge motivated by the increasing importance of high pressure phenomena in advanced engine design. Presently, pressure effects in chemical kinetics are represented via empirical parameterizations loosely based on direct measures of inelastic processes of mostly stable molecules. At sufficiently high pressures, bimolecular reactions can interrupt the unimolecular decay of reaction products and adducts that have negligible lifetimes and importance at low pressure. Consequently, an exciting science opportunity exists to more rigorously understand the collision-induced flow of internal energy in molecular radicals in high pressure combustion environments. To meet this challenge will require new ways to measure the energy redistribution of reactive species with typically many isomers, each of which may have different inelastic properties. Collisions of these radicals with trace species, such as other radicals, may have significantly different consequences than collisions with more numerous stable species such as N_2 or O_2.

The ability to detect a variety of molecules under combustion conditions not only enables fundamental investigations of chemical reactivity but also contributes to sensor development for real-time intracycle feedback in advanced engine control strategies discussed elsewhere in this report.

Calculations. The principal challenge is to integrate novel theoretical techniques into automated systems that can be applied to kinetics and thermodynamics problems with reduced direct human involvement. Here is a great scientific opportunity to develop novel expert systems with efficient electronic structure and kinetics methods to enable computers to comprehensively enumerate all relevant possible reaction pathways for a given set of reactants and then systematically and iteratively characterize the relevant pathways on the PES and corresponding kinetics or thermodynamics. This solution could perhaps involve point selection on the PES driven by the kinetics, or progressions through inexpensive to expensive electronic structure and kinetics methods to arrive at calculated kinetic and thermodynamic properties with error estimation. Any automated system will occasionally fail and must be flexible enough to learn from failures. Automated systems are also likely to uncover previously unconsidered processes in larger molecule reactions.

A related challenge is the adaptive integration of kinetic and thermodynamics information at each 4D simulation point in multiscale simulations of combustion systems. Such systems from ignition to burnout cover an enormous range of chemistries, only a very small fraction of which is relevant to any given simulation point. Here too is a great scientific opportunity to develop, modify, and test new and existing methods to reduce large chemical mechanisms at each 4D point to what is relevant to advance the simulation. Because of the uncertainty in any determination of kinetic and thermodynamics properties, part of this challenge is to develop ways to propagate these uncertainties to other scales in the simulation. The development or adaptation of reduction methods to parallel computer environments may also be important.

Multiphase Chemistry and Dynamics

The challenge of multiphase combustion is to develop experimental methods that probe the physics of turbulent multiphase flows or reveal chemical reactivity at phase interfaces and to develop the theoretical techniques that can reproduce and interpret this information. Fundamental scientific questions of heterogeneous chemistry arise in many poorly understood aspects of combustion, including heterogeneous chemical reactions in evaporating sprays preceding ignition and reactions in boundary layers or thin films near surfaces of combustors. The basic chemical and physical processes that govern these systems are not understood in detail. Spatially and temporally resolved measurement, including chemical composition, in all phases of a high-density multiphase system, such as that represented by the turbulent evaporating and reacting spray from a fuel injector or the reaction of gas phase molecules with liquid films at a “dirty” piston surface, is a major scientific opportunity with the potential to both foster groundbreaking change in fundamental physics and chemistry and enable revolutionary technical developments in combustion of novel fuels.

Developments in chemically responsive imaging and detection techniques that use previously difficult-to-access regions of the electromagnetic spectrum will help answer this challenge. These new methods may include NMR flow imaging, THz spectroscopies, or broadband Raman imaging. As one example, X-rays penetrate high-density turbulent gas flow without the drastic refractive blurring suffered by optical wavelengths, and detection near atomic resonances provides information on oxidation states and chemical bonds (see sidebar on X-rays in combustion science). Combining chemical specificity with sub-microsecond time resolution and sub-micron spatial resolution in both gas and condensed phases would give truly unprecedented information about heterogeneous and interfacial chemistry and dynamics. New versions of multiphoton microscopies, with depth profiling provided by the laser focus, can give temporally resolved information on chemical species at a well-defined position. Application of these and other novel chemically selective, spatially and temporally resolved techniques to laboratory systems, perhaps in individual droplet combustion or experiments with carbonaceous nanoparticles, will elucidate generally applicable physical and chemical laws that will inform modeling of real devices. Model system studies, such as gas collisions with deposited or assembled carbon nanoparticles, could mimic soot aggregation with size and site specificity. The measurement of real devices with these methods will be an exquisitely demanding test for increasingly rigorous theoretical models.

From a theoretical perspective, this challenge of chemistry and dynamics across multiple phases requires the development of multiscale models. These models will include the transition from descriptions of bimolecular gas phase collisions to gas surface collisions and could involve novel ways to bridge time scales from internal rearrangements within particles to particle/particle agglomeration collisions, and continuum descriptions that would couple in radiation effects. For example, a first-principles approach to soot modeling could be envisioned that includes PAH chemistry, soot inception, heterogeneous chemistry, aerosol dynamics and particle size distribution, soot oxidation and soot radiation. The physics of differential evaporation from fuel mixtures, segregation of chemical species at interfaces, and heterogeneous chemical reactions of fuel droplets before ignition are some of the areas that will be addressed by studies of multiphase systems. This fundamental scientific knowledge will produce stringently validated, physically motivated models of heterogeneous processes under turbulent, high-pressure conditions. Technological advances enabled by such models may include controlling ignition chemistry by manipulation of differential evaporation, adaptive injectors that respond to fuel changes, or development of renewable catalytic surfaces that remove the unburned hydrocarbons in the boundary layers near combustor surfaces.

Characterization of complex combustion systems, in particular for multiphase systems, requires simultaneous knowledge of many variables. This complexity naturally lends itself to multiplexed detection and analysis tools. Techniques that inherently provide multiplexed information, such as Fourier-transform spectroscopy and time-of-flight mass spectrometry, have been applied to time-resolved multiple-species detection in controlled laboratory reactors and in simple combustion systems. The next step in complexity, combining multiple measurements with spatial imaging as well as temporal resolution, will help capitalize on many of the scientific opportunities related to novel combustion of non-traditional fuels. The algorithms to analyze and digest the multidimensional datasets that result are under continuing development, and an overarching technical and scientific challenge is offered by the need to manage the increasing complexity of the datasets, to share them among collaborators and between experimentalists and modelers, and to provide faithful representations of reduced dimension or of averaged quantities for model comparison and calculation across differing scales of length and time. Different representations of the same chemical and physical phenomena may be naturally appropriate to various modeling treatments, simulation codes, or analysis of certain datasets.

Turbulent Reactive Flows

While computational combustion is now established as a powerful scientific and engineering approach, the early goal of achieving quantitative (predictive) capabilities for research- or engineering-level simulations of combustion has not been reached, and remains both a high-impact objective and a formidable task. Achieving this goal requires meeting several basic science challenges, including challenges in the areas of chemical kinetics and thermodynamics, liquid fuel spray dynamics, turbulent ignition, and combustion.

A leading challenge is to develop robust and reliable models of turbulence-spray and turbulence-chemistry interactions, which remain essentially unsolved despite being the focus of intensive research in the past. Turbulence-spray and turbulence-chemistry interactions play a central role in IC engine cycles, since their dynamics determine the quality of the fuel-air mixture preparation and of the subsequent combustion process. Current spray models are limited to descriptions of the dispersed region, i.e. the region downstream of the break-up points in the liquid jet where primary droplets are formed. Current ignition and combustion models are limited to chemical descriptions of simple fuels (i.e. small molecules) at low-to-moderate pressure conditions, and to physical descriptions of fast-chemistry regimes (i.e. premixed or non-premixed turbulent flames with small-to-moderate deviations from chemical equilibrium).

To provide predictive computational capabilities, we must extend the turbulent spray models to treat the dense region, including the liquid flow inside the injector nozzle. Progress in this area will require new developments, including the following: (1) theoretical descriptions of the two-phase flows dynamics under high liquid injection speed and high gas pressure conditions; (2) theoretical descriptions of the evaporation processes under extreme conditions that include possible cavitation and flash-evaporation processes; (3) methodologies to simulate liquid-gas interfacial processes and small-scale droplet dynamics (at scales that are unresolved by a computational CFD approach); and (4) high-resolution experimental and numerical capabilities used both for fundamental studies and model validation.

A related important challenge is to develop robust and reliable ignition and combustion models adapted to the wide range of combustion regimes observed under HCCI and LTC engine conditions, including propagation-controlled (premixed) combustion modes, mixing-controlled (non-premixed) combustion modes, kinetically controlled (flameless) combustion modes, or mixed modes. Progress in these areas requires many new developments, including the following: (1) kinetics and thermodynamics models for more realistic fuel compositions at lower-temperature and higher-pressure conditions; (2) validated theoretical descriptions of heterogeneous chemical processes (including the surface chemistry occurring at the piston/cylinder walls, and at the surface of solid soot particles); (3) new methodologies to construct detailed chemical kinetic mechanisms; (4) new methodologies to simplify these detailed mechanisms and produce computationally efficient, tractable chemical models that may then be integrated into four-dimensional CFD tools; (5) theoretical descriptions of turbulence-chemistry interactions that are not limited by a fast-chemistry assumption; and (6) high-resolution experimental and numerical capabilities used both for fundamental studies and for model validation.

Progress will build upon the emerging area of chemical digital libraries that has been promoted in recent years by the combustion chemistry community ([PrIMe]; [Frenklach 2007]; [CMCS]). Digital libraries play a dual role as a data/software store and a collaboratory, and thereby function as a much needed coordination framework in the area of combustion kinetics, as well as an interface between combustion chemists and reacting flow researchers. Progress will also build upon the hierarchical, tightly integrated, building-block strategy that has been adopted in recent years by the turbulent combustion community, and an outstanding collaborative framework established between experimental and computational scientists [TNF; Barlow 2007].

CONCLUSION

Our overall vision for future research is the development of predictive combustion models that will accelerate and influence the transition from conventional fuel/engine systems to alternative fuels and advanced engine designs. Such models can only be predictive if they are grounded on fundamental experimental and theoretical characterizations of chemical reactivity. We envision research aimed at developing two kinds of combustion models: (1) laboratory flame models with rigorous incorporation of turbulence and (2) engine models with realistic turbulence descriptions.

We envision laboratory flame simulators that use first-principles approaches free of turbulence models. Such simulators must be DNS-based and grounded on fundamental chemistry information at all scales. At maturity, DNS simulators will be the approach of choice for detailed simulations of ignition and combustion, and the natural companion of detailed experimental laboratory studies (i.e. fundamental studies performed in canonical configurations under both atmospheric and engine-relevant temperature and pressure conditions). Our vision includes research efforts aimed at the following: (1) expanding the knowledge base in kinetics and thermodynamics into regimes of larger molecules, higher pressures, and heterogeneous chemical processes; (2) expanding the capabilities of chemical models towards methodologies for automatic generation and reduction of detailed chemical kinetics models; (3) expanding the knowledge base in liquid jet dynamics into the break-up regime; (4) expanding the capabilities of multi-phase flow models towards methodologies to describe freely moving liquid-gas interfaces as well as droplet/particle dynamics; (5) expanding the knowledge base in multi-scale modeling towards methodologies that can couple quantum-scale and continuum-scale descriptions; and (6) expanding experimental diagnostics capabilities towards achieving high spatial/temporal resolution of chemical and physical processes occurring under high pressure and multi-phase conditions.

We envision engine simulators based on first-principles approaches that use turbulence modeling and are informed by the laboratory combustion studies discussed above. Such simulators must be LES based for computational feasibility. At maturity, these simulators will provide a unique and revolutionary tool that can be applied to a full characterization of the operating space (i.e. the load and speed map) of an engine configuration, and thereby push computational combustion beyond the current limits of a diagnostic tool, and turn it into a design tool used for optimization and control. Achieving the goal of LES-based engine simulators will require adding more accuracy and realism to current LES modeling capabilities, as well as applying these capabilities to both in-cylinder processes and processes taking place in the intake, fuel injection systems, and exhaust. Our vision for LES includes research efforts in areas that are similar to the ones listed above for DNS simulators, with the additional level of difficulty resulting from the fact that in LES, small scale dynamics remain unresolved. Our vision also includes efforts aimed at expanding the capabilities of turbulent-chemistry interactions models towards a description of multi-mode combustion.

In summary, achieving the goal of predictive combustion models requires meeting several basic science challenges in the areas of combustion chemistry, liquid sprays, and turbulent combustion. It is important to emphasize that the new technological focus on alternative fuels and non-traditional IC engine strategies also corresponds to a much broadened parameter space in terms of fuel composition and thermodynamic conditions, and therefore corresponds to a dramatic increase in the level of scientific complexity. This increased level of complexity has in turn a negative impact on the discovery-to-technology cycle and creates the risk of an unbridgeable gap between basic research and technology development. Therefore, in addition to achieving scientific progress in individual technical disciplines, there is an urgent need for an unprecedented level of integration of fundamental knowledge and expertise both across discipline boundaries (from physical chemistry to CFD) and across scales (from quantum-scales to IC engine scales) (see [CBCS]).

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GRAND CHALLENGE

GRAND CHALLENGE

The Workshop participants identified the Grand Challenge as the development of a validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications.

Energy, economic, and environmental security in the United States requires the development of a science-based, predictive, combustion modeling capability that enables a "dual-revolution" in the design and utilization of 21st century fuels in advanced engines for transportation. Currently, transportation consumes the second largest percentage of energy in the U.S., accounting for nearly 60% of our nation's use of petroleum, an amount equivalent to all of the oil we import. The enormous infrastructure investment virtually guarantees that the internal combustion (IC) engine will remain the primary power source for transport throughout the next 30-50 years, even as new fuel sources and advanced engine designs evolve.

Within IC engines, the length scales that are relevant range from the size of an atom, angstroms, to the device size, tens of centimeters; the range of time scales is commensurately broad spanning a factor of one billion. At each scale, different instruments measure unique phenomena, different modeling approaches simulate these events, and the depth of fundamental scientific understanding varies widely. Building a framework to encompass all these data, models, and concepts, and to ensure the overall accuracy and fidelity of both microscopic and macroscopic predictions, is a grand scientific challenge requiring 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, peta-scale computing will be enabling.

At the most fundamental level, the chemical bonds of fuel molecules store energy in a convenient, stable form. The chemical conversion of fuel and oxidant to products proceeds principally through a complex set of free-radical reactions. Effective combustion of hydrocarbon fuels maximizes energy output and production of H_2O and CO_2 while minimizing formation and release of unwanted emissions such as NO_x and soot. Ideally, one could measure the reaction rate and product yields as a function of temperature and pressure for each contributing reaction in isolation from any potentially obscuring interference. In practice, this is not possible due both to the sheer number of reactions and the broad temperature/pressure range of combustion. Moreover, we do not now have sufficient experimental control to allow many reactions to be studied individually. As a result, the strategy must be to experimentally characterize prototype fuel-molecule reactivity in great detail, and to demand that reaction-rate theory reproduce these 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. Yet, for both existing and evolving fuel streams, hundreds of chemical species and many thousands of reactive steps contribute to combustion—manual calculation and accounting over all such contributing reactions is clearly an impossible task, and computer-based expert systems that automate calculation and error estimation of the chemical details become crucial. Indeed, it is this chemistry that dictates the rate of combustion, the emissions profile, and engine-knock and compression ignition behavior in existing and advanced engines for transportation.

By analogy, however—to use a time-honored aphorism of politics and real estate— all chemistry is local, and the level of complexity that must be addressed by a predictive combustion model significantly exceeds that summarized above. Fuel and air rarely mix homogeneously; ignition occurs in localized regions and proceeds outward; and turbulence, transport, and radiative properties interact interdependently with the energy-releasing chemistry. For example, in IC engines, the microscopic reaction chemistry affects the development of the macroscopic turbulent flow field, and the change in temperature due to the altered flow dramatically affects the reaction rates. In diesel engines, thermal radiation dominates heat transfer, by virtue of the high levels of in-cylinder soot. At the higher pressures of evolving engine concepts, gas-phase spectral radiation properties and turbulence-radiation interactions will attain greater significance.

Compared to current engines, combustion processes in next-generation engines are likely to be characterized by much higher pressures, lower temperatures, and higher levels of dilution and/or excess air. Combustion processes in these environments are largely unknown. Furthermore, the combination of unexplored thermodynamic environments and new physical and chemical fuel properties results in complex interactions that are also not understood even at a fundamental level. Both intermolecular and intramolecular energy transfer will impact the local reactive environment. At high pressure, mean-free collision paths become extremely short, and qualitatively new reaction intermediates, termolecular (and beyond) collision events, and diffusion-limited versus kinetic-controlled fuel oxidation chemistry may become determinant. Additionally, evolving fuel streams will contain more oxygenates, napthenes, and olefins. Key aspects of the combustion kinetics of these compounds are unknown even at atmospheric pressure. For alcohols, esters, and ethers from biofuels, their more polar nature also affects physical properties, such as evaporation, viscosity, lubricity, heat transfer, corrosivity, and storage.

The present level of understanding and modeling of the spray dynamics in liquid-fuel combustion is inadequate for designing and optimizing new engine technologies for use with 21st century fuels. The wide range of physical and chemical properties of new fuels demands that the present empirical spray models be replaced by a fundamental first-principles understanding of spray breakup and the subsequent vaporization, mixing, and chemical processes, which will require a revolutionary new understanding of the fundamental fluid mechanics and chemical reactivity in these multiphase problems. New insight into the physics and chemistry of spray evolution must be based on innovative probes of turbulent sprays at high pressure in unprecedented detail. This understanding has the potential to enable ground-breaking technical advances in control of combustion processes for future fuels, including on-board adaptive combustion employing “smart” fuel injectors that adjust to changing fuel characteristics and load conditions.

Condensed-phase and heterogeneous processes in combustion of 21st century fuels in advanced engines are not limited in scope to spray dynamics. Surface chemistry takes place within engines, in catalytic converters, and during the formation and burnout of soot, yet it remains the least understood aspect of combustion chemistry. The qualitatively distinct operating regimes of advanced engines will offer both uncertainties and opportunities in surface chemistry. Conceptual understanding and predictive capabilities for surface phenomena will lead to more optimal engine designs for future fuels. For example, at the high pressure, lower temperature and more lean conditions of advanced engines, a significant opportunity arises to optimize the engine combustion system design to lessen soot emissions through improved scientific insight into in-cylinder soot formation and destruction processes. Furthermore, we may envision employing advances in nanostructure synthesis, functional specificity, and deposition techniques to coat cylinder walls with oxidation catalysts so as to reduce unburned hydrocarbon emissions and manage surface deposits and heat transfer properties. Further research to provide fundamental understanding of heterogeneous catalysis occurring in aftertreatment on-board converters will be required by the changes occurring in future emissions streams.

The Grand Challenge summarized herein for the development of validated, predictive, computer-based models of combustion is much more about scientific understanding than about increased computer cycles applied to existing DNS and LES codes. This challenge focuses on the fundamental necessity of producing validated models that provide correct, actionable predictions with quantifiable uncertainties. Success requires a broad array of discovery research and coordinated scientific inquiry that integrates experiment, theory, modeling and simulation. The scientific community possesses neither the conceptual understanding nor the diagnostic tools necessary to even define the optimized set of validation experiments that fully advance knowledge acquisition, let alone perform these studies. Quantitative diagnostic methods need to be developed at all scales, from individual reactive encounters, to idealized yet controlled molecular ensembles, to in situ combustion chambers. High-pressure environments and the extraordinary breadth of future fuel streams present truly daunting challenges. Achieving this Grand Challenge requires an aggressive, multidisciplinary, coordinated, experimental and theoretical research program.

The Workshop participants identified the Grand Challenge as the development of a validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications. High-fidelity multi-scale modeling will play a key role in enabling the transition from hardware-intensive, experience-based fuel formulation and engine design to simulation-intensive, science-based design. Multi-scale approaches are required to reduce the dynamic range of scales to a computationally tractable task and to model the effects of unresolved processes and reduced descriptions on resolved scales. Ultimately, the realization of this Grand Challenge will revolutionize design and implementation of transportation strategies based on internal combustion engines.

The Priority Research Directions in the next section provide detailed descriptions of many, but not all, of the critical components required to address this Grand Challenge.

PRIORITY RESEARCH DIRECTIONS

COMBUSTION UNDER EXTREME PRESSURE

ABSTRACT

The next generation of clean, fuel-flexible and efficient engines will operate at pressures considerably higher than those commonly seen in engines today. At these pressures many of the fundamental assumptions underlying present combustion modeling become invalid. Basic research is needed to characterize the physical properties and chemical oxidation mechanisms of current and future transportation fuels at high pressures in order to understand reaction initiation and propagation under these conditions. Fundamental investigations of transport and flow phenomena at high pressure, and their coupling to chemical reactivity, will be essential in describing these advanced engines. A thorough fundamental understanding of the chemistry and physics of new fuels in high pressure regimes will require new developments in experimental, theoretical and numerical techniques. The ability to predict fuel/species properties, reaction rates, and ignition behavior is crucial for developing clean and efficient combustion engines.

EXECUTIVE SUMMARY

Combustion of hydrocarbon fuels for practical transportation systems has historically operated over a range of pressures from atmospheric to peak levels of 30 - 100 bar, and all of the experimental, theoretical and computational modeling methods that have been developed to characterize combustion depend on phenomena that occur over these pressures. The most basic concepts of thermal autoignition, flame propagation, flame quenching on engine walls, liquid jet penetration and breakup into sprays, liquid droplet evaporation and aerodynamic drag, and even ideal gas kinetic theory all are based on experience and theory at pressures relatively close to atmospheric. However, as pressures increase significantly to levels considerably greater than 100 bar, many of these conceptual pictures begin to change or disappear, and they must be replaced by new realizations in order to be able to design engines, burn fuels cleanly and efficiently, and simulate their combustion in engine models.

Conventional estimation methods for hydrocarbon fuels are not adequate for determining the physical properties and chemistry of new fuels at high pressures. Advances are needed in the understanding of the complex internal and external energy transfer and dissociation processes occurring in excited molecules at high pressure. A better description of the coupling and interaction of high pressure flow and molecular transport processes with chemistry is also necessary, especially as the relative timescales for fluid mechanics, transport and chemical reaction change. Chemically reacting flow simulations at high pressures will require new algorithms and techniques; the increased computational demands for modeling transport, flow, turbulence, and chemistry at elevated pressures go beyond mere increases in spatial resolution.

Experimental investigations are needed to clarify the physical nature of dilute, high-pressure reaction initiation and evolution. New experimental approaches will be required to obtain high pressure measurements and to isolate reaction and collisional kinetics. Obtaining the necessary spatial and temporal resolution to make these measurements *in situ* is a formidable challenge even at atmospheric pressure and much more difficult at pressures of 100 bar and higher, as is the unraveling of the convoluted spectral signatures of complex molecules in multi-species environments. Existing spectroscopic databases must be extended to include extreme conditions, and species-selective detection techniques must be developed to support this work.

Summary of Research Direction

Future engine concepts for efficient and clean combustion [Aoyagi, et al. 2006; Hiroshi, et al. 2004; Pirault, et al. 2005] incorporate ultra-dilute mixtures at pressures considerably higher than are employed in current IC engine technologies. Dilute mixtures keep peak combustion temperatures (and hence pollutant formation rates) low, while high pressures minimize energy loss during combustion [Edwards, et al. 2006] and restore power density lost via dilution. Fuel concentrations as low as 0.1% and pressures as high as 500 bar are within the present conceptual range of practical devices. Under these conditions, the fundamental physical nature of the combustion process is not understood, and observable heat release characteristics often do not correspond either to a conventional flame-like combustion process or to a bulk, homogeneous combustion process. Moreover, many new engine concepts are highly dependent on the ignition properties of the fuel for their successful implementation and control [Westbrook, 2000]. Ignition and flame propagation of alternative and renewable fuels, as well as of the changing feed stocks of conventional fossil-based fuels, are very likely to be much different at very high pressures than under the more familiar, lower pressure conditions of current engines. For example, changes in phenomenology and chemical behavior with increasing pressure are reasonably familiar from studies of supercritical fluids and combustion. Under such conditions, distinctions between gas and liquid phases become moot, new equations of state must be used, and elementary reaction rates must reflect the fact that molecular species mean free paths before collision with other species become very short. This type of redefinition of fundamental concepts, which occurs at pressures above about 200 bar for supercritical combustible gases, requires a re-examination of the basic assumptions that govern the physics and chemistry related to combustion; and the need for this type of re-examination increases as the combustion pressure increases. Understanding the physical nature of the combustion process at extreme pressures and developing the capability to predictively model ignition and combustion evolution for a wide range of new fuels are prerequisites to the identification of optimal operating conditions, engine geometries, reactant combinations, and ignition and control strategies that will enable successful development of clean, efficient future engines.

This priority research direction describes targeted efforts to develop the knowledge base required to understand and predict the nature of the combustion process under highly dilute, high pressure conditions. Substantial research activity is needed for predicting the physical properties and reaction mechanisms of these fuels at high pressures, including the impact of high pressure on collisional relaxation processes and their relationship to unimolecular relaxation and dissociation processes. This research direction requires advances in experimental techniques, theory and analytical methods, and in numerical simulation techniques. Accordingly, there is considerable linkage between this research and research into diagnostic development, multi-scale simulation techniques, and informatics.

It is very likely that current engines and fuels will continue to be in common use for many years, with the transition to higher pressures and novel fuels taking place gradually. As a result, the need for improved understanding of combustion and fuels at elevated pressures will overlap use of current fuels, including conventional gasoline, diesel fuel, and jet fuels. This primary research direction therefore includes research on the high-pressure phenomenology and other factors involving these conventional transportation fuels and also next generation, alternative fuels.

Physical properties of fuels at elevated pressures

Determining physical properties at extreme pressures, where empirical testing is especially difficult or impossible, is a challenge requiring new theoretical methods. Quantum-chemistry methods of molecular simulation hold promise for predicting phase equilibria and transport properties [Westmoreland, et al. 2002], and may ultimately allow prediction of phenomena such as evaporation rates and gas-chromatographic elution times. For pure and mixed simple molecules having simple interaction potentials, vapor-liquid phase equilibria, boiling points, and critical points can be predicted reasonably well at near-atmospheric pressures. Further advances in equilibrium ensemble methods, conductor-like screening models, *ab initio* molecular dynamics, and quantum-mechanics/molecular-mechanics methods are required to extend these capabilities to higher pressure for more complex molecules and mixtures. We need also to understand and be able to predict transitions from separate phases to supercritical behavior and other collective phenomena. Moreover, advances in this area will also support the first-principles calculation of high pressure reaction rates required to develop the combustion models described below.

High pressure chemistry of conventional and alternative fuels

Many alternative fuels contain large molecular species and increased fractions of compounds, such as oxygenates, napthenes, and olefins. Key aspects of the combustion kinetics of these compounds are poorly known and often are quite different at elevated pressures from their properties at near-atmospheric conditions. At elevated pressures, larger molecular weight species are more likely to exist as multiple isomers that lead to different chemistry. It is essential therefore to understand the kinetics of high-pressure large-molecule reactions that involve multiple sites for radical attack and have numerous competing isomerization and dissociation channels. For example, large aromatic molecules are more likely to decompose into two radicals at low and atmospheric pressures, but as pressure increases they decompose increasingly via ring-breaking reactions that do not increase the number of species. It will also be important to delineate the balance at high pressures between oxidation and decomposition for the larger fuel-generated radicals. A combination of theoretical and experimental approaches will be required to develop an accurate understanding of the high pressure kinetics of new fuels. For example, photoionization may be able to distinguish separate isomers whose ionization thresholds are within 0.1 eV of each other. Identifying isomers, however, will most likely require new experimental techniques and high level electronic structure calculations.

An improved understanding of the complete oxidation kinetics of the primary fuel-generated radicals is essential to model ignition. The oxidation chemistry is not well understood beyond the first oxidation step, even for conventional fuels at low pressure. Elucidating the changes of the major chain branching reaction sequences with pressure is essential for understanding ignition and quenching phenomena. Clarification of the intermediate stages of oxidation is impeded by the difficulty in experimentally isolating the key peroxy and hydroperoxy radical intermediates. Experimental procedures for detecting, isolating, and reacting these intermediates are needed.

Theoretical studies of the rates and product branching ratios for the reactions of O_2 with hydroperoxy radicals are also needed [Bozzelli and Sheng 2002]. Again, synergistic new experimental techniques, laboratory facilities, and theoretical studies should be pursued. For example, experimental measurements of key species concentrations under nearly isolated reaction conditions coupled with master equation simulations of key reaction channels can be used to validate chemical models [Taatjes 2006].

Potentially novel behaviors of chemical reactions of new and conventional fuels at high pressures may be important. Isolated binary collision concepts may not be valid, and diffusion-limited reagent processes may occur. The formation of radical-complex precursors may become important mechanistically [Lee et al. 2006]. Scaling up of reaction times suggests that rates of collisions that transfer/remove energy or initiate reactions may occur on timescales competitive with unimolecular decomposition times. The number of distinct chemical species may change in subtle but significant ways with pressure and temperature [Miller and Klippenstein 2006] and appropriate procedures for treating such variations in chemical mechanisms are required. Pressure dependences of molecular and radical decomposition reactions, frequently treated in current kinetic models by simple falloff models, may exhibit much more complex behavior at high pressures where collisional effects are not well understood. Detailed studies of the energy transfer process are needed since the branching between different products can depend significantly on the details of the energy transfer process. In addition, the larger sizes of the fuel molecules suggest that formation of multiple radical sites may be competitive with unimolecular decomposition rates. The kinetics of these diradical species could lead to new ring closure processes, and a new field of bimodal kinetics may need to be defined, including the kinetics of multiple oxidized radical sites on the same molecule and simultaneous oxidized and cleaved sites in individual fuel fragments.

Scientific Challenges

Theoretical challenges

Significant theoretical, analytical, and algorithmic challenges must be overcome to enable first-principles calculations of fuel properties and rate constants at high pressures using quantum-chemistry based molecular simulation techniques. Specific challenges include accurate representation of interatomic and united-atom interaction potentials, efficient inclusion of long-range interactions of highly polar molecules, the development of theories describing dissociation of large, weakly bound free radicals at high temperatures, energy transfer processes in large, excited-state molecules, and non-statistical reactions. Algorithmic and computational challenges also arise. Moreover, high-performance computing will be required to deliver transport properties and to provide accurate predictions as the number of atoms increases.

Additional theoretical challenges arise in the description of the coupling of chemistry to the fluid motion and individual species transport. For dilute systems at high pressures, fluid dynamic time scales can be comparable to chemical time scales. Hence, exothermicity, nonadiabaticity, and partial or completely diffusion-controlled reactions—potentially leading to extinction—can become important. Development of formalisms and simulation techniques to efficiently capture these effects will be a major challenge.

The basic phenomenology of combustion processes will be affected by large increases in operating pressures, questioning whether high pressure combustion will occur via flames, homogeneous autoignition, or other collective processes. The basic foundations of combustion at high pressures must be understood in order to optimize the coupling of engines and fuels in the future.

Experimental challenges

Developing an increased understanding of the high-pressure chemistry of conventional and alternative fuels, creating kinetic models describing their oxidation, and characterizing the physical nature of the combustion process will require the development of suitable facilities as well as significant advances in experimental techniques. New approaches and improvements in existing techniques are needed for producing controlled-temperature environments for combustion at high pressures—possibly resulting in the definition of new experimental configurations suitable for collaborative data depositories. Existing technologies such as shock tubes, rapid compression machines (or motored engines), and heated static cells with spark or laser ignition must be modified for use at high pressures.

Historically, kinetic models of combustion chemistry have largely been developed by comparing experimental measurements with modeling predictions for low-pressure flames, shock tubes, and reacting flows [Smith et al. 1999]. New quantitative, temporally and spatially resolved composition and temperature diagnostics for combustion of new fuels are required to obtain data for kinetic mechanism development and validation at high pressure. Effective diagnostics will need to detect complex reactant, product, and combustion intermediate species in multi-species environments. Large molecules will likely exist in several isomers and have numerous internal energy states, hampering species-specific detection methods due to spectral line broadening and overlap of emission and absorption features. New methods are needed to identify isomers in new fuel mixtures. Furthermore, high pressure conditions will lead to spectral broadening that will interfere with current optical diagnostics. Extension of current spectral data bases is required to support these efforts. Additionally, diagnostic methods for measuring instantaneous temperatures are needed for characterizing the local thermal state.

Application of *in-situ* techniques will be particularly challenging. At high pressures, gradients in physical properties can be very steep. It will be necessary to develop experimental diagnostics that are capable of resolving the spatial structure of the reaction front. Diffraction limitations may require the development of new optical techniques to capture these gradients. High temporal resolution will be required to measure combustion intermediates and to probe the transient development of the reaction front. Difficulties in propagating optical beams through boundary layers and high-pressure turbulent media will also need to be overcome. New methods will be needed to characterize experimentally the influence of turbulence and mixing on the reaction front and how these factors influence reaction propagation and interact with the chemistry.

High pressure facilities will be needed to study the evolution of liquid fuels as they are introduced into combustion chambers, to determine whether processes such as jet penetration, droplet shedding or vaporization, and fuel/oxidizer mixing occur via familiar or completely new mechanisms. For example, how do liquid sprays evolve when injected into supercritical fluids?

POTENTIAL SCIENTIFIC IMPACT

Overcoming the scientific challenges enumerated above will have broad impact on our fundamental understanding and ability to predict molecular properties, reaction dynamics, and combustion processes of new and conventional fuels under dilute high-pressure conditions. Progress in quantum-chemistry based molecular simulation will improve our ability to predict not just fuel/species properties but also allow the direct prediction of reaction rates. Significant advances in our understanding of the chemistry of large molecules with numerous isomers, including reaction/oxidation pathways, energy transfer processes, and decomposition processes, will also be forthcoming, as will new methods to treat collisional processes under conditions where simple binary collision concepts are not valid. The dominant physical processes influencing the structure and propagation of reaction fronts at small Damköhler number will also be clarified.

Additionally, innovations in the methods employed to further advance science are likely to result—including advances in analytical and modeling methods, numerical algorithms, and experimental techniques. Fundamental spectroscopic data will also be generated. These new methods and data can potentially impact a diverse set of fields of scientific enquiry.

POTENTIAL IMPACT ON 21ST CENTURY TRANSPORTATION FUELS

The scientific knowledge gained will provide a foundation from which optimal fuels can be defined, and engine concepts to best utilize these fuels can be developed. The ability to predict accurately the properties and combustion behavior of virtually any fuel will allow engine-fuel system concepts to be evaluated efficiently. Furthermore, these advances will permit: (1) assessment of the influence of additives or new compound groups on fuel performance, and (2) the development of fuel-flexible engine designs. Better understanding of the physical nature of the combustion process and the thermochemical conditions required to obtain reliable combustion initiation and complete oxidation will lead directly to specification of engine operating conditions and geometries that minimize emissions and optimize efficiency. This understanding will also enable improvements in the design and operation of current conventional technologies and potentially lead to the development of transitional technologies.

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UNDERSTANDING AND EXPLOITING SURFACE CHEMISTRY IN TRANSPORTATION SYSTEMS

ABSTRACT

Basic research is needed to make it possible to understand, predict, and exploit surface chemistry to enable efficient, low-emissions transportation. The key need is the development of new tools and concepts that would permit measurement and/or control of surface nanomorphology and chemistry on the length and time scales and under the temperature and pressure conditions relevant for engines. Simultaneous development of suitable computational chemistry methods for modeling these microscopically complex systems would advance the field of engine combustion from its current mostly Edisonian approach to a predictive science. The opportunity presented by new fuel sources and advanced engine concepts offers such an overwhelming design and operation parameter space that only those technologies that build upon a predictive science capability are likely to yield a product within a useful timeframe. Advances in surface chemistry science may enable significant improvements in energy efficiency and emissions control.

EXECUTIVE SUMMARY

Surface chemistry plays a major role in the performance of many combustion devices, but it remains the least-understood aspect of combustion chemistry. The inception, growth, aggregation, and oxidation chemistry of soot and other particulates critically affect diesel and jet engine performance; and particulate emissions adversely impact health. Catalytic combustion, ignition, and reforming make it possible to operate combustion devices at conditions where ordinary flames would be unstable. Catalytic converters and related exhaust treatment devices make it possible for high power-density engines to operate with acceptable emission levels. Surface chemistry is also crucial to the production and utilization of next-generation fuels and may offer a means to improve ignition timing and reduce the emissions load placed on exhaust-system catalytic converters by tailoring in-cylinder wall structures and/or fuel additives. Thus advances in surface chemistry that elucidate the formation, transport, and destruction pathways for particulates, NO_x, and residual hydrocarbons in engines offer the opportunity to promote greater fuel efficiency and thus significantly reduce the life-cycle greenhouse and toxic emissions of a transportation system. This priority research direction defines a focused effort to elucidate the fundamental surface chemistry that underlies so many crucial energy technologies.

SUMMARY OF RESEARCH DIRECTIONS

Particulates

Mitigation of soot emissions is critical for the practical development of novel engines using non-traditional fuels. The ability to predict the composition and concentration of particulate matter with confidence requires accurate measurement and modeling of the evolution of the spatio-temporal distribution of important gas-phase precursors and particulate species. Although models have been developed for soot inception in conventional engines with traditional fuels, the current models are over-simplified and largely untested experimentally. Research focused on measurement and mechanistic modeling of the kinetics and thermodynamics of soot-forming reactions is critical for revealing the detailed chemistry of organic precursors underlying soot nucleation. These mechanistic approaches must be extended to particle inception, growth, and oxidation, particularly under the high-pressure conditions proposed in most advanced engine concepts. As soot cools it is coated by residual hydrocarbons in the cylinder and exhaust manifold. New fuels may introduce new compounds to these coatings, further complicating a poorly understood phenomenon. A fundamental understanding of soot-coating formation and oxidation in both the cylinder and exhaust manifold is needed

Current engines using traditional fuels produce significant concentrations of sub-micron particulates [Kittelson 1998]. These particulates are thought to pose a substantial health risk [HEI 2001], reduce regional and local air quality [Seinfeld and Pandis 1998], and significantly impact the Earth's climate [IPCC 2001]. Soot production may be enhanced with the use of next-generation fuels containing higher aromatic fractions. Experimental probes of soot growth are in their infancy. The small particle size and complex morphology make detection difficult. There is pressing need for measurements of particle size, shape, and composition, and the chemical identity of the species involved in the growth process. Testing of mechanisms for soot growth has yet to be performed with sufficient detail to unambiguously establish key pathways and to uncover potential methods for disruption. The role of other elemental components (e.g., Fe, Zn, V, and S) in the fuel and engine environment is currently unknown. Present particulate emissions standards reflect these large uncertainties; it is possible that the standards could change dramatically as the state of knowledge improves—with major economic and societal impacts.

Fundamental advances need to be made in both theoretical and experimental methodologies for studying soot formation. New chemical and physical models will be required for processes that occur over wide ranges of spatial and temporal scales. Reactive force fields need to be developed for treating the bond making and breaking processes between closed- and open-shell (radical) species. Calculations of the relevant reactions may involve non-adiabatic and excited-state dynamics to a degree never before addressed in computational chemistry. The timescales for these events may lie beyond the reach of conventional molecular dynamics. In such cases, transition path sampling, metadynamics, and hyperdynamics may be useful, but novel statistical mechanical sampling may still be needed to probe the relevant timescales and reaction pathways. Oxidative degradation of particulates and organics deposited on particulates must be studied both *in situ* and in flow reactors employing multiple diagnostics. Optical probes, including developed techniques such as laser-induced incandescence, must be calibrated for high-pressure operation; and new approaches based on VUV and X-ray sources to probe particulate size, shape, and composition require development and application. In short, the opportunity to minimize particulate effects in novel engines employing evolving fuel streams requires detailed physical and chemical insight into particulate formation and destruction pathways.

Surface Coatings for Combustion Devices

Many opportunities are available to manipulate surface chemistry to improve combustion devices. In the combustion chamber, the surface coating could help control heat transfer and lubricant flows, reduce deposit formation, and reduce wear. Surface coatings that inhibit deposit formation through either chemical or physical means could significantly improve engine systems in the near term. Additional concepts include coating walls with oxidation catalysts to reduce unburned hydrocarbon emissions and integral fabrication of thermoelectric devices into the wall surface to utilize the significant waste heat through the walls. Advances in nanostructure synthesis, functional specificity, and deposition techniques offer the promise of high-surface area coatings that may serve to both catalyze reactions and exert physical control through pore-size characteristics. Further, many new engine concepts rely on sensors that allow feedback and active control; a focused effort on fundamental surface chemistry research will dramatically enhance our ability to rationally design these structures and coatings.

The dominant transportation-fuels and emissions-control technologies employed are based on surface chemistry, often in the form of heterogeneous catalysis. Many methods are available for measuring and/or calculating the stable species on a clean, flat, uniform surface of known composition. In most real systems, however, the surface morphology is not flat, the chemical composition and the location of the reactive site are not known, and one can only indirectly determine which reaction intermediates may be important. Indeed, recent studies have shown that the usual static view of surface chemistry can be wildly wrong: (1) the morphology can change dramatically depending on the partial pressures in the gas phase above the surface [Somorjai 2003]; (2) many reactions proceed via dynamic reaction fronts rather than homogeneously across the surface as is usually assumed in models [Rotermund 1997]; (3) the thermochemistry of surface intermediates can depend significantly on the local environment; and (4) some important reactions proceed in a submarine fashion—one reactant migrates into the solid surface, and then emerges to attack the surface-bound reactant from beneath the surface [Ceyer 2001]. Such details are determinate, and not merely phenomenological, in directing surface adsorption, transport, and reactivity.

Research is needed to develop experimental methods with high sensitivity, high spatial resolution, and fast time response for measuring the morphology, composition, coverage, transport, and reactivity for surfaces of technological interest, under conditions similar to those in an engine. Some of these measurements might be made using advanced light-source techniques. Studies are needed for the activity, stability, and cycling of deposited nanostructures with desired catalytic and absorptive properties as functions of temperature and pressure. Novel materials and concepts for heat management on coated cylinder walls are desired. Finally, improved methods for reliably computing surface structure, reactivity, and gas-surface interactions will drive the design of experiments and their interpretation and ultimately provide accurate models for the behavior of the entire system.

Catalytic Combustion, Ignition and Reforming and Catalytic Exhaust After-treatment

At present, catalytic combustion and ignition are not widely deployed, and catalytic reforming is performed primarily at refineries. Currently available catalysts, and the novel engine designs they make feasible, cannot compete with well-developed existing technologies. However, even a relatively small breakthrough in these catalysts (e.g., increasing the thermal stability of combustion catalysts by a few hundred degrees) could open up a wide range of completely new opportunities in both vehicular and stationary power applications. Existing combustion catalysts already make it feasible to “burn” fuels at temperatures and dilution ratios where gas-phase combustion is unstable or impossible, and where NO_x and particulate formation rates are negligible. Improving these catalysts to make their operating temperature match those required by high-efficiency jet engines or by efficient internal combustion engines would open up a new low-emissions, high-efficiency operating space not currently accessible. Such a breakthrough has the potential to completely transform the jet engine industry and may facilitate the development of new engines that could displace conventional spark-ignited or diesel engines. Also, improvements in catalytic reforming may allow on-board conversion of some liquid fuel to H_2, enabling significant increases in compression ratios, power densities, and efficiencies for SI engines and/or enhanced ignition timing control in HCCI/LTC engines.

Current engine designs and operating conditions are highly constrained by the need to employ after-treatment devices to minimize toxic gas and particulate emissions. One existing limitation is that the engine must be operated inefficiently in order to maintain the exhaust stream within the operating range of the after treatment catalyst. The most famous example is an ordinary gasoline spark-ignited engine, where the requirements of conventional three-way catalysts force an efficiency loss of about 20%. For diesel engines, the best currently available exhaust catalysis technology requires co-feeding urea or ammonia into the exhaust, with a very significant associated increase in the complexity of both the exhaust system and the fueling infrastructure. An additional practical necessity is that exhaust catalysts in vehicles must maintain high performance for decades, which is only feasible if the surface structure is self-regenerating.

Each of these technology constraints argues for a focused basic research effort to discover new catalyst formulations and structures that operate over a broader range of conditions so as to accommodate both new fuel sources and advanced engine concepts. These studies would specifically address improved methods for minimization of unburned hydrocarbons, NO_x, and particulate emissions, and they would employ the rapid advances in nanostructure synthesis and functional specificity as a central strategy. Diagnostics that probe molecular-level reactions but operate at temperatures and pressures in the engine and exhaust manifold must be developed. New knowledge need not be exact to provide insight; and trends that drive informed next steps, e.g., prediction of bi-metal catalytic efficiencies [Norskov 2006], will be highly valued.

SCIENTIFIC CHALLENGES

Current models of soot formation are oversimplified and do not adequately describe the complex chemical and physical processes that lead to soot production and burnout during engine operation. These processes span large scales in space and time, which necessitates the development of multiscale models of soot evolution including inception/nucleation, growth, and oxidation. This model development must rely on quantitative measurements of multiphase systems for boundary conditions and validation. Such measurements will require new techniques for detection of gas-phase precursors, particle size, concentration, morphology, and composition of soot material. Complementary improvements in computational chemistry techniques are also needed to facilitate understanding of these highly complex systems.

The development of tools and concepts to promote a molecular-level understanding of chemistry at surfaces under realistic engine and exhaust-stream conditions is paramount. Changing fuel streams and evolving engine designs offer great opportunities for discovery and rapid utilization of new knowledge in surface chemistry. A strategy component that seeks to discover enhanced catalytic properties unique to the nanoscale represents a new approach to emissions reduction in transportation systems. Efforts to narrow the divide between surface scientists probing ultra-high-vacuum molecular events and catalysis researchers characterizing and developing real technologies would permit the entire surface chemistry community to become much more effective.

POTENTIAL IMPACT ON 21st CENTURY TRANSPORTATION FUELS

Internal combustion engines will remain the primary power source for auto and truck transportation in the U.S. for many years to come. Given this fact, and the evolving nature of both fuel resources and engine designs, a science-based approach to energy efficiency and emissions control is critical to the energy and economic security of the nation. This priority research direction defines a focused effort to elucidate the fundamental surface chemistry that underlies so many crucial energy technologies.

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BREAKTHROUGH DISCOVERY TOOLS

ABSTRACT

Alternative fuel use in novel engine and gas turbine designs for 21st century fuels will require fundamental new understanding of in-cylinder and combustor chamber processes, including fuel mixture preparation, ignition, combustion, and pollutant formation. New experimental tools are needed that provide currently unavailable high-fidelity spatially and temporally resolved (four-dimensional—4D) data on turbulent combustion processes. These tools should be applicable in a hierarchy of configurations that range from model systems to practical engines. The information obtained with new diagnostics tools will lead to new scientific understanding of alternative fuel combustion. Studies based on these new diagnostics will enable validation of state-of-the-art science-based combustion simulations. Those simulations are needed to enable globally optimized fuel economy and pollutant reduction strategies, especially for new fuels and new non-traditional combustion concepts for ground and air transportation.

EXECUTIVE SUMMARY

Economic and national security goals require new fuels in combination with novel combustion strategies that offer the potential for transformative improvement in fuel economy and dramatic reductions in emissions as compared to today’s conventional IC engines and gas turbines. The combination of unexplored thermodynamic environments and new physical and chemical fuel properties results in complex interactions among multiphase fluid mechanics, thermodynamic properties, heat transfer, and chemical kinetics that are not understood even at a fundamental level. This deficiency severely limits our ability to predict the behavior of these systems from first principles, as well as our ability to optimize them. Overcoming these shortcomings places new demands on experiments and computations. The predictive capabilities of existing models for engine combustion are significantly deficient. The lack of diagnostic tools for furthering our understanding of the controlling processes under engine-relevant conditions has hampered development of computational models to investigate engine combustion and to design new engine concepts. Thus new diagnostic techniques are imperative to study combustion of alternative fuels under the high pressures and temperatures in engines as well as in model devices. Quantitative diagnostics methods need to be developed to allow time-resolved, multi-dimensional measurements in multiphase flows of simultaneous flow field and scalar distributions. The scalars of interest include temperature, fuel molecules, key intermediate combustion species, and pollutants. Successful implementation of these diagnostics will provide benchmark experimental data of high reliability for traditional and alternative fuels that will be used to develop and validate the predictive capability of engine and gas turbine combustion models.

SUMMARY OF RESEARCH DIRECTION

Demands are increasing for quantitatively accurate, predictive models that include and exploit the effects of alternative-fuel composition on combustion performance and emissions in novel combustion strategies. Advanced engine development increasingly relies on three-dimensional, time-dependent (4D) modeling [Drake and Haworth 2007]. Diagnostic methods need to be developed to validate model predictions and to uncover new physical and chemical phenomena. These diagnostics must provide simultaneous, quantitative measurements of time-resolved multi-dimensional velocity and scalar distributions, e.g. pressure, temperature and chemical species, in both model devices and practical combustors. Optical methods with the potential to resolve processes at small time and length scales, in particular those that are laser-based, are promising candidates to achieve these goals. High-repetition rate laser-based imaging techniques of temperature, species, and velocity distributions can address many of the requirements if they can be made quantitative at high pressures and temperatures. The known target molecule photophysics, needed for quantitative interpretation of the measured signals, is not understood for conditions of interest. Measurement techniques must be developed for molecules that cannot currently be measured, but that are identified through simulations or other experiments as important for novel engine concepts when using alternative fuels. New diagnostics approaches as well as enabling technology, e. g. new light sources, need be developed. Finally, the hardware for new techniques should be miniaturized into “keyhole” devices that enable measurements in otherwise inaccessible areas.

SCIENTIFIC CHALLENGES

The use of alternative fuels in next-generation engines will feature nontraditional, mixed-mode, multiphase turbulent combustion under previously unexplored physical, thermal and chemical conditions. The influences of physical and chemical properties of alternative fuels on combustion processes and engine performance remain largely unknown. New diagnostic methods are needed to bridge these gaps. In each of the following subsections, a key diagnostic challenge is identified.

Four-dimensional measurement capabilities at high repetition rates

Evaporation, mixing, ignition and combustion of alternative fuels are controlled by their often unknown physical and chemical properties. The impact of these properties needs to be understood in detail for validation of comprehensive simulation tools. The resolution of large spatial gradients found in complex engine geometries requires instantaneous three-dimensional measurement capabilities. There are current technological barriers, especially due to the limited availability of laser sources and detectors that enable routine measurements at rates above 10 Hz [Hult 2002]. Frame rates on the order of 10 kHz are required to resolve critical temporal variations during gas phase mixing and combustion; for spray investigations, frame rates higher than 100 kHz will be needed. Ultimately, simultaneous measurements of several quantities are required to understand the interaction between them. Laser-induced fluorescence and Raman scattering are among the most promising candidate techniques for scalar measurements and particle image velocimetry techniques, including holographic approaches, for velocity measurements [Fajardo 2006]. Fast cameras that can capture thousands of frames for sustained periods of time need to be improved for these purposes to allow higher spatial resolution of large-scale measurement areas. Furthermore, with the exception of broadband-absorbing molecules like fluorescence tracers [Smith and Sick 2007], the selective, high-speed detection of molecules of interest requires tunable laser sources delivering pulse energies sufficient for such measurements. Such sources are not commonly available (Figure 1).

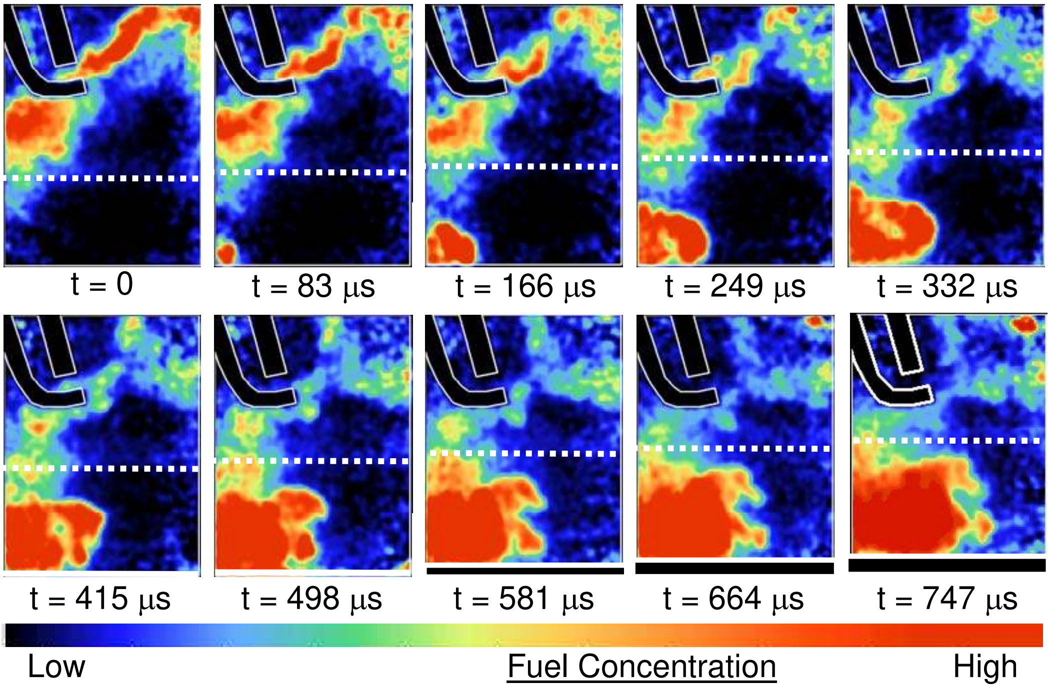

Figure 1. A sequence of qualitative fuel distribution images in a direct-injection gasoline engine shows the strong spatial and temporal variation of the fuel vapor as it passes the spark plug and mixes further with the in-cylinder air. Planar laser-induced fluorescence of a tracer molecule has been used for this two-dimensional measurement. [Smith 2007]

Temperature is a critical and sensitive parameter for auto-ignition and combustion. For example, 5K accuracy is required to study auto-ignition. Currently, there is no sufficiently accurate and precise temperature imaging technique that works under engine conditions. A promising candidate technique might be based on laser-induced fluorescence, possibly of nitric oxide or small organic molecules, like ketones or single ring aromatics. Detailed knowledge of the chemical and photophysical properties of these molecules will be paramount to achieve the required uncertainty limits.

Time-resolved three-dimensional (4D) measurements can also be developed based on chemiluminescence. Chemiluminescence signals from small molecules can be used to track combustion progress qualitatively or to detect areas of potentially increased soot formation. The extraction of fuel/air ratio information from chemiluminescence signals has been pursued [Hardalupas 2004], but quantitative understanding of chemiluminescence signals is far from adequate for diagnostics purposes at high pressures. The effect of alternative fuels on the production of chemiluminescent molecules remains unknown. The detection of 3D chemiluminescence by a 2D camera plane prevents full 3D data acquisition. The resolution of 4D data at high frame rates will require new detection and analysis methods, likely based on multiple detectors and computationally efficient 3D reconstruction algorithms [Han 2006].

Photophysics of molecules and atoms at high pressures and temperatures

Quantitative interpretation of optical signals requires that we understand pressure, temperature and species effects, i.e. inter- and intramolecular energy transfer processes. The effort for such corrections can be considerable even under atmospheric conditions [Barlow 2007]. For most molecules, the photophysics required to predict signals under engine temperatures and pressures is insufficiently known [Koban 2005]. Measurements of the energy transfer processes are needed to build theoretical signal prediction models. Understanding the photophysics will enable the development of robust, reliable, and quantitative diagnostics techniques. This condition applies equally to laser-based techniques and those that are based on chemiluminescence. Related to this need is the interpretation of infrared emission and absorption that controls radiative heat transfer. This requirement will be increasingly important at the high pressures that are expected for novel combustion engines (Figure 2).

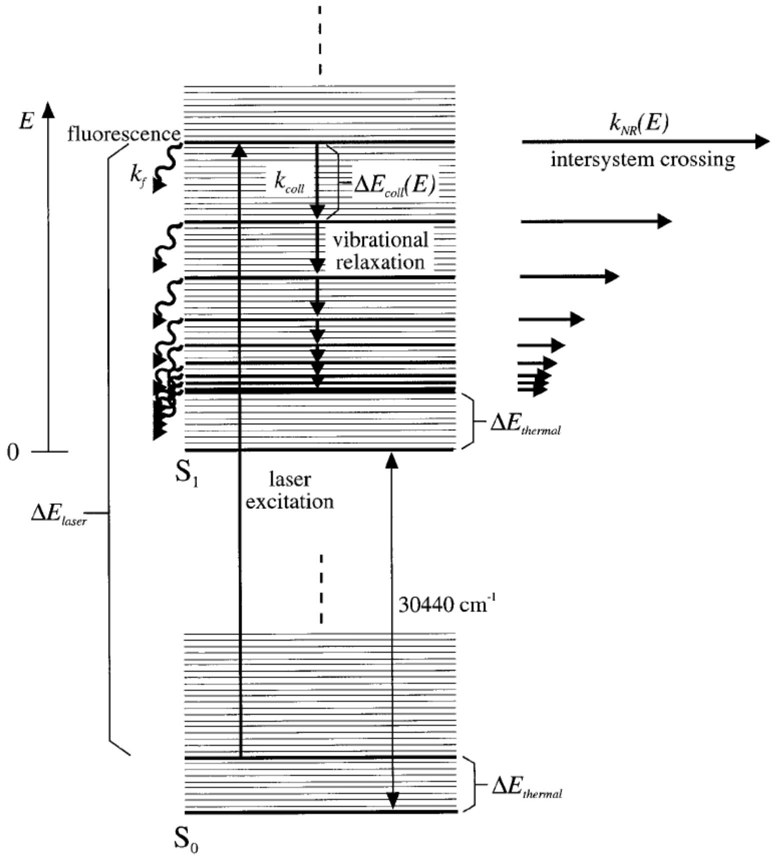

Figure 2. Energy diagram for acetone, a molecule that is frequently used as a fluorescence marker to visualize mixing processes. [Thurber 1998]

Detection of “new” molecules

The use of alternative fuels brings with it new chemical species not found, at least in appreciable amounts, when burning traditional hydrocarbon fuels. There are critical deficits in our knowledge and understanding of “cool flame” ignition and Low Temperature Combustion reactions, critical concepts in new high efficiency, low emission engines. Key molecules that are part of these reactions include peroxides, allylic radicals, and formaldehyde. Oxygenated fuels, like ethanol, are prone to produce aldehydes, irritating substances that may be emitted with the exhaust. Practical quantitative techniques for their measurements remain essentially unknown, particularly under engine conditions, with the exception of some limited, qualitative measurements of formaldehyde (e. g. [Graf 2001]). Thus, these critical molecules escape detection, and new detection techniques have to be developed for their measurement. Enabling X-ray light sources (e.g., the Advanced Light Source, www.als.lbl.gov) and techniques such as nonlinear spectroscopy and multiplexed frequency comb-based spectroscopy [Mazzotti 2005] need to be explored to access information on critical species and interfacial systems.

Keyhole diagnostics for real engines

The use of keyhole diagnostics, such as endoscopes and optical fibers, enables the application of optical diagnostics to real engines and gas turbines without the need for major, if any, modification of the engine. Currently, size, restricted illumination and signal collection solid angles, optical distortion, and damage thresholds limit the usefulness of such techniques. Diode-laser-based sensors have shown great promise for robust, rapid detection of in-cylinder gas properties [Mattison 2006; Kranendonk 2006], but further development of advanced laser sources are required to probe additional molecules of interest for detailed exploration of causes of inefficiency and pollutant formation under realistic engine operating conditions. In particular, selectively probing these molecules under high-pressure conditions is not yet possible, perhaps requiring hyperspectral sources [Sanders 2005] and sophisticated data processing techniques. Advances in miniaturized diagnostics applicable to essentially unmodified engines are a critical need. Validation data for complex simulations of alternative fuel use in real combustion devices must become available.

POTENTIAL SCIENTIFIC IMPACT

Targeted development of novel combustion processes for new fuels

Fundamental understanding of injection, vaporization, fuel/air mixing, combustion initiation, combustion progress, and pollutant formation will be the key to achieving the optimal combustion performance of engines, irrespective of their design and the fuel they will use. The space and time resolved information obtained with new diagnostics tools will lead to physical understanding and to model and simulation tool development. Breakthrough diagnostics will enable validation of ultimately predictive simulations, based on such methods as large eddy simulations (LES) and direct numerical simulations (DNS). Those simulations are needed to facilitate the search for globally optimized fuel economy and pollutant emissions, especially for new fuels and new non-traditional combustion concepts for ground and air transportation.

Many modern and envisioned engine concepts operate with very dilute fuel/air mixtures, which are vulnerable to ignition failure and extinction. These failure modes are highly fuel specific. A significant contribution from data obtained with new diagnostic tools will be the understanding of turbulence-chemistry interaction (see [Frank 2002] for studies at atmospheric pressure) under high pressure, high temperature conditions, and in reaction regimes for new fuels that have not yet been explored. This interaction controls critical steps in engine performance, i.e. ignition, burn duration, pollutant formation, etc. New diagnostics for high pressure, high temperature conditions and those for molecules that currently cannot be detected can also assist measurements of rate coefficients in experiments that isolate critical reactions affecting flame extinction, combustion efficiency, and pollutant formation.

Improved photophysical models at high temperature and pressure

The high-temperature and pressure photophysics of even small molecules (e.g., water, carbon monoxide, acetone, biacetyl, toluene, formaldehyde, etc.) is inadequately understood at present. Detailed evaluation of photophysical properties such as collision cross sections for a variety of molecules will enable the use of theoretical models for extracting quantitative information from optical diagnostics, such as laser-induced fluorescence, absorption spectroscopy, and chemiluminescence imaging. Current databases for such photophysical properties are based largely on atmospheric measurements and are known to be inadequate at high temperature and pressure. Successful development of theoretical models for accurate signal processing from a wide range of diagnostic techniques will enable quantitative measurements under conditions that are relevant for engine operation.

POTENTIAL IMPACT ON 21st CENTURY TRANSPORATION FUELS

Successful development of novel combustion technologies using alternative, as well as traditional fuels has the potential to significantly reduce U. S. demand for petroleum in the transportation sector. The recommended research directions on diagnostics will provide the critical tools that will enable scientists and engineers to rapidly develop and evaluate novel engine design and control strategies that take advantage of 21st century fuels. Models are required to quickly and reliably evaluate and optimize performance when using new fuels. Investigations of physical and chemical processes in engine combustion under realistic conditions will yield essential experimental data for the development and validation of physics-based, predictive models. Enhanced understanding of chemically reacting flows characteristic of combustion will help in overcoming near-term and long term barriers to increased fuel efficiency and lower emissions within the transportation and power generation sectors. Hence, advanced diagnostics are critical for enabling and accelerating the implementation of new engine technologies in concert with the use of new fuels for achieving energy independence.

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MULTISCALE MODELING

ABSTRACT

High-fidelity multiscale modeling will play a key role in enabling the transition from hardware-intensive, experience-based engine design to simulation-intensive, science-based design. Several scientific challenges must be addressed to make this transition while accommodating new fuel types and engine combustion systems. For example, engine combustion processes involve physical and chemical phenomena that span a wide dynamic range ($\sim 10^9$) in spatial and temporal scales. Multiscale approaches are required to reduce the dynamic range of scales to a computationally tractable task and to model the effects of unresolved processes on resolved scales. In addition, the introduction of alternative fuels requires models that capture and discriminate new physical and chemical fuel properties. The new fuels will be used in next-generation engines that, compared to current engines, are characterized by higher pressures, lower temperatures, and higher levels of dilution and/or higher levels of excess air. The combination of unexplored thermodynamic environments and new physical and chemical fuel properties results in complex interactions among multiphase fluid mechanics, thermodynamic properties, heat transfer, and chemical kinetics that are not understood even at a fundamental level. A successful outcome for multiscale modeling would enable predictive device-scale models that can be used to develop and optimize next-generation, high-efficiency, low-emissions engines that use non-petroleum-derived fuels.

EXECUTIVE SUMMARY

Next-generation reciprocating-piston IC engines using alternative fuels offer the potential to improve U.S. energy security and maintain global competitiveness while reducing well-to-wheels energy consumption, criteria pollutant emissions, and greenhouse-gas emissions. Compared to current engines, combustion processes in next-generation engines are expected to be characterized by higher pressures, lower temperatures, and higher levels of dilution (trapped residual gas from previous engine cycles and/or recirculated exhaust gas – EGR) and/or higher levels of excess air (fuel-lean). The combination of unexplored thermodynamic environments and new physical and chemical fuel properties results in complex interactions among multiphase fluid mechanics, thermodynamic properties, heat transfer, and chemical kinetics (aero-thermo-chemical interactions) that are not understood even at a fundamental level. These unknown parameters place new demands on simulations, and severely limit our ability to predict the behavior of these systems from first principles as well as our ability to optimize them. There is an urgent and growing demand for simulation-based approaches that capture these complex aero-thermo-chemical interactions, and in particular, that capture and discriminate the effects of variations in fuel composition. Because the dynamic range of scales that can be captured computationally is limited, multiscale approaches will be required to model the effects of unresolved scales on resolved scales for spatially and temporally resolved (four-dimensional - 4D) simulation and modeling. Key fundamental scientific challenges that must be addressed to advance 4D multiscale modeling for alternative fuels in next-generation engines are discussed herein.

SUMMARY OF RESEARCH DIRECTION

Device-scale three-dimensional, time-dependent (4D) modeling is relied on increasingly in advanced engine development [Drake and Haworth 2007]. Current practice is to “tune” models to match experimental engine measurements under specified conditions, then to exercise the models in a narrow range about the calibration points. While this approach is suboptimal, it is inevitable given the limitations in current fundamental physical understanding of in-cylinder processes. The introduction of alternative fuels and novel combustion processes exacerbates these limitations.

High-fidelity multiscale spatially and temporally resolved (four-dimensional - 4D) modeling is one approach that, in close collaboration with experiments, can close the knowledge gap and ultimately lead to truly predictive device-scale models that can accommodate and discriminate the effects of alternative-fuel composition on combustion performance and emissions. Key fundamental scientific challenges that must be addressed are identified and discussed in the following section.

SCIENTIFIC CHALLENGES

Wide dynamic range of scales

The length scales that are relevant in IC engines range from angstroms (atomic/molecular scales) to several centimeters (device size); the range of time scales is commensurately broad. Engine combustion processes thus involve physical and chemical phenomena that span a wide dynamic range ($\sim 10^9$) in spatial and temporal scales. By comparison, a dynamic range of ~1,000 in length scales is a practical upper limit for current tera-scale computing; peta-scale computing and algorithmic advances may push this limit to ~10,000. Multiscale approaches are required to model the effects of unresolved scales on resolved continuum scales for 4D simulation and modeling.

At each scale, phenomena are measured using different instruments, and are simulated using different modeling approaches. Building a framework to encompass all these models and data, and to ensure the overall accuracy and fidelity of the predictions, is a major challenge. The challenge is particularly acute in cases where phenomena at different scales are coupled. For example, in IC engines, the microscopic reaction chemistry affects the development of the macroscopic turbulent flow field, and the change in temperature due to the altered flow dramatically affects the reaction rates.

Addressing this multiscale challenge is particularly important for fundamental insights and successful predictions of the effects of alternative fuels. Changes in fuel composition directly affect phenomena at several scales (e.g., at microscopic scales, the changes affect some reaction rates; at larger scales, changes in bulk liquid properties affect fuel injection/evaporation). Understanding how changes at specific scales affect the overall performance of an engine requires very careful coupling across the scales.

This multiscale challenge has several components. From an applied mathematics and systems engineering perspective, the challenge is to couple disparate submodels operating in different regimes. Solving this challenge in turn leads to issues of optimization and inverse modeling, subject to constraints involving stiff differential equations.

Complex interactions

Next-generation, alternative-fuel engines will feature nontraditional, mixed-mode, multiphase turbulent combustion under previously unexplored pressure, temperature and chemical conditions. The influences of physical and chemical properties of alternative fuels on combustion processes and engine performance remain largely unknown. Turbulent combustion traditionally has been categorized either as premixed or as nonpremixed [Poinsot and Veynante 2005]. Advanced engine designs already blur these boundaries [Drake and Haworth 2007]. The novel physical and chemical properties of alternative fuels and the unfamiliar thermochemical environments (higher pressures, lower temperatures, dilute and/or fuel-lean mixtures) anticipated for next-generation engines accentuate existing physical and modeling uncertainties. These engines will operate in heretofore unexplored regimes in which standard thermochemical approximations (e.g., ideal-gas behavior), transport properties, and conventional notions of autoignition and flame propagation may no longer be appropriate. The nature of the physical properties must be determined. This knowledge of the physical properties then must be distilled into models that can accommodate and discriminate among the various modes of combustion: e.g., quasi-homogeneous kinetically controlled, premixed flame propagation, nonpremixed flame, turbulent-mixing-controlled, or some as yet unidentified mode.

Another physical aspect worth highlighting is thermal radiation. Thermal radiation is a dominant mode of heat transfer in diesel engines, by virtue of the high levels of in-cylinder soot [Musculus 2005]. Many of the next-generation engine concepts involve considerably higher pressures compared to today's diesel engines. At elevated pressures, gas-phase spectral radiation properties and turbulence-radiation interactions will become more important (Modest 2005). We anticipate that high-end spectral radiation and turbulence-radiation interactions models will be required to meet the levels of accuracy needed for next-generation 4D computational combustion tools.

Novel numerical algorithms and error estimation

The advent of tera-scale computing power made it possible to use direct numerical simulation (DNS) to gain fundamental physical and chemical insight into fine-grained turbulent-chemistry interactions in laboratory-scale turbulent flame configurations [e.g., Pantano 2004; Hawkes et al. 2006]. New numerical developments will be required to adapt current DNS solvers to peta-scale computing and beyond. Scalable, accurate, and efficient algorithms also are needed to treat spatial disparities resulting from multiscale phenomena.

A particularly important issue is to develop a framework to understand and quantify the propagation of uncertainties and errors in physical properties, models, initial and boundary conditions, and numerics, in order to place rigorous error bounds on the simulation outputs. This lack of "error bars" to date has precluded quantitative predictability, and makes it difficult to identify which submodels should be targeted for improvements. Better understanding of the multi-scale coupling would also allow the design of experiments focused on validating and verifying the models for cross-scale coupling.

Data management, analysis, and visualization

Huge datasets are created by the application of advanced 4D simulation tools. Tools are needed to manage and process the data, to extract physical insight from the raw data, and to distill the physical information into models that are suitable for device-scale simulations. Research, development, and deployment of multiscale analysis and visualization tools for understanding turbulent combustion from large, simulated and measured datasets are required. Knowledge discovery tools that enable automated analysis and discovery of salient features in simulated or measured data are essential [Akiba et al. 2005; Edelsbrunner and Harer 2006]. The new tools must be interoperable, scalable to petabytes of data, and must enable automated parameterization and discovery of multiscale interactions (e.g., turbulence-chemistry-radiation-spray-particle interactions).

Device-scale modeling

Ultimately device-scale models will be required for engine development and optimization. We anticipate that there will be a transition from current Reynolds-averaged simulation (RAS) approaches toward large-eddy simulation (LES). LES is of particular interest for alternative fuels, with their increased emphasis on discriminating the effects of fuel composition on combustion performance and emissions. In any case, effective simulation-based fuel/engine design will require that device-scale models be implemented within an optimization strategy. Using petascale (and beyond) computing systems with 10^5 to 10^6 processors, one can envision performing multiple (thousands) of design iterations in which each iteration corresponds to a high-fidelity, multiphysics/multiscale simulation.

Workforce development

In addition to the technical challenges, there are significant workforce development issues. An individual scientist seldom has expertise at more than one scale; even the language describing phenomena changes from one scale to another. Correctly coupling one scale to the next requires a workforce familiar with the approximations and methods used at each scale, as well as collaboration with the mathematicians and/or systems engineers developing the overall model.

POTENTIAL SCIENTIFIC IMPACT

Successful resolution of the challenges outlined above would provide new fundamental understanding of, and models for, the fuels and conditions that are anticipated to be relevant for next-generation, high-efficiency, low-emissions engines. Well-documented benchmark simulation data would be available for complex multiphase turbulent combustion systems at relevant conditions. The methodology of establishing a general framework for information communication between models of different length and time scales, and the overall model uncertainty management, would represent a substantial contribution to the study of complex multiscale systems.

POTENTIAL IMPACT ON 21ST CENTURY TRANSPORTATION FUELS

A documented archive of numerical data would be available for configurations relevant to next-generation engine combustion systems and fuels. Application of the new tools would provide engineers insight into combustion processes; in particular, to utilize the opportunity provided by the availability of new fuels to promote U.S. energy independence. Broadly applicable, comprehensive, predictive device-scale models would be available for the development and optimization of next-generation combustion systems and fuels using 21st century computing technology.

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BASIC RESEARCH NEEDS FOR SMART ENGINES

ABSTRACT

The present change in fuel properties (because of the emergence of non-traditional and alternative fuels), concurrent with the development of advanced engines that rely on fuel chemistry to an unprecedented degree, offers the opportunity and challenge of simultaneously optimizing fuel and engine technologies. An engine that can dynamically alter its configuration and its fuel stream would answer this challenge. Developing such an engine will require fundamental research into technology for sensing fuel and combustion properties, new knowledge of separations and fuel transformation chemistry, and materials science for new combustion strategies. Most importantly, the basic combustion science underlying the control strategies that will be used in such an engine, linking fuel properties with optimum combustion conditions, will provide a new general high-level description of engine combustion.

EXECUTIVE SUMMARY

Commercial fuels contain tremendous variability in chemical composition. Historically, engines have been developed to work specifically with different types of fuels in diesel compression-ignition, gasoline spark-ignition, or aviation-fuel turbine combustion. Collectively, the fuel molecules are blended to meet legislated physical and chemical targets. The combustion properties of the individual molecules vary greatly, however, in ways that are presently poorly understood (especially in advanced high-efficiency, low-emission engines). Future fuel classes may be less distinct and have significantly greater variability in their chemical and physical properties, both to avoid the cost, energy, and greenhouse-gas emissions that result from more-extensive refinery processing, and because of the blending of unconventional streams, such as those produced from biomass, oil sands, oil shale, and coal. An opportunity exists to create "smart" engines that are equipped to analyze fuel characteristics and operating conditions and can adjust their configuration and/or the incoming fuel components in real time. Smart on-board sensors would analyze the composition of the fuel, engine performance, and emissions (*real-time* soot, HC, CO, NO_x). On-board processing of this information would guide chemical and/or physical transformation of the fuel stream, for example via catalytic reactions or low energy separations, and modification of combustion parameters, such as valve timing, compression ratio, or injector characteristics, in order to maintain optimum performance and low emissions for a range of fuels and operating conditions.

Creation of such a revolutionary capability will require new basic research into advanced spectroscopic and analytic methods for detection of fuel properties, combustion characteristics, and exhaust composition; materials for separations and methodologies for on-board chemical transformation of fuels; a fundamental understanding of the fuel properties that affect performance in traditional and novel combustion regimes; and a knowledge of the rationale and relationship between these fuel properties and available control measures. This last goal will emerge from continuing progress toward a predictive understanding of engine combustion and its impact on design, flexibility, self-monitoring, and optimized operation of current and emerging combustion devices.

SUMMARY OF RESEARCH DIRECTION

An historic opportunity to simultaneously optimize both sides of the fuel-engine system through development of fuel-sensitive advanced combustion strategies is offered by the ongoing change in fuel composition because of the replacement of traditional light sweet crude resources by non-traditional fossil and alternative fuels, coupled with a revolution in engine technologies. Current engines use mostly open-loop control strategies that require extensive calibration prior to engine deployment to ensure compliance with efficiency and emissions constraints. The control parameters that are used are relatively limited, and engines managed in this way do not perform well outside of the calibrated region (e.g., because of fuel-property changes), nor do they tend to maintain compliance as they age. One way to exploit the present opportunity is to develop an adaptive engine that can dynamically perceive, adjust, and optimize its hardware configuration and fuel properties in response to changing operational requirements.

A shift in engine flexibility of this magnitude will require basic research to provide substantial advances in three major areas. First, the necessary fundamental understanding must be developed to enable on-board, real-time analysis of fuel, combustion, and exhaust properties to be used as control inputs. New methods must be devised for detection of physical, chemical and thermodynamic properties of gaseous and condensed-phase species in the fuel stream, the combustion chamber, and the exhaust. Second, basic research is needed into robust and specific chemical transformation, and separation technologies are needed to modify fuel, additive, and exhaust-gas compositions to facilitate optimal engine performance. Finally, control strategies must be invented to employ the advancements in sensors, separations, and transformations discussed above to enable a self-optimizing, fault-tolerant engine of the future. The evolution of this strategy will certainly involve advances in nanoscale science and will be the key scientific prize from research into smart engines and adaptive combustion, a revolutionary approach to simultaneously optimizing fuels and combustion technologies for clean and efficient utilization of non-traditional energy resources.

SCIENTIFIC CHALLENGES

Fundamental Understanding for Evolving Fuel/Engine Configurations

Underlying any development of adaptive combustion is the need for fundamental knowledge about the response of engines both to changes in fuel characteristics and to adjustments in combustion parameters. Detailed predictive modeling of real combustors is a long-standing and still-elusive goal. The fundamental combustion research that is needed to enable adaptive combustion and smart vehicles is an abstraction from, and a coalescence of, aspects of a fully detailed model. We need to know which fuel properties should be measured and which combustion parameters should be adjusted. We also need to know the response function to determine the correct parametric modification for a given change in fuel properties. The strategy for obtaining this knowledge is distinct from the present methods of devising chemical mechanisms for individual pure fuels and combining them to describe the behavior of mixtures and real fuels. To illustrate, imagine that a complete mechanism existed for the combustion chemistry of all (thousands of) possible components of the fuel stream. Utilization of this information to adapt combustion conditions as the input composition changed would then require real-time full chemical speciation of the fuel, a preposterously large task. Rather, the generally applicable and “high-level” properties of the fuel that affect performance must be revealed, and these are the properties that must be measured. It is critical that the fundamental principles underlying the importance of these properties be understood in order to permit development and extension of a control model to fuels (or combustion conditions) that have not been specifically validated.

Fundamentally new research opportunities occur when the fuel and the combustion strategy can be simultaneously optimized, but the increase in the parameter space will require new conceptual and algorithmic methods for data analysis and automated recognition of large-scale property correlations. Adaptive-learning algorithms and automatic optimization tools may provide a means to control real engines based on end-product metrics of performance, efficiency, and emissions. The control history of such an engine provides data on the response function connecting a chosen (not necessarily optimal) set of sensor inputs and a set of available control parameters. Predictive modeling and rapid (combinatorial) laboratory measurements of a wide range of fuel characteristics and combustion properties is envisioned; the dimensions of this problem will necessitate high-throughput computation and analysis tools. Real engines may not be scalable to sufficiently high-throughput applications, and they may not provide sufficient control of chemical environment, fluid mechanics, or physical parameters to determine fundamental principles for the effects of fuel characteristics on combustion. Surrogate systems and idealized combustion reactors will be required and must be validated for comparison to real-scale systems. Finally, the interpretation of this wealth of data will likely employ a systems approach of complex and collective phenomena; crucial knowledge will derive both from a sum over individual physical or chemical details and from decoding macroscopic observations.

Basic Research for Smart-Engine Sensors

Successful sensing for control in adaptive combustion will rely in part on fundamental spectroscopic and diagnostic work for in-cylinder measurement of properties such as pressure, temperature, heat-release, and particulate loading distributions. Resilient methods for rapid measurement of gas-phase composition of exhaust (e.g., CO, hydrocarbons, NO_x and soot) and intake composition will be required. Fuel adaptability will require real-time characterization of fuel parameters in the liquid phase, including physical parameters, such as volatility or density, and chemical parameters, such as carbon-hydrogen ratio, oxygenation, or functional group distributions. Sensing for smart engines may require methods to measure general “high-level” properties applicable to any fuel, rather than molecule-by-molecule specific details. New methods of measurement are required for laboratory experiments to generate a knowledge base for control algorithm development as well as for real-time sensors aboard the smart vehicle or inside the smart combustor. Micro-and nano-scale discoveries and engineered devices will likely play a role in developing these sensors; micro-combustors have been designed already for hydrocarbon sensing [Moormnan et al., 2003].

Basic Research for Adaptive Combustion

Adapting the combustion process to a variable fuel stream under changing load conditions will demand engineering effort in such areas as actuators for injector modification and variable compression ratio (see Figure 1). Fundamental research is required to enable the “smart” engine to adapt the characteristics of the fuel through separations or pre-combustion processing [Oakley et al. 2001]. Fuel could be reformulated in the tank to tailor its suitability to a certain advanced combustion strategy [Zhao 2004], the benefits of which could be further enhanced by controlling the composition of the exhaust gas fraction that is recirculated to the intake manifold. Basic research is needed for the chemistry of modification of a range of possible fuels using waste heat from the exhaust or coolant, for example by distillation, catalytic separation or reaction, or reforming by partial oxidation [Subramanian and Schmidt 2005], similar to strategies developed for fuel cells [Deluga et al. 2004; Zhan and Barnett 2005]. Implementation of these measures also will require considerable research into materials and separations and development of the fundamental knowledge needed to apply the measures to improve performance. A “smart” engine must understand how to utilize the various molecular streams produced on-board or introduced as additives. For example, designing an additive that can be modified catalytically on-board the vehicle to optimize a combustion property such as ignition timing [Hashimoto 2006] would entail basic research into catalysis and the combustion chemistry of novel compounds. New developments in efficient, low-temperature catalysis for processing a wide range of fuels, materials for storage of fuel components, and function-specific membranes or nanostructures for fuel separations are required to accomplish fuel modification.

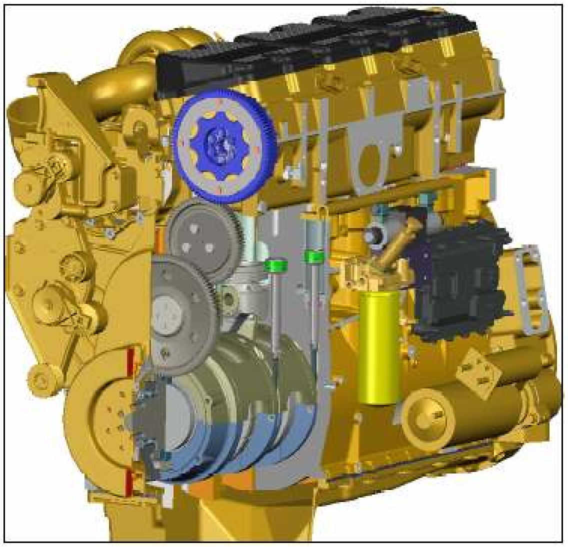

Figure 1. Prototype engine employing a variable compression ratio [Duffy 2006].

Additionally, new demands on engine characteristics will require new fundamental knowledge well beyond the operating domains of our current transportation technologies. As one example, the use of waste heat for fuel processing may compel higher exhaust temperatures and hence decreased heat loss to the cylinder walls. Managing heat transfer *per se* is important for adaptive combustion because it directly affects the timing and efficiency of compression ignition [Filipi et al. 2004], and reducing heat loss can increase the efficiency of energy extraction [Farrell et al. 2006]. Deposit formation changes heat transfer [Güralp et al. 2006], and the characteristics of the deposit are sensitive to fuel additives [Zerda et al. 2001; Smith et al. 2002]. Basic research into the heat transfer properties of surfaces and surface coatings, heterogeneous chemistry of deposit formation, and condensed-phase material transformations under high temperature and pressure is required to enable combustors with engineered heat transfer properties that are also resistant to deposit formation.

POTENTIAL SCIENTIFIC IMPACT

Fundamental combustion models that could discern relevant fuel properties and useful control variables, and could relate these properties and combustion parameters to performance and to one another, would constitute a high-level general description of engine combustion of unprecedented scope. Algorithmic development for recognition of correlations in control strategies and development of combinatorial strategies for fuel property/performance analysis would provide benefits for (and draw lessons from) similar problems of optimizing other complex and collective systems.

POTENTIAL IMPACT ON 21ST CENTURY TRANSPORTATION FUELS

The advancements outlined in this PRD could yield improvements in engine efficiency, low exhaust emissions, and fuel flexibility comparable in magnitude to the aggregate experienced over the past century. In addition, the robust and inexpensive sensors, chemical separation and transformation technologies, and control strategies developed in this work could be used in a wide variety of applications distinct from combustion engines. All of these breakthroughs could have profound beneficial impacts on energy security, air quality, and the economy.

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PHYSICAL AND CHEMICAL PROPERTIES FOR COMBUSTION OF 21ST CENTURY TRANSPORTATION FUELS

ABSTRACT

The next generation of transportation fuels is likely to be much different from current practical fuels. These fuels will be produced from sources such as oil sands, oil shale, coal, and fuels derived from biomass, all of which are fundamentally different from current petroleum-based fuels. The differing physical properties of nontraditional fuels will affect critical phenomena such as transport and mixing, evaporation, and spray breakup. Furthermore, reliable operation of advanced clean, fuel-flexible and efficient combustion engines that employ compression ignition will rely to an unprecedented degree on the details of fuel chemistry. As the effects of these physical and chemical properties on combustion, especially in advanced engines, is in many cases poorly understood even for traditional fuels, advances in measurement methods, theory, and modeling are necessary to determine the physical and chemical properties required for new fuels and combustion technologies.

EXECUTIVE SUMMARY

Transportation fuels derived from coal, oil sands, oil shale, and biodiesel sources from North America all may have the capabilities of satisfying the nation’s fuel needs, but fuels produced from these different sources have unique physical and chemical properties that result from their geologic characteristics or biological origins. Fuel composition differences lead to differences in physical properties, combustion performance, and emissions characteristics. Another layer of complexity derives from some new combustion technologies under development for our next generation of engines, often involving very high pressures and sometimes supercritical fluids. Adapting to these technology changes will require crucial physical, chemical and kinetic properties that are presently unavailable and, in some cases, unmeasurable. Key theoretical advances, measurement techniques, and information integration are necessary to deal with the new molecules, large molecules, mixtures, and extreme conditions of combustion temperature and pressure.

A significant change in the new fuel mix is the addition of oxygenated fuels from biomass, notably alcohols, esters, and ethers. Current bio-derived fuels and blending stocks retain their oxygen content in chemical components that are more polar than hydrocarbons. Their stronger intermolecular interactions affect evaporation, viscosity, lubrication, heat transfer, corrosivity, and storage, along with reaction kinetics and thermochemistry. Existing estimation methods and established measurements for hydrocarbon fuels are not adequate for determining behavior of many new fuels.

This priority research direction (PRD) will involve scientific studies that will lead to the development and evaluation of formalisms for computing chemical kinetics and physical and chemical properties of next-generation transportation fuels, including development of new design tools for mathematical modeling. The elements of this PRD will enable clean and efficient combustion of traditional and non-traditional fuels by providing the tools to design advanced combustion systems.

SUMMARY OF RESEARCH DIRECTION

Many proposed new alternative fuels contain large molecular species, with increased fractions of compounds such as oxygenates, napthenes and olefins, whose chemical properties and combustion kinetics are poorly known. Each type of alternative future fuel has its own unique features or chemical signatures; biomass-derived fuels from celluloses and lignins have high polymeric characteristics, oil sands fuels have unusually high naphthenic content, and oil shale and coal liquid fuels have more aromatic content than conventional petroleum-based transportation fuels. A combination of theoretical advances, kinetic modeling, and experimental studies will be required to develop an accurate understanding of their properties.

Physical properties for next-generation fuels

A key goal for clean, efficient use of next-generation fuels is accurate prediction of their physical properties. Presently, most fuel properties are measured by empirical testing or correlation with easily measured characteristics like vaporization curves, flash point, and pour point. In light of the large variations in composition of potential future fuels, there is a clear need to develop scientifically based methods for fuel property prediction, rather than building on pure-species properties and applying linear or nonlinear combination rules. A first-principles prediction from molecular characteristics is needed to enable robust prediction of combustion performance for new fuels. While group-contribution methods have been used to estimate phase equilibrium and thermochemistry, advances in quantum chemistry techniques are needed to describe properties of future fuels.

Advanced molecular simulation holds the promise of predicting phase-equilibrium and transport properties quantitatively from statistical mechanics, extending to properties like evaporation rates and gas-chromatographic elution times. Rather than building on the pure-species physical property and applying linear or nonlinear combination, these methods must use intra- and intermolecular interaction parameters with stochastic variation of spatial changes (Monte Carlo equilibrium-ensemble methods) or spatiotemporal changes (molecular dynamics). For pure and mixed simple molecules having simple interaction potentials, vapor-liquid phase equilibria, boiling points, and critical points can be predicted reasonably well. Non-equilibrium molecular dynamics, however, are needed to predict transport properties of complex mixtures of large molecules in the gas and liquid phase. Key scientific challenges include representation of accurate interatomic and united-atom interaction potentials, efficient inclusion of long-range interactions like dipole-dipole and van der Waals interactions, and quantitative accuracy.

Quantum-chemistry methods are advancing toward predictive abilities, but further advances are required. The Conductor-Like Screening models COSMO and COSMO-RS for phase-equilibrium properties combine quantum mechanics with an ideal solvated molecule as reference rather than pure compounds. *Ab initio* molecular dynamics and quantum-mechanics/molecular-mechanics (QM/MM) methods can potentially deliver transport properties but will require algorithmic development and high-performance computing. All of these challenges are made more challenging by the complex molecular structures and large sizes of the components of future transportation fuels.

Thermochemistry and kinetic models for combustion of new fuels

Prediction of combustor performance, including ignition, combustion, and emissions characteristics, with next-generation transportation fuels requires development of species thermochemistry, elementary-reaction kinetics, and full and reduced reaction models for fuels and their intermediates that have not been simulated before and about which little is known.

The scientific challenges include advances in quantum-chemistry methods, new theories for collisional energy transfer, new reaction theories, and experiments to validate or challenge these predictions. Existing quantum-chemistry methods quickly must trade off accuracy for molecular or transition-state size as the number of atoms increases, for example as N^7. Many crucial combustion reactions are known to occur nonadiabatically over complex energy surfaces, rearranging by virtue of high nonthermal energy states and mediated by poorly understood collisional energy transfer. Despite a substantial body of measurements of elementary-reaction kinetics for relatively small species [Taatjes, 2006; Bozzelli and Sheng, 2002], few experiments or theoretical studies exist for even modestly large molecules above room temperature, and many of those include reactants without product identification. We must understand the kinetics of reactions that involve multiple sites for radical attack and have numerous competing isomerization and dissociation channels. It will be important to delineate the balance between oxidation and decomposition for large fuel-generated radicals. While paraffinic species have received considerable attention to date, other classes of components with significant content in future transportation fuels have received little or no attention on kinetics, including components such as aromatics, naphthenes, cyclic alkanes, and olefins, as well as large polycyclic aromatic and paraffinic molecules and radicals. Such studies are needed over the full range of temperatures (room temperature to 3500K), pressures (1-1000 bar), and compositional ranges that will be encountered in future transportation engine systems.

Predicting performance of transportation fuels requires special knowledge of the chemical kinetics of large molecules, for which many theoretical issues are unresolved. These unresolved issues include the following:

- Dissociation of large, weakly bound free radicals cannot be described satisfactorily at high temperature using rate constants, as dissociation is intrinsically coupled to internal energy relaxation. We must determine adequate methods for describing the rates of such reactions in simulation models.
- Large molecules frequently have many isomers. In a typical chemically activated unimolecular reaction involving low isomerization barriers, a collision complex may explore large portions of the potential energy surface (many different potential wells), and the rate coefficients and product distributions of such reactions depend critically on the collisional energy transfer properties of highly excited rotational-vibrational states of the various isomers. At present, no unifying theory describes energy transfer in highly vibrationally excited states of molecules. Such a theory is essential if we are to automate rate-constant calculation.

- A general methodology is needed for solving two-dimensional master equations for multiple-well systems and to obtain rate constants from the results (i.e. with energy E and angular momentum J as independent variables and not just E).
- Extensions of chemical reaction rate theory and models to very high combustion pressures are uncertain with currently available theories, and new treatments are needed for systems in which isolated binary collision concepts may not be valid, and diffusion-limited reagent processes may occur. Rates of collisions that transfer/remove energy or initiate reactions can occur on timescales competitive with unimolecular decomposition times, and the number of distinct chemical species can then change in subtle but significant ways with pressure and temperature [Miller and Klippenstein 2006]. Appropriate procedures for treating such variations in chemical mechanism are required.

New Experimental Approaches

Suitable facilities and new diagnostic methods are required for experimental measurements of chemical kinetics in high pressure combustion, specially controlled temperature environments, and the ability to detect complex species in multi-species environments with new *in situ* methods. Improvements in spatial and temporal resolution of detection for products and intermediates will also be necessary.

New diagnostic methods are required for quantitative and time-resolved measurements of reactants, intermediate species, products and temperature of novel fuels. A suite of species-specific methods needs to be developed for species identification in a multi-species environment. Diagnostic methods include both sampling-based and *in situ* optical methods. Gas chromatography with mass spectroscopy effectively samples stable reactant and product species. Tunable photoionization coupled with mass spectrometric analysis can identify isomers. For example, it may be possible in photoionization to distinguish separate isomers whose ionization thresholds are within 0.1 eV of each other, but this will require new experimental techniques and possibly high level electronic structure calculations to identify the isomers. Candidate optical methods include emission or absorption in the ultraviolet, visible and infrared regions, or extinction in the case of particulate loading experiments. Emerging technologies using X-ray emission, ultrafast lasers, and single-molecule spectroscopy may also prove useful. New methods that are based on multiple wavelength or multiple spectral band methods using multiple techniques, such as combined Raman and IR spectroscopy, will provide more spectral information and cross correlation to disentangle overlapping species and/or to monitor growth and decay of specific functional groups (e.g., carbonyl) in reactive intermediates. Diagnostic methods for measuring instantaneous temperatures are needed for characterizing local thermal equilibria.

New diagnostic techniques need to be developed, tested, and applied in research facilities. Once developed, they will serve as important tools for heterogeneous systems, such as sprays, and for practical systems, such as engines. Diagnostics for such systems must overcome significant difficulties in propagating optical beams through boundary layers and high pressure turbulent media. In addition, application of diagnostic methods will likely require extension of current spectral databases. The presence of large molecules with high levels of internal energy hampers current methods of species-specific detection due to spectral line broadening and overlap of emission and absorption features.

Surrogates and reduced models for fuels of the future

Use of new mathematical models can aid decisions on fuel properties to maximize engine performance and minimize emissions. For example, should aromatics in fuel be minimized for future engine designs and what minimum cetane should be required for engine performance? Are octane number and cetane number suitable parameters to characterize fuel performance in homogeneous charge, compression ignition (HCCI) engines? Once optimal fuel characteristics are defined, researchers can use the predictive model to evaluate the impact of including new groups of compounds in a fuel formulation.

A parallel approach to combustion measurements or fully detailed models of real fuels is to mimic these fuels with surrogate mixtures, a suite of a small number of chemical compounds containing most of the functional groups in realistic fuels [Violi et al, 2002]. Physical and combustion properties of the surrogate are then thoroughly measured for a wide range of temperatures, pressures, and combustors. Because fewer fuel compounds are involved, surrogates provide a cleaner basis for developing and testing models of the fuel properties in practical combustors. Use of a well-defined surrogate also provides a fuel with a known, repeatable composition for careful experimental studies. Variability in compositions of future alternative transportation fuels can easily reflect the unique compositions of each type of fuel. For example, biodiesel fuel surrogates can be represented by increased levels of sample methyl ester, oxygenated species, while a surrogate for oil sand fuels would contain higher levels of a selected cyclic paraffin component. Additional strategies for predictions of NO_x and SO_x emissions would require suitable surrogate reaction pathways. The technique of creating and using surrogate mixtures for transportation fuels is in the very early stages of development, and advances and refinements are needed.

While reaction mechanism reduction techniques have received considerable attention in recent years, better methods of automatic mechanism reduction are still needed and will be in particular demand for the very large fuel molecule systems that are characteristic of practical transportation fuels to be used in the future. Existing mechanism reduction tools are not easy to use, and packaged software tools are not generally available; more advances are needed.

SCIENTIFIC CHALLENGES

Key scientific challenges center on advancing theory and modeling of properties, necessarily including design and use of experiments to test the predictions. Significant challenges include the following: dealing with high pressure; large molecules that are real fuels; heteroatom content; and new fuel molecules and blends. In addition, new tools and data are required for making property predictions and measurements for high densities and pressures. With adequate predictive power, such models can be used to develop new fuels, combustors, and experiments to test and expand the models themselves. Advances are required in quantum chemistry, molecular simulation, theories of nonideal mixtures, collisional energy transfer, reaction theories, and parallel computation, and measuring chemical species using traditional spectroscopic techniques. Theoretical challenges include the following: our ability to describe potentially nonstatistical reactions and partial or completely diffusion-controlled reactions, and the effects of large exothermicity. We must also collect, organize, archive, and access experimental and computational data for these fuels and under conditions that will require advanced cyberinfrastructure development.

An important emerging problem in combustion modeling is that ignition reactions can occur at relatively low temperature (T=700-1000K) that are different in numerous ways from the subsequent high temperature reactions (T=1000-2500K), so extrapolation of high temperature chemistry to the low temperature ignition regime is not valid. Large molecules exist in numerous isomers, leading to many possible reaction channels and to complications relating to the definition of what are distinct chemical species. Synergistic experimental and theoretical efforts are needed to understand the chemical and energy transfer pathways under these conditions. A full understanding of secondary reactions is also essential for unraveling the complex chemistry in this temperature regime. Developing an improved understanding of the radical oxidation chemistry, and particularly the second O_2 addition kinetics, is important and challenging. These efforts will be challenged in part by isomer identification, thermochemistry, and kinetics.

POTENTIAL SCIENTIFIC IMPACT

Intellectual merits of this research direction include advances in fundamental insights into the basis and consequences of intermolecular interactions, kinetic aspects of oxygen-atom substitution within hydrocarbons, and thermodynamics and kinetics at high pressures. Advances in high-accuracy calculation of physical, thermochemical, and kinetic properties will necessarily identify new computational and physical bases for these advances.

This research will lead to an understanding of the chemistry and energy transfer processes of complex molecules in novel regimes of temperature and pressure. New experimental and theoretical approaches will be developed for mechanism discovery of complex combustion systems. This research will identify and quantify a new class of reactions found in low temperature combustion of large molecules, possibly including non-statistical behavior.

POTENTIAL IMPACT ON 21st CENTURY TRANSPORTATION FUELS

Engine manufacturers have demonstrated that existing fuel and combustor models can improve design, development, and operational performance. Development of properties as described above are crucial for advancing the technology for clean, efficient use of next-generation fuels. These new fuels will be quite different from traditional, petroleum-based fuels and will contain many components that have received very little study to date. The fundamental knowledge gained through this research will allow prediction of low-temperature reaction, ignition, flame propagation, extinction, and emissions phenomena. The measurements provide information about key reactions and validate models of analogous reactions. New techniques can be applied to inhomogeneous kinetic systems, such as injection sprays, and to practical systems, such as engines. Altogether, these advances and new techniques will expedite development of clean and efficient engines.

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AUTOMATED DISCOVERY OF FUEL CHEMISTRY KINETICS

ABSTRACT

The complexity of alternative transportation fuels necessitates the development of new methodologies to describe their combustion, so that efficiencies and pollutant emissions can be accurately predicted. Theoretical chemistry can be used to predict the rates of the elementary reactions that compose the detailed kinetic mechanism for these fuels. An accurate description of the often intricate mechanisms of large-molecule reactions requires a characterization of all relevant transition states, a task now performed by manual search. Development of automatic means to search for chemically relevant configurations is the computational-kinetics equivalent of improved electronic structure methods. Automatic methodologies are also required to reduce the computational complexity of detailed mechanisms for use in multiphysics simulations of engines.

EXECUTIVE SUMMARY

Most alternative transportation fuels consist of mixtures of many large molecular weight compounds, and their combustion involves hundreds of species and thousands of reactions. This leads to two related challenges for which new methodologies are required. The first is to develop detailed mechanisms, which require accurate reaction rates and thermochemistry for each of the reactions involved. The second is to reduce this detailed description to one that is computationally tractable in engine simulations.

Current automatic mechanism generators can provide approximate rate coefficients based on simple empirical rules [Van Geem et al. 2006], but many of them are not of sufficient accuracy. Moreover, important but unexpected pathways may not be included. The development of an automated procedure that employs more advanced statistical, dynamical and quantum chemical methods [Wagner 2002] would yield a means for the determination of complete and accurate elementary rate coefficients for critical chemical reactions. Expert systems, which accumulate kinetic and thermodynamic information from theory and experiment [Ruscic et al. 2004], can greatly increase accuracy, reliability and self-consistency, and can realistically quantify the uncertainties involved. An integral part of these methodologies is a comprehensive validation procedure (involving experimental data on both homogeneous and diffusive systems – e.g., laminar flames), which provides feedback to the expert system and the underlying theoretical methods.

The development of methodologies to reduce the computational complexity of these detailed mechanisms is essential for simulations of combustion in commercial devices. These methodologies can exploit both a reduction in the level of description of the chemistry and novel computational algorithms for their efficient implementation.

SUMMARY OF RESEARCH DIRECTION

Automated Elementary Rate Coefficient Generation

The development of predictive combustion models for alternative fuels requires accurate elementary reaction rate coefficients for thousands of elementary reactions, with many of these rate coefficients being completely unknown [Curran et al. 2002]. Recent advances in theoretical chemical kinetics provide the means for accurately predicting the kinetics of chemical reactions from first principles [Miller and Klippenstein 2006; Klippenstein et al. 2006]. Current implementations of these approaches require considerable human effort related to the manipulation of data from various software, and the manual search for transition states often relies on individual investigators' (necessarily incomplete) "chemical intuition," possibly omitting important nonintuitive pathways. The comprehensive automation of these procedures to yield a program that directly produces a truly complete kinetic phenomenology for any given set of reactants would constitute an extraordinarily powerful tool in computational kinetics, opening new possibilities for exploring fundamental reactions and exciting opportunities for mapping out the combustion chemistry of alternative fuels.

Expert Systems

Predictive modeling of combustion of 21st century fuels will require efficient utilization of the best available knowledge from multiple chemical scales. Chemical scales relevant to accurate descriptions of the chemistry of alternative fuels include spectroscopy, thermochemistry, kinetics, generation of comprehensive chemical mechanisms, and reduction of chemical mechanisms. New and robust methodologies are required to ensure that knowledge passed from one chemical scale to the next is in the form of accurate, reliable, and self-consistent data, accompanied by well-characterized uncertainties.

An expert system (ES) is one means to efficiently generate reliable and self-consistent knowledge at each scale. The central role of an ES is to derive the best self-consistent set of data, based on statistically and scientifically sound methods of analyzing all available experimental and theoretical determinations and their interdependencies, and incorporating corrective validation feedback received from other scales [Ruscic et al. 2005]. New research will be required to develop expert systems for the critical chemical scales for combustion of novel fuels, and to design architectures so that the ESs at various scales are able to interactively and dynamically exchange information.

Validation of Kinetics

A kinetic mechanism may be compiled by an "expert system" in which the choice of the values of the rate constants has been made based on first principles. This mechanism then needs to be validated against experiment in a comprehensive and rigorous manner. This validation is an essential step towards the development of an accurate mechanism, for in most cases there are significant uncertainty factors associated with the rate constant determination. For the challenges of novel fuel combustion, comprehensive validation schemes must be developed that test a mechanism against experimental data obtained for a large number of combustion phenomena and over a wide range of parameter space. Additionally, rigorous mathematical approaches could identify the controlling kinetic subsets for a given phenomenon and set of parameters, thereby providing feedback into the expert system for possible rate constant revisions. The mechanism validation should consider data obtained in both homogeneous reactors and flames, and for thermodynamic conditions ranging from standard atmospheric to extreme ones relevant to conventional as well as new-concept engines.

Mechanism Reduction

Spatially and temporally resolved computer simulations play a vital role in the development of improved IC engines [Drake and Haworth 2007]. In order to apply knowledge of alternative fuels chemistry to such high-level simulations, it is essential to have computationally tractable, reduced descriptions, based on the detailed mechanisms. Among the current approaches to achieve this goal are: graph methods to generate skeletal mechanisms by discarding unimportant species and reactions [Lu and Law 2005; Pepiot and Pitsch 2005]; dimension-reduction techniques, e.g., based on quasi-steady state assumptions [Chen 1988] or based on dynamical systems [Maas and Pope 1992; Lam and Goussis 1994; Ren et al. 2006]; and computational storage/retrieval algorithms [Pope 1997; Tonse et al. 1999; Chen et al. 2000; Velijkovic et al. 2003]. There is a need to develop automatic reduction and storage/retrieval methodologies with controlled accuracy that can be applied to the large detailed mechanisms for alternative fuels.

SCIENTIFIC CHALLENGES

There are several difficult steps involved in the automation of the standard theoretical procedures for predicting rate coefficients. Most importantly, there is a need to develop expert systems for discovering all the key connections (transition states) between wells and for accurately predicting the thermochemistry of these stationary points. Some work is also needed on generalizing the procedure for defining and extracting rate coefficients from solutions of the master equation describing the time dependent populations in each of the molecular complexes. For nonadiabatic processes, procedures for automatically determining the seams connecting surfaces and for estimating the rates of surface hopping are needed. For highly exothermic reactions, direct dynamics procedures may prove useful in describing the branching arising from rapid processes for which statistical theories are not appropriate.

The need to consider large molecules also presents various scientific challenges. It is often not feasible to apply accurate quantum chemical methods to the study of large molecules. Methods for accurately generalizing from small molecule studies to large molecules need to be developed. Careful and detailed extensions of group additivity concepts may continue to prove useful [Westmoreland et al. 2002]. These extensions may be based on detailed results for the smaller systems with the automated rate procedure. Large molecules also frequently have multiple isomers, and which isomers should be considered as separate species may change with temperature and pressure. Large weakly bound free radicals are generally not stable at high temperature, and the proper rate coefficient description is then intimately connected to the internal energy relaxation process. Thus, there is a need to understand the collisional energy transfer process for such large molecules and particularly the dependence on both energy and angular momentum.

New methods and efficient algorithms are required that can derive accurate, reliable, and self-consistent sets of data with well-defined and comprehensibly characterized statistically significant uncertainties by utilizing and analyzing all available experimental and theoretical knowledge pertinent to a given chemical scale, as well as by taking corrective action based on validation feedback from other scales. Novel methods of analyzing data should also incorporate approaches and algorithms that will, by analyzing the existent data, discover weak spots of knowledge and initiate new theoretical computations and new experiments. Finally, expert systems imply active curation of experimental and theoretical data on each level of chemical scale. Development of expert systems will necessitate the parallel development of supporting computer-science infrastructure, such as adaptive web-services for information exchange, efficient job streamlining and scheduling that uses the appropriate mix of local and non-local (e.g. using the Grid) computational resources.

For conventional transportation fuels, fundamental experimental databases that may be used for validation purposes are practically non-existent. There is an even greater lack of data for alternative fuels, such as, for example, synthetic and bio-derived fuels that only recently have emerged as viable. Typically, such fuels have large molecular weights and low vapor pressure, which makes their experimental handling rather difficult especially under the high pressures and temperatures encountered in engines. Such large molecules are on one hand susceptible to thermal decomposition, even at relatively low temperatures, and on the other must be heated enough to be maintained in the gaseous phase. A concerted experimental effort may be required to generate reliable kinetic and thermodynamic data over a wide range of conditions to validate mechanisms for emerging fuels. The validation process includes additional complications stemming from uncertainties associated with the mass diffusion of large non-spherical molecules. Thus, existing transport theories need to be extended in order to satisfactorily predict the fuel diffusion, whose effect could be of the same order compared to kinetics.

The challenge is to develop a general methodology that reduces the computational complexity as much as possible, while maintaining accuracy within prescribed bounds. Techniques from dynamical systems may be useful for this purpose (see, e.g., Ren et al. 2006). Storage and retrieval can greatly reduce the computational burden of treating combustion chemistry. The vast memory of massively parallel computing systems may increase the efficiency of such approaches, but also requires the development of new, adaptive parallel algorithms [Lu et al. 2005].

POTENTIAL SCIENTIFIC IMPACT

The ability to automatically and efficiently predict rate coefficients will have valuable impacts on all areas of gas phase chemistry. This capability would constitute a fundamentally new tool for accurate computational kinetics. Predictions from a first-principles approach, in synergy with experiment where available, will yield greatly improved kinetic models [Miller et al. 2005]. The new channels discovered in theoretical studies of the CH + N_2 [Moskalev and Lin 2000] and C_3H_3 + C_3H_3 reactions [Miller and Klippenstein 2003] provide illustrations of important new and unexpected pathways that are likely to be uncovered in such studies. Especially noteworthy is the impact the results could have on atmospheric chemistry and on chemical vapor deposition studies. Finally, the ability to predict rate coefficients for many classes of reactions should also lead to an improved understanding of chemical reactivity.

We envision the development of expert systems in spectroscopy, thermochemistry, rates of elementary chemical reactions, comprehensive chemical models, and models with reduced dimensionality that will be broadly applicable to other areas of chemistry. The efficient use of laboratory and computational resources by using expert systems will suggest new experiments and computations that will most efficiently increase the knowledge content most critical in a particular application.

The kinetics and combustion community has accomplished much over the last 20 years through the use of advanced laser diagnostics and computational tools. Specifically, for the first time fundamental combustion experiments for small fuel molecules, such as H_2, CO, and C_1-C_4 hydrocarbons can be predicted satisfactorily from first-principles. Extending this experimental and theoretical expertise to large molecules of relevance to transportation fuels will definitely "push the envelope" of the associated science, as a complicated and untested range of molecules will be studied. This approach is not merely "incremental" but presents a challenge in its own right because of the large number of new species and kinetic pathways that will be investigated. Even modest success along these lines will be a major step forward scientifically.

POTENTIAL IMPACT ON 21st CENTURY TRANSPORTATION FUELS

The combustion of alternative fuels will involve large classes of reactions whose kinetics is poorly known. The development of an automatic rate constant generation procedure will allow for the quantitative prediction of the kinetics of such reactions.

Expert systems will provide accurate chemical models for combustion of alternative fuels and will thereby contribute a central element in the development of new-generation computational combustion models for IC engines.

The development of methodologies to reduce the computational complexity of detailed chemical mechanisms for alternative fuels is essential for simulations of engine performance, including pollutant emissions.

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SPRAY DYNAMICS AND CHEMISTRY FOR NEW FUELS

ABSTRACT

The present level of understanding and modeling of the critical spray dynamics in liquid-fuel combustion is inadequate for designing and optimizing new engine technologies for use with alternative fuels. The wide range of physical and chemical properties of new fuels demands that the present empirical spray models be replaced by a fundamental first-principles understanding of spray breakup and the subsequent vaporization, mixing, and chemistry, which will require a revolutionary new understanding of the fundamental fluid mechanics and chemical reactivity in these multiphase problems. New insight into the physics and chemistry of spray evolution will need to be based on innovative probes of turbulent sprays at high pressure in unprecedented detail. This understanding has the potential to enable ground-breaking technical advances in control of combustion processes for future fuels.

EXECUTIVE SUMMARY

The evolution of fuel sprays plays a defining role in controlling the efficacy of ignition and the uniformity of combustion and hence in determining both combustion efficiency and the formation of soot and toxic partially oxidized and unburned hydrocarbon pollutants emitted into the exhaust stream. The physics and chemistry of this multiphase problem are difficult to probe experimentally, to understand theoretically, and model rigorously. This problem is particularly critical in the design of new engines for emerging fuels because key processes such as the physical breakup of the liquid spray, the mixing of vaporized fuel with the cylinder gases, and the chemistry at droplet interfaces under high pressure will change—in ways that cannot at present be reliably predicted—with the new chemical and physical characteristics of non-traditional fuels. A priority research direction is to develop rigorous models for spray dynamics, fluid flow and droplet breakup, and fuel droplet interfacial chemistry, evaporation, and mixing, supported by new and powerful experimental spatial (sub-micron), temporal (sub-microsecond), and chemical characterization of complex multiphase flows. These experiments will be needed to validate unprecedented detailed models, requiring full multi-scale simulation from the first-principles equations governing the critical processes, consistent with device-scale resolution of flow fields. The overall research goal is to develop methodologies to computationally predict and design optimally shaped sprays for engine combustion of new fuels based on their physical and chemical characteristics. These new models, and the related experimental measurements that test and validate them, would provide a critically needed fundamental understanding of turbulent multiphase fluid dynamics, cavitating liquid flow, and molecular interactions and reactivity across phase boundaries. This level of understanding may permit extraordinary new technologies, such as smart fuel injectors that adapt to changing fuel and load conditions, to permit fuel-flexible advanced engines to run cleanly and efficiently on a range of alternative fuels.

SUMMARY OF RESEARCH DIRECTION

To develop and deploy non-traditional and alternative fuels requires an understanding of how their physical and chemical characteristics influence engine performance and emissions. Advanced knowledge and modeling capabilities of fuel sprays are essential in this evaluation. The introduction of alternative fuels will greatly increase the number of physical and chemical parameters that characterize fuel performance in engines. At present the fundamental physics that determines the course of initial spray breakup is not well determined. New modeling capabilities are required that will provide enhanced accuracy over current methodologies and greatly augment the ability to distinguish between favorable and unfavorable fuel characteristics. This type of fundamental characterization of alternative fuel combustion is crucial for devising new science-based test metrics, beyond octane and cetane number, for fuels to be used in advanced engines.

Advanced understanding and modeling capabilities of flows inside fuel injectors will offer the opportunity to optimize and even custom design injection systems. These designs can be tailored to specific fuel characteristics, engine design, and engine operating conditions for more effective mixture preparation. Integrating the injector modeling with in-cylinder fuel spray and combustion modeling would provide the ability to completely evaluate the effects of fuel characteristics on engine performance and emissions. Furthermore, with measurement of segregation of species at the surface of droplets, it would be possible to determine the extent of fuel component separation in the liquid before ignition. Characterization of the fluid dynamics itself is already a substantial and critical scientific challenge. Advanced injector devices under consideration will allow use of even more complex pulsed sprays, with air-assist and multi-component fuels in ultra-high-pressure injection. Highly informative detailed multidimensional measurements of vapor and liquid phase composition in evolving sprays combined with rigorous modeling are required to generate a new level of understanding for prediction of fuel injection and mixing in combustion of novel fuels.

High-Resolution Measurements

Multiphase imaging. New methods are needed for spatially and temporally resolved chemical and physical characterization of liquid and vapor phases in spray combustion; for example, powerful new imaging capabilities that simultaneously capture liquid spray evolution and droplet sizing with sub-micron resolution at sub-microsecond timescales. Progress can be made by applying existing techniques [Adrian 1991; Miles and Lempert 1997; Linne et al. 2006] to new fuels, but diagnostics exploiting new architectures (e.g. ballistic imaging of structures and acceleration of the liquid interface [Linne et al. 2006]) and wavelength ranges (e. g. magnetic resonance; X-ray absorption, microscopy, and scattering [Cai et al. 2003];THz, infrared, and Raman microscopies) will also be required (see Figure 1). The fundamental physical processes of spray breakup remain poorly known; multiphase imaging techniques that can resolve velocity fields will be particularly valuable.

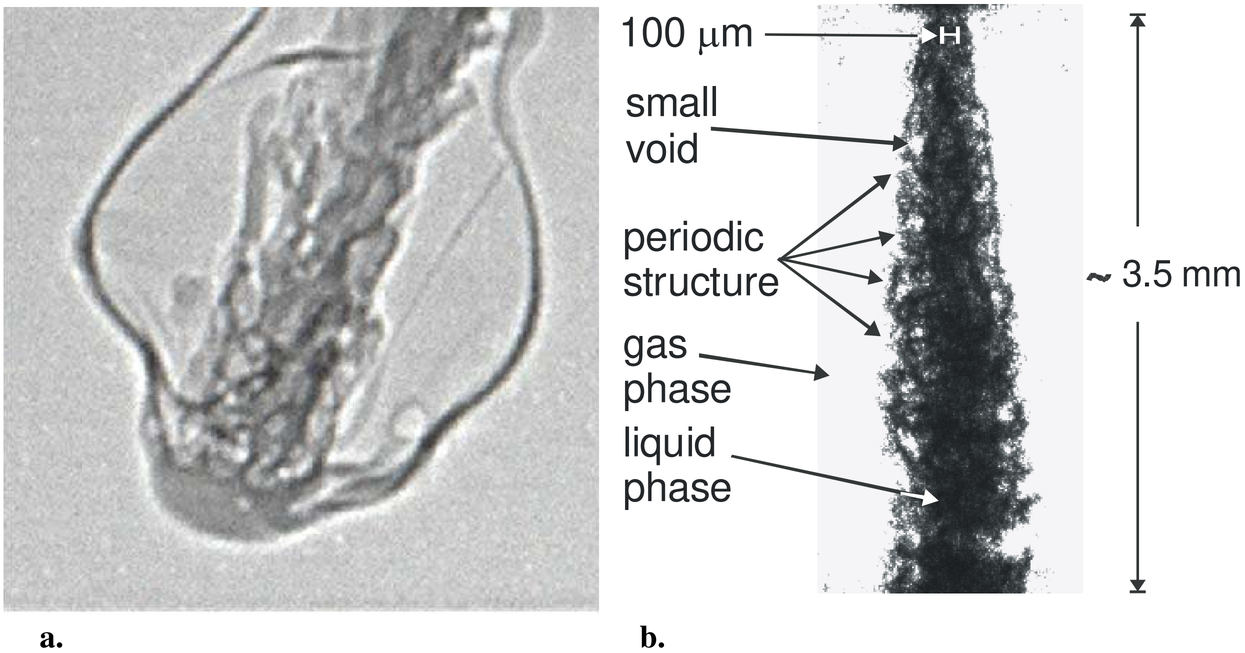

Figure 1. Imaging techniques for the liquid core in an atomizing spray. a.Instantaneous structure of the leading edge of an impinging spray (entering from the upper right), detected by using single-shot ultrafast X-ray phase-contrast imaging with 300 ns resolution. Complex structure is observed in the dense spray. (J. Wang, Argonne National Laboratory) b. High spatial (25 μm) and temporal (3 ps) resolution ballistic image of the near field of an atomizing diesel fuel spray (Sturman), showing cavities and periodic structure in the liquid core. [Linne et al., 2006].

In addition to overall spray visualization diagnostics, individual droplet temperature [Omrance et al. 2004] and liquid surface morphology-shape parameter measurements are needed to be able to validate spray vaporization and breakup/coalescence models. Advanced diagnostics are also needed for the assessment of multi-component fuel vaporization processes under high-pressure conditions, including processes that occur under supercritical conditions. The role of supercritical phase transition phenomena in practical sprays is not well understood, particularly for multi-component fuels [Okong'o and Bellan 2002].

Chemical species information will also be important, especially for characterizing the dilute-spray region. As one example, coherent X-ray scattering near atomic resonances could give three-dimensional snapshots for particular oxidation states, giving spatial and chemical characterization at unprecedented levels of detail. The data that naturally arise from X-ray measurements [Messer et al. 2005; Muntean et al. 2005] provide bond distribution information (e.g., number of C=C double bonds), which may serve as a natural "reduced" description of complicated chemistry, suitable for inclusion in detailed computational fluid dynamics codes. Chemically sensitive spectroscopies, combined with scattering measurements, could follow the size and composition history of a single droplet in a turbulent multiphase flow. These methods could follow the development of the spray flow all the way through to gas-phase mixing phenomena at high pressure.

Fundamental chemistry and physics. Experimental studies of a combination of fundamental, well-controlled systems and real combustors will be needed to develop the physically rigorous theory required for reliable prediction of the fluid dynamics and chemistry that operate under the harsh conditions of an igniting spray. Such studies of fundamental and applied systems will be critically important for the development of novel, fuel-efficient engines that use alternative fuels. The reactivity of fuel molecules at the surface of droplets under a high-pressure oxidizing environment, reactions at liquid films relevant to spray impingement on chamber walls, and liquid and interfacial chemistry contributing to deposit formation also need to be investigated. Interface- or film-specific methods, such as harmonic generation [Shen 2000] or infrared ellipsometry [Gensh et al. 2005], can be applied to fundamental investigations of differential evaporation, species segregation, and surface chemistry at liquid-gas interfaces under the high pressure and temperature conditions relevant to spray combustion.

Observational insight into the primary and secondary breakup of liquid sprays remains a key research need. Investigations of spray breakup must be performed under a wide range of conditions, using well-characterized flow fields. Of particular interest for developing physical understanding relevant to new engine designs will be studies of the impact of injector designs, nozzle cavitation, turbulence, and aerodynamic contributions on spray breakup. Consideration of alternative fuels will additionally require similar studies of the influence on spray evolution of fluid characteristics, such as viscosity, surface tension, and volatility. Furthermore, a basic molecular-level understanding of these critical characteristics for pure fuels and complex mixtures will be required to predict performance of novel future fuels. Experiments to explore fundamental fluid properties in the vicinity of critical thermodynamic conditions will be extremely valuable.

First-principles models

At present, the description of spray breakup depends largely on empirical models and averaged descriptions of the turbulent flow (see Figure 2). For reliable prediction of performance with new fuels, fundamental modeling approaches using detailed methods, such as direct numerical simulation (DNS) techniques [Chen et al. 2006], will be required. Efficient numerical algorithms for tracking the evolution and development of free surfaces will be required for in-depth understandings of liquid breakup and coalescence processes. High-order numerical methods must be developed to solve the equations that describe liquid sprays for all quantities of interest, such as velocity, pressure, temperature, and chemical composition. Simulations must begin with a molecular-level understanding of fundamental physical properties and be carried out from first-principles. In conjunction with the advanced experimental investigations, these models will give unprecedented insight into sprays. A detailed DNS capability is required to study flow inside and just down stream of injectors (including cavitation physics), the liquid spray jet inside the engine combustion chamber, liquid-jet break-up and atomization, spray-drop dynamics, multi-component fuel vaporization, gas-phase fuel-air mixing, and ignition kinetics. To accommodate studies of sprays in very high-pressure ambient conditions, consideration of thermal radiation may also be required. In addition to improving fundamental understanding, DNS results can help develop and test large-eddy simulation (LES) models [Pitsch 2006] for device-level simulations. To support this effort, data reduction and analysis algorithms must be designed for strong coupling between model computation and theory development, including pedigree and uncertainty propagation.

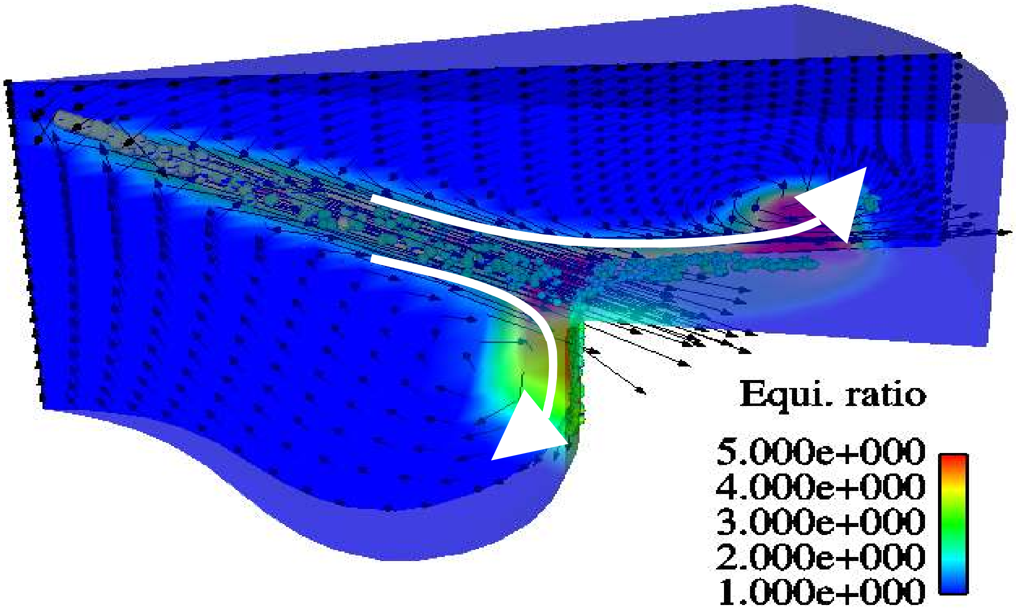

Figure 2. Typical diesel spray calculated with a discrete droplet spray model employing empirical submodels for break-up and Reynolds-averaged Navier-Stokes (RANS) based transport and dispersion simulation. (Courtesy of Prof. R. D. Reitz, University of Wisconsin)

SCIENTIFIC CHALLENGES

The spatial and chemical distribution of gases and liquids in high-pressure, high-speed fuel sprays dominate the heterogeneous chemistry before and during ignition. Until now, direct experimental access to these parameters has been very limited, and hence a first-principles description of these sprays, including interphase momentum, heat, and mass transfer, has not been possible. As a result, the structure and dynamics of fuel sprays have not been validated, and creative high-end modeling of these phenomena, which ultimately may enable the design and optimization of adaptive injectors for flexible-fuel operation of advanced engines, has not been possible. Beyond the instantaneous composition and distribution of gas and liquid in these systems, the evolution of composition in the multicomponent mixture is of great importance but remains mostly unmeasured and poorly characterized. Further, evolution pathways are expected to change with fuel chemistry; the physical characteristics of the fuel will alter the initial spray breakup, and chemical changes will affect the reactive processes in the dilute zone. A description and characterization of fuel flow from inside the injector through the spray breakup and evaporation is urgently needed to accurately predict fuel-to-air mixture requirements and optimize fuel utilization. The new fuels that are the subject of this report present even greater challenges as they often have lower volatility, may contain reactive sites in the fuel molecules (e.g., esters in biodiesel), and include multiple components with widely varying properties. The time-resolved distribution of the mass and composition in the multicomponent mixture is of great significance as liquid-phase chemical changes could occur before ignition. A final issue is modeling of supercritical conditions, as this area is currently poorly developed and will be important in high-pressure applications.

POTENTIAL SCIENTIFIC IMPACT

A fundamental understanding of the physical and chemical processes that occur in high-speed liquid fuel sprays will form a theoretical framework to organize knowledge that will be gained from the development and application of advanced spray measurement techniques. The theoretical framework will provide the context and background for developing more accurate first-principles based models for fuel-spray processes, including fundamental characterization of all of the key processes that occur in fuel injection and spray evolution. The complex liquid flow processes inside the fuel injector, including cavitation, will be accurately modeled so that ad hoc spray-jet boundary conditions at the exit of the nozzle can be avoided. The fluid mechanics of cavitation, especially inception, are poorly known; this fundamental physics will now become accessible. There will be significant new insights into the complex processes that occur at liquid-gas interfaces, including multi-component vaporization. The reactive composition changes that occur during spray ignition will provide important information for creating and improving elementary reactivity theories at phase boundaries.

POTENTIAL IMPACT ON 21st CENTURY TRANSPORTATION FUELS

As the range of available fuels increases, flexible-fuel operation will become an important feature of engines. Design and evaluation of this flexibility requires advanced knowledge and modeling of fuel sprays. With sufficient understanding, fuel properties could be evaluated on the engine, and real-time adaptability of the fuel injection process could be developed. Active control of spray quality, shaping, and injection parameters (e.g., injection pressure, phasing, and duration) will be accomplished with intelligent injection algorithms to provide fuel flexibility without adversely affecting performance and emissions. This advance would provide the revolutionary capability for a fully optimized flexible-fuel engine that will operate both cleanly and efficiently.

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CONCLUSION

CONCLUSION

The modern American society is built on the assumption of inexpensive and convenient transportation for people and goods. For the past 100 years, petroleum-based fuels derived from light, sweet crude oil have provided the energy for America's, and indeed for the world's, transportation needs. Environmental, economic, and security concerns, coupled with the specter of a finite supply of oil, are driving a shift to alternate fuel sources. These new sources, whether oil shale, oil sands, biodiesel, or ethanol, all have combustion characteristics that vary from those of traditional fuels. With the requirement for controlling pollutants at the parts-per-million level, changes in fuel composition may have a significant impact on the ability for vehicles to meet stringent environmental regulations at competitive costs. A first principles understanding of 21st century fuels will enable the optimal design of engines for the clean and efficient combustion of these new fuels.

At the same time that new fuel sources are entering the market, new engine cycles are also appearing that promise to increase efficiency by 30% or more. Such enhanced efficiency will reduce environmental impacts and enhance security. Methods such as HCCI offer diesel-like efficiency with the environmental acceptability characterized by current gasoline fueled vehicles. These new concepts rely on subtle control mechanisms that require a fundamental understanding of combustion science for their optimal implementation. To maximize efficiency and minimize pollution, these new engine concepts typically operate under very dilute and very high pressure conditions compared with current designs.

The Challenges

New fuel sources provide a significantly different mix of chemicals than are found in traditional sources, including a higher fraction of aromatic compounds and oxygenated species. The chemistry of these new compounds is poorly characterized, particularly under the high pressure conditions relevant to next generation engine designs. New theoretical and experimental efforts are needed to characterize the unique chemistry of these new fuel components. In addition to their chemical properties, the physical properties of these species must also be determined over the full range of pressures and temperatures of these engines.

The ultimate challenge in combustion science is to produce predictive models of combustion systems that can be used for device design. Significant challenges remain in developing the multiscale models that can address the 8-10 orders of magnitude in space and time relevant to combustion. The complexity of future fuels adds to these challenges. Significant advances in high performance computing and algorithm development are needed in addition to scientific understanding to fully develop predictive models. A coordinated set of experiments, based on new diagnostic methods, will be needed to validate these models under the high pressure conditions relevant to real devices. These experiments present unique challenges that will require a new generation of techniques and instruments to probe the detailed physics and chemistry of high pressure combustors. New theoretical tools will be needed as pressures exceed 100 atm and traditional binary collision models begin to fail.

Outlook

Due to a combination of the high energy density of liquid hydrocarbon fuels and the well developed and pervasive infrastructure for their combustion utilization in transportation, combustion powered transportation is likely to remain a mainstay for the next 50 years. A diminishing supply of light sweet crude oil combined with increasing availability of alternative fuels will lead to a substantial shift in the fuel composition at the same time that new high efficiency engines are being introduced. For internal combustion engines to provide environmentally acceptable impacts and be compatible with national security and competitiveness needs, substantial investments in combustion science are needed. Progress over the last 25 years has shown that predictive modeling of combustion lies within our grasp for laboratory scale devices. To extend this predictive modeling to practical combustion devices utilizing 21st century fuels will require sizeable effort in both theory and experiment; however, the path to success is clearer now than ever before.

APPENDICES

APPENDIX 1 – TECHNICAL BACKGROUND

BES Workshop on Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels

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(Prepared as background material for the workshop.)

CONTENTS

INTRODUCTION - MOTIVATION AND OPPORTUNITIES

Energy Needs

Our nation requires a secure, economical, and environmentally acceptable energy supply to uphold our standard of living, ensure our national security, and maintain our economic competitiveness. Currently 85% of our nation's energy comes from hydrocarbon sources including natural gas, petroleum, and coal. America's total energy use as of 2005 was split among transportation (28%), industrial use (32%), residential use (22%), and commercial use (18%). While total energy consumption has increased, this distribution has remained fairly constant over the last 50 years as shown in Figure 1. Transportation accounts for one of the largest uses of energy; indeed when electric power is factored out, transportation is the largest single user of energy. For transportation, 97% of transportation energy derives from petroleum. Of total petroleum consumption, 44% is used for gasoline, 14% for diesel, and 8% for aviation fuel. The fraction of petroleum imported into the U.S., 60%, is roughly equal to that consumed in the ground transportation sector. The transportation sector's dominant role in consumption suggests that efficiency improvements in this sector can have a large impact on the nation's energy use. The monolithic nature of transportation energy use, liquid fuels used in internal combustion engines, means that unlike industrial energy use, a relatively small number of technologies and fuel sources need be considered.

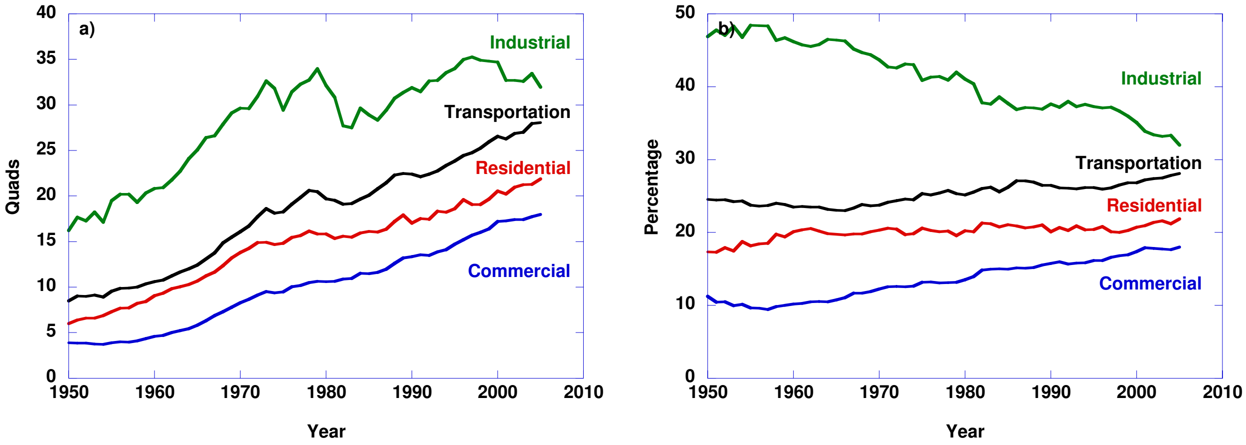

Figure 1. a) Energy consumption by end use in the United States from 1950 to 2005 in quadrillion BTUs (Quads). b) Relative energy use by end use in the United States from 1950 to 2005. Source: Energy Information Administration, Annual Energy Review 2005, Report No. DOE/EIA-0384(2005).

Petroleum plays the central role in the current transportation energy picture and indeed in the world's total use of energy. The total demand for energy is expected to increase steadily throughout the world with particularly large increases in the demands from emerging economies, as shown in Figure 2. Total oil use is projected to grow from 162 Quads in 2003 to 239 Quads in 2030 with 60% of that increase being used in transportation.

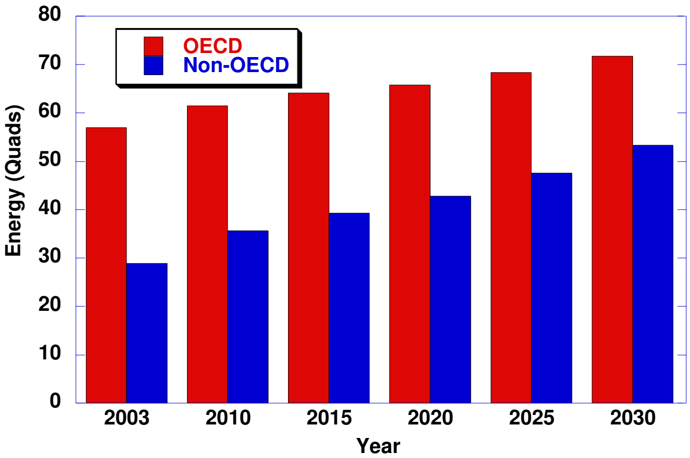

Figure 2. Projected worldwide transportation energy use in Quads from 2003 to 2030. OECD is the Organization for Economic Development and Cooperation. OECD member countries represent the developed world and non-OECD member countries the developing world. Source: Energy Information Administration, Annual Energy Review 2005, Report No. DOE/EIA-0484(2006).

While energy demand is increasing steadily, oil prices have remained relatively stable until recently, as shown in Figure 3. After adjusting for inflation, oil prices have historically stabilized in the range $20-$30/barrel with the exception of the 1970's oil crisis and current prices. The peak in the 1970's has largely been attributed to OPEC production restrictions. The current rise in prices does not correspond to artificially limited production. With projections of a steady rise in demand, new sources of liquid hydrocarbon fuels will be needed to maintain energy prices near their historic values.

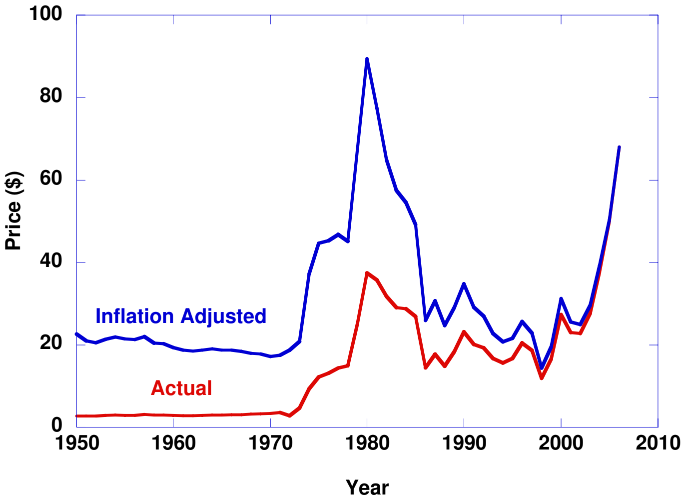

Figure 3. Oil prices 1945 to present in actual dollars and inflation adjusted dollars.

Table 1 lists the largest known oil reserves. At current consumption rates, about 18 billion barrels per year, these reserves would last for approximately 70 years. As noted above, consumption is projected to increase by 50% in the next 20 years. While new reserves are continuing to be added, the rate of new discoveries is declining, as shown in Figure 4. Various estimates with different assumptions have been made regarding the peak of oil production and lifetime of reserves. Although there is disparity in these estimates, oil is certainly a finite resource. Most estimates indicate that the "end of oil", as we now know it, will occur in the next 50-100 years.

Other than the oil sands of Canada, the reserves shown in Table 1 lie in countries with complex to unfriendly relations with the U.S. The ever-increasing reliance of the U.S. on energy from such regions is a national security issue. Diversifying our energy sources to include more domestic fuels would enhance U.S. security, generate new industries and jobs, and protect our economy from geopolitical upheaval. Essentially all of the alternative fuel sources can be domestically produced or are found in stable, friendly regions.

Table 1: Largest known oil reserves.

Rank	Country	Proved reserves (billion barrels)
1.	Saudi Arabia	261.9
2.	Canada	178.8[1]
3.	Iran	125.8
4.	Iraq	115.0
5.	Kuwait	101.5
6.	United Arab Emirates	97.8
7.	Venezuela	77.2
8.	Russia	60.0
9.	Libya	39.0
10.	Nigeria	35.3

NOTES: Proved reserves are estimated with reasonable certainty to be recoverable with present technology and prices. 1. Includes 174.5 billion barrels of oil sands reserves. *Source: Oil & Gas Journal,* Vol. 102, No. 47 (Dec. 10, 2004). From: U.S. Energy Information Administration. http://www.eia.doe.gov/emeu/international/petroleu.html .

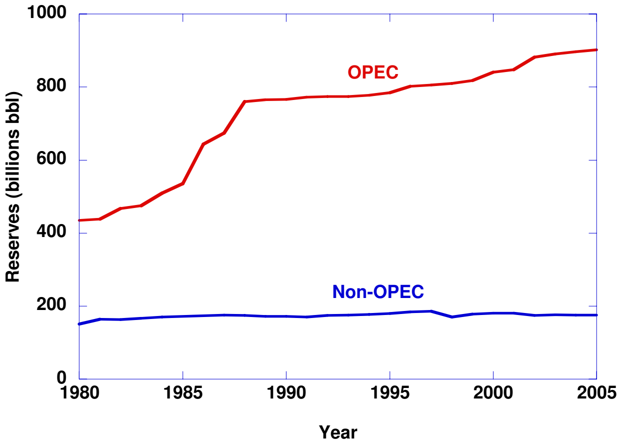

Figure 4. Proved oil reserves 1980-2005, not including Canadian oil sands**,** from BP Statistical Review of World Energy, June 2006, http://www.bp.com/statisticalreview.

Energy Consequences

Energy use has consequences that extend beyond immediate applications. Environmental impacts can be particularly significant. Urban smog is largely attributed to combustion byproducts. The adverse health effects associated with smog have led to considerable regulation in this country to limit the emissions of NO_x, hydrocarbons, and other pollutants from internal combustion engines. Controlling these emissions while maintaining high efficiency is a challenge for combustion scientists and engine manufacturers. Regulations continue to tighten, with new diesel emissions regulations to come into effect in 2010.

Increasingly, human activity and in particular anthropogenic emission of CO_2 are linked to global climate change. Recent studies have shown very strong correlations between the atmospheric temperature and atmospheric CO_2 and methane concentrations over hundreds of thousands of years, as shown in Figure 5.

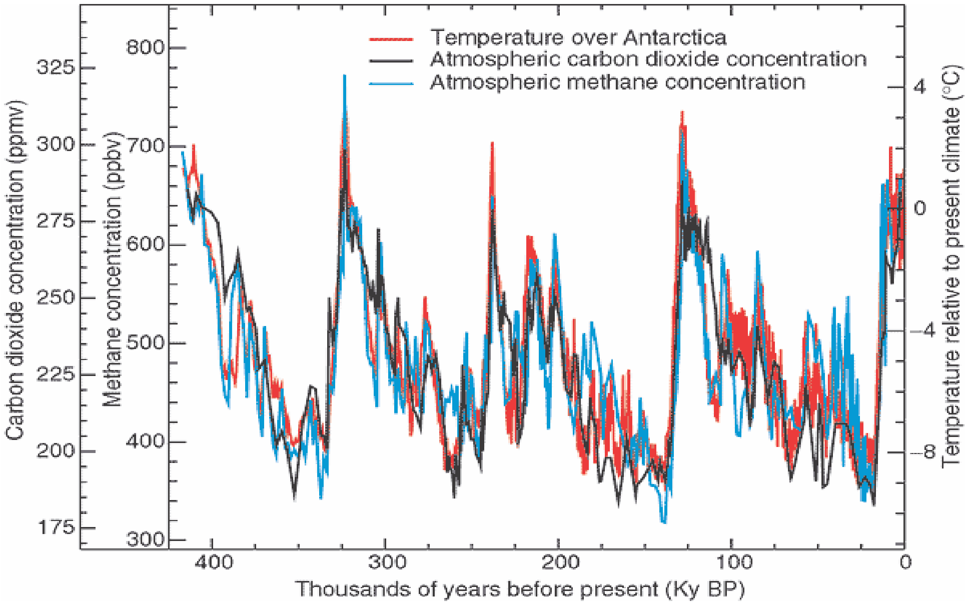

Figure 5. Correlation of atmospheric temperature over Antarctica with carbon dioxide and methane concentrations. Source: Petit J.R., Jouzel J., Raynaud D., Barkov N.I., Barnola J.M., Basile I., Bender M., Chappellaz J., Davis J., Delaygue G., Delmotte M., Kotlyakov V.M., Legrand M., Lipenkov V., Lorius C., Pépin L., Ritz C., Saltzman E., Stievenard M. (1999). "Climate and Atmospheric History of the Past 420,000 years from the Vostok Ice Core, Antarctica". Nature **399**: 429-436.

Given this strong correlation and growing evidence that CO_2 is causally related to global warming through the greenhouse effect, the rapid rise in atmospheric CO_2 concentration over the past 50 years is noteworthy. As shown in Figure 6, atmospheric concentrations have risen to over 370 ppm, well above the historical peaks of 300-325 ppm shown in Figure 5 associated with past cycling from periods of warming to ice ages. The long atmospheric lifetime of CO_2 (50-200 years, US EPA) indicates that essentially permanent, significant reductions in anthropogenic CO_2 emissions are required to bring CO_2 levels back to their historic range within even a few generations.

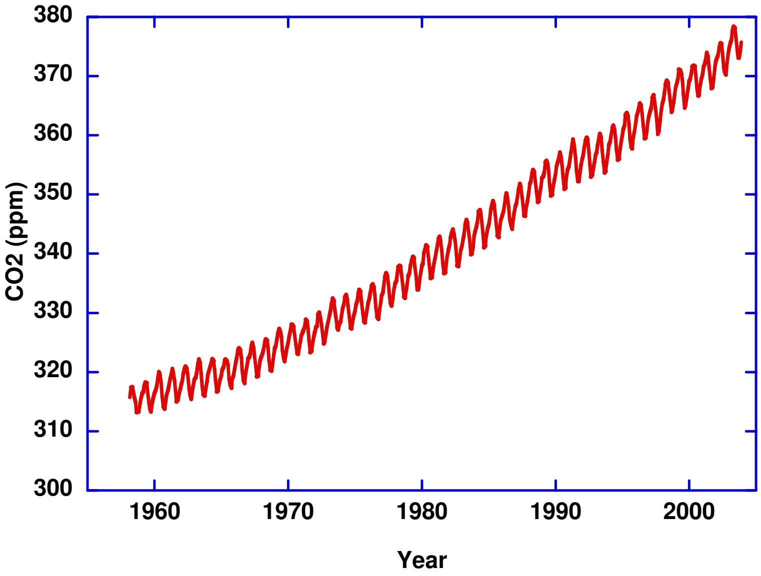

Figure 6. Measured CO_2 concentration for the last 45 years at Mauna Loa, Hawaii. Source: C. D. Keeling and T. P. Whorf, "Atmospheric CO_2 Concentrations - Mauna Loa Observatory, Hawaii, 1958-2002," Numeric Data Package NDP-001, Oak Ridge, TN, Carbon Dioxide Information Analysis Center, Revised August 2003, http://cdiac.esd.ornl.gov/ndps/ndp001.html

Anthropogenic greenhouse gas emissions come primarily from energy production. In 2002, U.S. greenhouse gas emissions were dominated by energy-related CO_2 emissions. These emissions accounted for 82.8% of U.S. greenhouse gas emissions in that year. Combustion accounts for essentially all of this CO_2. Increases in efficiency can reduce these emissions, and switching to renewable fuel sources such as biofuels can further reduce or eliminate the net CO_2 emissions.

Combustion production of energy also contributes to local pollution, most notably by providing many of the raw materials for photochemical smog production. The two major classes of local pollutants from combustion are nitrogen oxides, NO_x, and soot and unburned hydrocarbons. These species are tightly regulated and great strides have been made in reducing their outputs in recent decades. A combination of improved combustion technology and exhaust after treatments have reduced and nearly eliminated these emissions from gasoline spark-ignited engines. Diesel compression ignition engine emissions have proven more difficult to control in part because catalytic aftertreatment systems are not practical for these engines. New regulations effective in 2010 will further tighten diesel engine emissions. The high efficiency of diesel engines makes it critical to meet these new regulations.

While not the focus of this document, energy use is integrally connected to our nation's and the world's economy. The U.S. economy in particular has been driven over the last 50 years by the availability of relatively cheap oil. We take for granted that transportation of goods and people is inexpensive, enabling the dispersion of the population in the U.S. over wide ranges. Our standard of living is based on the ability to move goods over great distances quickly and cheaply. Although there may be great controversy over whether the peak in oil production is near, there is little doubt that the supply of light, sweet crude, the cheap oil on which our economy is built, will peak in the next few decades. As new, typically more expensive sources of fuel come on line, efforts to produce higher efficiency can mitigate these effects, maintaining an economically acceptable infrastructure.

Path Forward

As combustion technologies move forward into the 21st century, several challenges lie ahead. Environmental acceptability will play a key role in an evolving regulatory climate. At the same time, reducing the U.S. dependence on foreign oil is likely to continue as a prime driver. These two forces push in different directions, particularly if carbon management regulation becomes a reality. For example, exploiting proven oil shale reserves could reduce U.S. dependence on foreign oil, but tapping these reserves would not reduce carbon emissions. Other developments hold the promise of addressing both issues simultaneously; for example, increases in efficiency would both reduce emissions and reduce foreign oil consumption.

Two developments in the fuel energy sector offer new challenges and opportunities: (1) utilization of non-traditional fuel sources, and (2) the creation of novel engine technologies. New fuel sources include bio-derived fuels, such as ethanol and biodiesel, and new fossil fuel sources, such as oil sands and oil shale. These new fuel sources offer a number of advantages and challenges. In addition to potentially reducing our dependence on foreign oil, they require substantially more processing from feedstock to fuel than traditional oil. As new engine technologies are developed, this processing becomes an opportunity to optimize the fuel stream for new engines and potentially to develop fuels substantially different from the current gasoline and diesel fuels. Indeed, new fuels may be required for some new engines to function within existing environmental regulations. Together these developments offer the potential for more efficient, cleaner transportation systems that use domestic energy sources.

EVOLVING ENERGY SOURCES

As shown in Figure 3, oil prices have remained relatively flat over the last 50 years after accounting for inflation. This inexpensive oil has driven our nation’s economy during that period. The only previous disruption has been the price spike in the 1970’s due in large part to price/supply manipulation by the OPEC cartel. The current rise in prices is not attributed to such manipulation, but rather to fears of supply shortages due to wars, politics, or natural disasters. Previously, price rises have been met with increased production that in turn lowers prices to their historic level. During the recent rise in prices, however, there has not been enough elasticity in production to create this balance. This circumstance is interpreted as one of the signs that a peak in light, sweet crude oil production is near. Regardless of whether or not peak oil production occurs in the near term, the current prices of oil make other fuel sources economically viable.

Although hydrogen may be a long-term fuel solution, currently a number of technical problems prevent its wide spread use, including insufficient methods for storage, fuel cell reliability and cost, and a proven, economical means of production. Liquid hydrocarbons remain an excellent fuel choice, particularly for the transportation sector. These fuels have the advantage of being relatively easy to store and transport with a large infrastructure in place today. Liquid hydrocarbons also have one of the highest energy densities of any practical fuel, as shown in

Table 2. It is worth noting that the high energy density of larger hydrocarbons results in part from their production of more CO_2, a more exothermic product than H_2O. Thus, one of the properties that make these fuels attractive for energy production also makes them a major contributor to anthropogenic atmospheric CO_2. The new alternative fuels do not in general share all of the advantageous properties of the current common fuels, gasoline and diesel, but neither do they necessarily share their disadvantages.

Table 2. Energy Density of Selected Fuels

Fuel	Energy density (MJ/kg)	Density (kg/l)	Energy density (MJ/l)
carbon (to CO_2)	32.8	2.20	72.16
carbon (to CO)	22.7	2.20	49.94
ethanol	29.7	0.78	23.31
hydrogen (liq)	142	0.07	10.08
hydrogen (2,000 psi)	142	0.01	1.42
methane (2000 psi)	55.5	0.11	6.11
methanol	22.7	0.78	17.84
nitromethane	11.6	1.14	13.22
octane	47.9	0.92	43.92
propane	50.3	0.58	29.32
coal, anthracite	31.4	1.55	48.67
coal, bituminous	23.9	1.35	32.27
coal, lignite	17.43	1.25	21.79
diesel	45.3	0.90	40.77
gasoline	45.8	0.74	33.89
jet a	43.3	0.80	34.64
kerosene	46.3	0.82	37.83
oil, crude (petroleum)	41.9	0.85	35.62
oil, heating	42.5	0.89	37.83

Source: Chemical Potential Energy, The Physics Hypertextbook™, 1998-2006, Glenn Eler, http://hypertextbook.com/physics/matter/energy-chemical/

Several classes of non-conventional fuels can be considered likely candidates for new fuel sources. Heavy fossil hydrocarbons are one potential source of new fuels. These include oil shale and oil sands as well as heavy crude oil. Coal is perhaps the ultimate "heavy hydrocarbon" and can also be processed to produce liquid fuels, as the Germans did in World War II. At the opposite extreme, natural gas can also be converted to liquid fuels. Potentially, more carbon-neutral fuels can be obtained through the production of biodiesel, ethanol, and other biofuels.

Heavy fossil fuel sources are distinguished from the traditional light, sweet crude oil by their higher average molecular weight and larger aromatic content. Several sources of heavy hydrocarbons are currently available or becoming available. Heavier crude oil is recovered from both existing fields and new discoveries, but is generally more difficult to recover and requires additional refining compared to light, sweet oil.

Oil Sands

Oil sands, also called tar sands, are high molecular weight hydrocarbons mixed with sand. Canada and other locations have very large deposits of oil sands that are just beginning to be exploited. In Canada alone, there are 175 billion barrels of proven reserves, making Canada second only to Saudi Arabia in proven reserves. Current fuel prices now make oil sands a viable source of fuel. Oil sands have undergone a different course of historical processing than traditional crude oil. Since oil sands have sat at or near the surface, they have not been under pressure, but instead have been exposed to microbes. Open pit mining is used to recover these deposits, which require considerable refining and "upgrading", generally increasing the hydrogen content, to produce usable fuels. These fuels have higher cycloalkane content than traditional diesel or gasoline.

Oil Shale

Oil shales are fossil hydrocarbons found in shale rock. The U.S. has substantial deposits of shale oil, particularly in the Rocky Mountain States. These hydrocarbons were successfully recovered by open pit mining in the 1980's, but were not a commercially viable fuel source. The hydrocarbons require substantial refining and upgrading to produce usable fuels. Rising fuel prices and new recovery techniques promise to make oil shale a viable alternative in the near future. In addition to traditional mining methods, followed by surface retorting to recover the oil, Shell Oil is now developing *in situ* refining methods. These new methods use in-ground refining to partially upgrade and liquefy the hydrocarbons, making it possible to recover the fuel source through pumping rather than mining. This new technology may prove more environmentally acceptable and perhaps more economically feasible as well.

Gas-to-Liquids

Liquid fuel production is also possible starting from natural gas using gas-to-liquids technologies (GTL), or at the other extreme coal using coal-to-liquids technologies (CTL). For the GTL process two general routes are possible focusing on methane, which makes up the bulk, 85-90%, of natural gas. Methane may be directly converted to liquid fuels through a high-activation energy process, or it may be first converted to synthesis gas (syngas) by reacting with steam at elevated temperature. The direct conversion process has not to date proven to be commercially feasible.

Syngas consists of a mixture of hydrogen and carbon monoxide suitable for further processing. Typically, steam reforming is carried out in heated, catalyst-filled tubes to produce a mixture of 5:1 hydrogen to carbon monoxide. The syngas may be directly converted to methanol, or through the Fischer-Tropsch process, it may be converted to a mixture of higher molecular weight hydrocarbons, which may then be further refined to produce useful fuels. The Fischer-Tropsch process is optimized for a 2:1 hydrogen/carbon monoxide mixture. The excess hydrogen from the syngas must be separated and may then be used for petroleum refining or other industrial processes, preferably in a co-located facility. Current fuel prices make GTL fuels economically competitive, with sustained prices of at least $25/bbl required.

GTL fuels have the potential advantage of having little or no sulfur content, substantially reducing the formation of particulates during combustion. GTL fuels may also be refined to produce low aromatic content, further reducing the toxicity of combustion emissions. Tuning the synthesis and refining processes can lead to improved fuel performance and reduced emissions compared to conventional fuels. For example, diesel fuels may be produced with higher cetane numbers than those for petroleum-based fuels and with lower emissions. NREL summary data show GTL diesel fuel yielding 11% lower PM, 13% lower NO_x, 28% less CO, and 22% less HC compared to No. 2 diesel. These reductions are the result of the substantially different chemical makeup of the GTL fuels. GTL fuels may also be used as additives to enhance the performance and/or reduce emissions of traditional fuels.

Coal-to-Liquids

In the U.S., coal is an attractive energy source because of its availability. The known U.S. coal reserves are approximately 2.5 times larger than the known Saudi Arabian oil reserves, based on heating potential. The CTL process is based on the GTL process after coal gasification. The coal gasification process requires high temperature, high pressure, steam, and oxygen to produce carbon oxides, hydrogen, and methane. The resulting gas may then be converted to syngas and used in the Fischer-Tropsch process. There are also methods for *in situ* processing of coal to liquid fuels. For CTL to be economically competitive, sustained petroleum prices of over $35/bbl are required.

Biodiesel

Biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. The transesterification process converts these bioderived oils and fats into fuel usable in standard diesel engines. Alcohol is used in the transesterification process, typically methanol or ethanol to produce methyl or ethyl esters, respectively. The resulting fuel, after purification to remove remaining fatty acids, alcohol, and glycerins, is a relatively simple mixture consisting of principally 5-10 esters. Biodiesel is governed by several standards, including the international standard EN 14214 and the US ASTM D 6751. These standards cover biodiesel derived from rapeseed oil, vegetable oil, and animal fat and ensure fuel uniformity, including removal of impurities, and specify the allowable sulfur content. The resulting fuel is significantly less toxic than petroleum with a LD50 of >50 mL/kg. Biodiesel also has the considerable advantage of being potentially carbon neutral.

In the U.S., the common raw materials are soybeans and restaurant grease, whereas in Europe, rapeseed is more common. Although vegetable oils may be burned in diesel engines directly, engine modifications are required. Table 3 presents the approximate yields of biodiesel from various feedstocks per acre of land cultivated. Note that actual yields can vary widely. Studies at the National Renewable Energy Laboratory (NREL) have shown that hydroponic algae is the most efficient source of biodiesel, but this source has not been commercialized.

Table 3: Approximate Yields of Biodiesel from Feedstocks per acre

Feedstock	US Gallons/acre
Soybean	40
Rapeseed	110
Mustard	140
Jatropha	175
Palm oil	650
Algae	10,000

Source: http://en.wikipedia.org/wiki/Biodiesel

Biodiesels may be used neat or blended with petroleum products to improve performance. Methyl esters have been shown to improve the cetane number of diesel fuel, and biodiesels generally have higher cetane numbers than conventional diesel fuels. Biodiesel is also a better solvent than diesel, yielding cleaner fuel and engine systems, although this may initially cause difficulties in vehicles previously run on standard diesel as old deposits are dissolved. Biodiesel also has lower emissions of particulate matter, unburned hydrocarbons, and carbon monoxide; see Table 4.

Table 4: Average Biodiesel Emissions Compared to Conventional Diesel

Emission Type	B100	B20
Regulated		
Total Unburned Hydrocarbons	-67%	-20%
Carbon Monoxide	-48%	-12%
Particulate Matter	-47%	-12%
NO_x	+10%	+2%
Non-Regulated		
Sulfates	-100%	-20%*
PAH (Polycyclic Aromatic Hydrocarbons)**nPAH (nitrated PAH's)**	-80% 90%	-13% - 50%***
Ozone potential of speciated HC	-50%	-10%

* Estimated from B100 result

** Average reduction across all compounds measured

*** 2-nitrofluourene results were within test method variability

Source: "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions," October 2002 (EPA420-P-02-001)

Biodiesel fuels are either very low in sulfur or sulfur free, depending on feedstock. Thus they are compatible with catalytic aftertreatment systems and are less prone to sooting. The flashpoint of biodiesel is much higher (>150ºC) compared to diesel (64ºC) or gasoline (-45ºC). Biodiesels are also biodegradable. Biodiesel typically has improved lubricity and ignition quality relative to diesel fuel in the U.S. The Fuel Injection Equipment manufacturers have adopted the use of the HFRR (ISO 12156-2:1998), and recommend that all diesel fuel meet a limit of 460 micron maximum Wear Scar Diameter (WSD). For the HFRR, a lower wear scar indicates better lubricity. As shown in Table 5, addition of biodiesel significantly improves the lubricity of standard Diesel Number 1 and Number 2.

Table 5: Improved Lubricity of Standard Diesel Number 1 and 2 by Adding Biodiesel

Percent Biodiesel	**Number 1**	**Number 2**
	HFRR Scar (microns)	**HFRR Scar (microns)**
0.0	536	671
0.4	481	649
1.0	321	500
2.0	322	355
20.0	314	318
100.0	314	314

"Fuels for Diesel Engines—Diesel Fuel Injection Equipment Manufacturers Common Position Statement", Signed by Delphi Diesel Systems, Stanadyne Automotive Corp., Denso Corporation, and Robert Bosch GmbH, issued June, 2000.

Some challenges related to biodiesels have also been identified. Diesel-engine emissions of nitrogen oxides (NO_x) increase by approximately 1% for every 10 vol% of biodiesel that is blended into diesel fuel. In cold-weather conditions, certain constituent compounds of biodiesel can form crystals in the fuel, resulting in gelling of the fuel. Biodiesel is also more susceptible to oxidative and biological instabilities than conventional diesel fuel, though these issues generally can be avoided by using the fuel promptly or by adding small amounts of stabilizer and biocide.

Ethanol and Other Alcohols

Ethanol has near-term potential to displace oil at a modest scale. If ethanol can be made from cellulosic and lignocellulosic materials, it has mid- to long-term potential as a significant renewable, carbon-neutral fuel source. Ethanol produced from agricultural feedstock is a carbon-neutral fuel. Traditionally, ethanol is produced by fermenting and distilling bio feedstocks that contain sugar or that can be converted to sugar. In the U.S., the primary feedstocks for this process are corn, barley, wheat, and other grains. For these feedstocks, only a small fraction of the plant material is converted to ethanol. Greater efficiency could be obtained if cellulosic material could be converted efficiently to ethanol, opening up the possibility of using such fast growing feedstocks as switch grass or the use of agricultural waste for ethanol production. Current major research efforts are focused on overcoming the challenges of cellulosic ethanol production.

Ethanol is currently finding limited use in U.S. fuels as either an additive to existing fuels or as a blended alternative fuel. Ethanol is blended at 10% or lower as an oxygenated additive, often displacing MTBE, to reduce engine knock. All current gasoline engines function well with blending up to 10%. Lightly modified engines are now commercially available that are able to use up to 85% ethanol blends, so-called E85. Substantial engine modifications are required to utilize pure ethanol because of its very high octane rating, 113, and poor cold start performance. The use of ethanol as an alternative fuel has generated controversy over the energy balance of ethanol production and use.

The supply of ethanol is steadily growing. According to the Renewable Fuels Association, the ethanol industry produced about 3.4 billion gallons in 2004, up from 2.81 billion gallons in 2003, a 21% increase. In February 2005, DOE/EERE's Biomass Energy Program estimated that U.S. agricultural and forest resources could potentially meet 30% of our current transportation fuel needs. (Figure 7, EERE fact sheet). Ethanol currently receives an incentive in the form of a partial exemption from the federal excise tax on gasoline. A 10% blend of ethanol receives a federal tax credit of 5.1 cents per gallon.

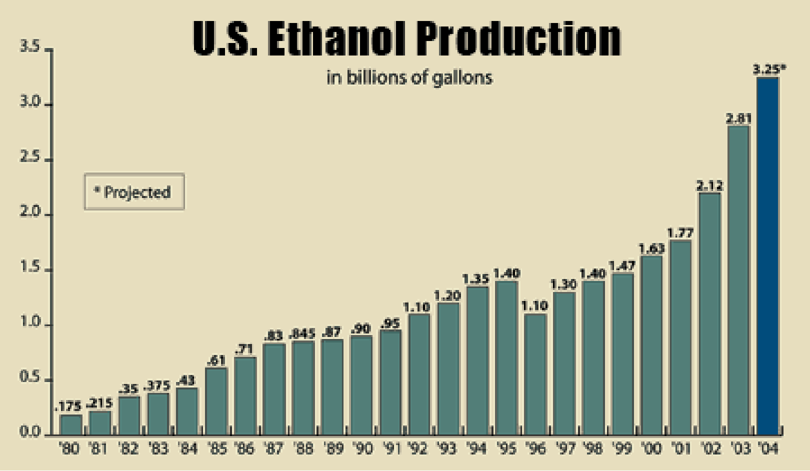

Figure 7. U.S. Ethanol Production (Renewable Fuels Association, "Ethanol Industry Outlook,"http://www.ethanolrfa.org/objects/pdf/outlook/outlook_2005.pdf)

The US government has mandated the increased use of ethanol. The Renewable Fuels Standard (RFS) is a policy that requires an increasing amount of renewable fuels to be used each year. The RFS in the recently passed federal energy bill mandates 7.5 billion gallons of ethanol to be used in the U.S. by 2012. In 2004, the U.S. used 3.4 billion gallons of ethanol. The RFS would streamline the current patchwork of fuel regulations we have across this country. States, regions— and in some cases cities— have different fuel requirements, and the RFS would allow renewable fuels to be used where they make the most sense instead of forcing the production of all these "boutique" fuels.

Ethanol has both advantages and disadvantages as a fuel. Reduced emissions with ethanol use have been documented, for example 20-30% reduction in CO (EERE fact sheet). The higher octane number of ethanol allows its use as an anti-knock agent and may enable the development of high efficiency engines utilizing high compression ratios impractical for gasoline engines. Ethanol does have a lower energy content than gasoline, about 2/3 by volume, reducing vehicle range with current engine technology. Evaporative emissions are also a problem due to its lower molecular weight. Ethanol also cannot be transferred or stored in the existing petroleum infrastructure due to materials compatibility issues. Ethanol is not the only alcohol that is a potential transportation fuel. Recent investigations have shown that butanol may be an even more promising bioderived fuel.

NEW ENGINE TECHNOLOGIES

Substantial efforts are currently under way to improve the efficiency of internal combustion engines (ICEs)—a sure path to reducing both fuel use and greenhouse gas emissions. Research is currently focused on gasoline- and diesel-fueled engines. In the U.S., DOE/EERE FreedomCAR and 21st Century Truck Programs are supporting research and development efforts with mid-term goals of a 50% increase in light-duty engine fuel efficiency and about a 25% increase in heavy-duty engine fuel efficiency, while meeting stringent new emissions regulations that take effect in the 2007-2010 timeframe. These advanced, high-efficiency engine technologies will also be applicable for hybrid-electric vehicles. Fully realized, the engine fuel efficiency improvements would reduce domestic petroleum consumption by an amount equal to one-third of current U.S. petroleum imports—an amount that exceeds all current U.S. imports from Persian Gulf nations. The increased efficiency would also reduce the total U.S. greenhouse-gas emissions by roughly 8%, which is greater than the 7% U.S. first commitment reduction called for under the Kyoto protocol.

The advanced engines rely on various strategies for achieving compression-ignition combustion of dilute fuel-air mixtures, which result in low peak combustion temperatures. These low-temperature combustion (LTC) strategies minimize the formation of NO_x and particulates, while retaining or improving high engine efficiencies associated with conventional diesel engine architectures. There are, however, major challenges for in-cylinder fuel-air mixture preparation and timing and controlling combustion over a wide range of engine speed and load, as well as during engine transients. Especially important with respect to a diversified fuel source future is that research-to-date indicates that fuel properties will influence the operation of these engines to a far greater extent than they affect conventional gasoline and diesel engines on the road today. Moreover, results suggest that tailoring fuel ignition characteristics holds promise for enabling a broader implementation of these high-efficiency combustion strategies over a wide range of operating conditions. Thus, optimization of both the fuel and the engine in a diversified fuel source future will require not only a thorough understanding of engine issues covered by current research efforts, but also an expansion of this understanding to include fuel effects and the development of capabilities to simulate and predict fuels effects on novel engine performance.

LTC strategies currently being implemented include lean diesel and gasoline direct injection (GDI) engines. Diesel engines already dominate the commercial transportation sector in the U.S., and in Europe command more than 50% of new car sales as well. The introduction of low-sulfur diesel fuel in the U.S. will enable the cleaner diesel technologies prevalent in Europe to penetrate the U.S. market. Like diesel engines, GDI engines control load by varying the fuel injected into the cylinder rather than throttling the engine airflow. By avoiding throttle losses, engine efficiency is increased. GDI engines typically use sophisticated engine control systems and operate in three distinct modes depending on engine load: ultra lean for low loads, stoichiometric at moderate loads, and homogeneous at high loads.

Homogeneous Charge Compression Ignition (HCCI) engines are a particularly promising novel LTC strategy and currently the subject of active research. These engines are in some ways a hybrid of diesel and gasoline engine technologies. They have the potential to produce low emissions with diesel-like efficiencies. Other characteristics are quite unique. Like a diesel engine, HCCI relies on compression ignition; the engine charge, however, is prepared to produce a premixed fuel-air charge similar to a spark ignition gasoline engine. Ignition then occurs volumetrically upon compression (Figure 8). Ignition timing is one of the key issues. Unlike diesel engines, which control timing by fuel injection, and spark ignition engines, which control timing by spark, HCCI engine timing must be controlled by charge preparation and the resulting ignition chemistry under compression. Thus, these engines can be thought of as chemistry controlled. Optimizing HCCI combustion or any compression-ignition LTC will require a detailed understanding of these ignition processes.

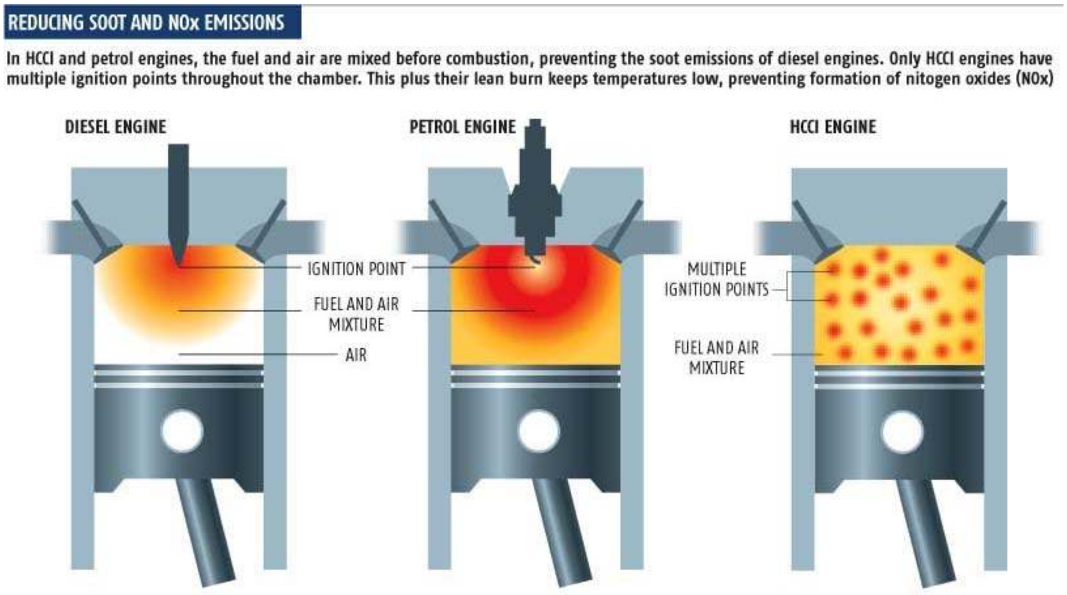

Figure 8. How an HCCI engine reduces soot and NO_x compared to petrol (gasoline) and diesel engines. Source: Department of Mechanical Engineering, University of California, http://www.me.berkeley.edu/cal/HCCI/.

Gas Turbines

Gas turbines are the heart of modern jets, providing the thrust it takes to lift and fly planes in civilian and military applications. In contrast to reciprocating internal combustion engines that are used in automobiles and trucks, the combustion process in gas turbines is continuous. Fuel is injected into the burners and mixed rapidly with air. The hot exhaust propels the actual turbine. Figure 1 shows a cross section of a single burner element of a gas turbine. While some of the complexities that plague reciprocating internal combustion engines are not present in gas turbines, they face their own set of challenges. In particular, operation at very lean (low fuel-air ratio) conditions to reduce the formation of nitrogen oxides puts combustion at the limit where stable combustion can be sustained. In a typical flight pattern, the intake air conditions can change dramatically from dry warm air at ground level to sub-zero temperatures at high altitudes with rain, snow, and hail. Engine reliability is obviously paramount. Engines must operate under all conditions without any degradation of performance. Maintaining combustion stability requires a detailed understanding of the combustion process. This requires an in-depth knowledge of how the nature and quality of the fuel in use affects performance.

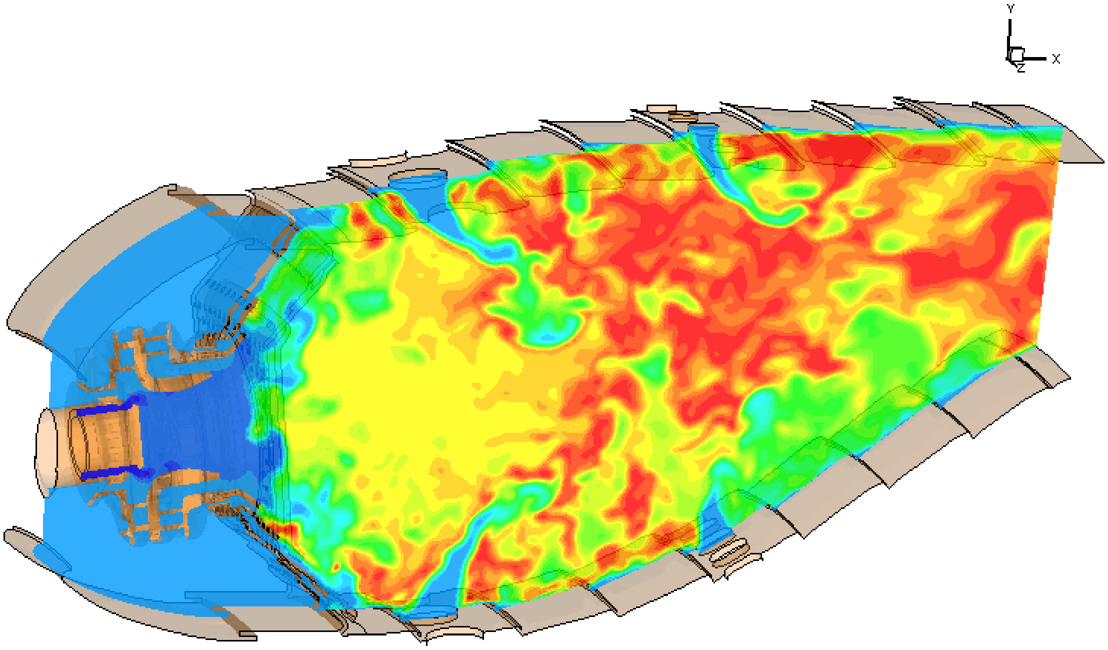

Figure 9. Cross section through a single burner element. A complete gas turbine houses many combustors. All have to work in harmony to ensure the overall stable performance of the entire engine (Image courtesy H. Mongia, GE Aviation).

With the increases in air traffic growth, the International Civil Aviation Organization has set emissions standards that have focused on the reduction of nitrogen oxides. Because current technologies cannot meet projected standards, turbine manufacturers have focused on new technology development.

Twin Annular Premixing Swirler (TAPS) mixer technology is a promising development in low-emission gas turbine technology [Mongia 2006]. As shown in Figure 2, TAPS combines two independently controlled flames. These flames, the pilot and cyclone, are designed for low-power and high-power operations and are merged to optimize the combustion properties. The flame and therefore combustion properties can be influenced by a number of design features, such as the number and orientation of swirlers (which stabilize the flames), the fuel injection device, and the degree of premixing of fuel and air. Engine tests incorporating TAPS technology have demonstrated substantial reduction of nitrogen oxides without increasing hydrocarbon emissions. However, significant research and development efforts are required to provide a detailed understanding of TAPS technology and the potential impact of new and evolving fuel sources on its emissions.

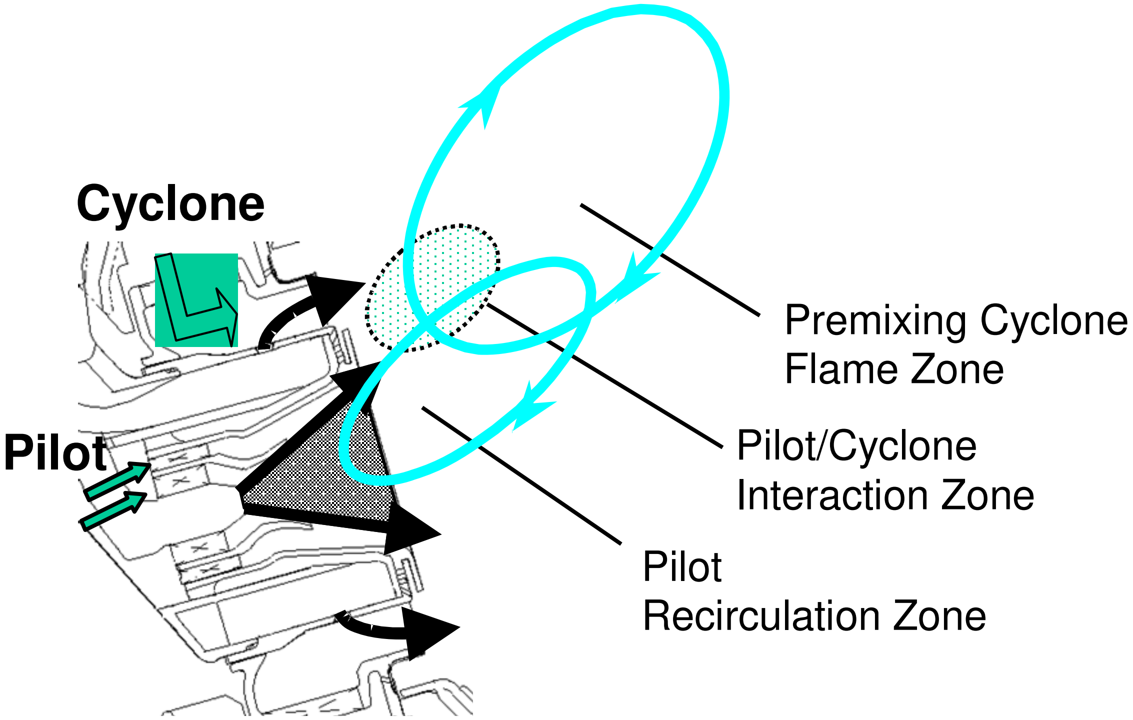

Figure 10. Cross section through a Twin Annular Premixed Swirler (TAPS) burner (Image courtesy H. Mongia, GE Aviation).

R&D CHALLENGES AND OPPORTUNITIES FOR NOVEL FUELS AND NEW ENGINES

Research needed to provide the science foundation for developing the next generation of fuels and engines encompasses the following: fundamental fuel, combustion, and interfacial sciences, more-applied topics related to fuel characterization and fuel-engine interactions, and modeling/simulation tool development. The topics discussed below are critical elements of the science foundation that needs to be developed.

Fuel Ignition Quality

Fuel ignition chemistry is especially important to the operation and control of high-efficiency, compression-ignition engines employing LTC strategies that are currently being developed. Unlike spark-ignition engines, where ignition timing is controlled by a spark, or diesel engines, where ignition occurs shortly after the start of fuel injection, chemical-kinetic processes occurring over a relatively long period of time play a prominent role in determining the timing of combustion in LTC engines. Optimal fuel ignition characteristics for these emerging high-efficiency engines are unknown and are likely to be different for different engine applications (e.g., light-duty *versus* heavy-duty engines).

A significantly improved understanding of the ignition and combustion chemistry of a wide range of potential fuels, including the chemical interactions that will occur in complex fuel mixtures, must be developed. A specific challenge is the “cool flame” first-stage ignition chemistry. The current understanding of cool flame ignition chemistry fails at the high pressures relevant to engines. Development of specialized experimental capabilities and diagnostics to directly investigate the temporal evolution of igniting mixtures would provide unique and invaluable insight into the core technical questions surrounding fuel-ignition chemistry. These investigations should also include both single-component fuels and complex real fuel mixtures. The challenges of conducting this research at relevant pressures and temperatures will be substantial. New fundamental studies in pressure diagnostics, basic spectroscopy, and optics may be needed to facilitate experiments under these conditions, and new computational chemistry and kinetics will be required to successfully understand and model these processes.

Emission and Deposit Formation

LTC at light engine loads can result in hydrocarbon (HC) emissions (e.g., aldehydes), and the use of fuel-air mixture stratification in conjunction with LTC can lead to particulate formation. Furthermore, deposit formation or fuel coking on injector tips can seriously degrade engine performance. Mitigating and avoiding these processes when using future fuels will require an improved understanding of the effects of fuel composition on the gas-phase and/or heterogeneous chemistry involved. Probing the interfacial chemistry of the heterogeneous processes at temperatures and pressures relevant to engines will be particularly challenging, because these conditions are not generally accessible by traditional surface science methods. Design of new experimental approaches that can probe the chemistry at these challenging interfaces would be a key to understanding the effects of fundamental fuel characteristics on interfacial processes. Computational prediction of the relevant heterogeneous chemistry is a formidable challenge that may require new theoretical developments. A thorough fundamental understanding of the interfacial chemistry is needed to permit predictive modeling of these important processes.

Fuel Performance in Engines

Current research on advanced engines is focused on using laser-based and optical diagnostics to provide an understanding of fuel injection, fuel-air mixture preparation, combustion, and emissions processes in engines employing LTC strategies, and how various engine parameters affect these processes. This research needs to be expanded to include fuel property effects encompassing the range of future fuel options. Limited results obtained to date suggest that fuels other than gasoline and diesel may enable more optimal and robust use of LTC strategies. A particularly important outcome of this research will be the definition of optimal fuel characteristics for emerging engines, a definition that may differ for heavy- and light-duty engines. Light-duty engines (used in automobiles, pickups and SUVs) typically run at higher speeds and lower loads than heavy-duty engines (used in trucks), and spray-wall or spray-flow interactions are more pronounced. Current research programs focus on fuel property effects on heavy-duty engines. A program focused on fuel effects on light-duty engines is needed. Light-duty engines consume about 45% of the total oil used in the U.S.

Diagnostics and Sensors for Engine Control

The challenges of combustion timing in the new LTC compression-ignition engines may require implementation of novel real-time strategies to adjust compression ratio, valve timing, intake pressure, or other operating conditions. These adjustments will need rapid feedback on in-cylinder conditions. New robust sensing methods may be required to accomplish these measurements, and research into fundamental spectroscopy, optics, and diagnostics may be required.

Ethanol-Fueled Engines

Ethanol is currently either used in conventional spark-ignition engines blended with gasoline in small quantities (<10%) or in fuel-flexible, spark-ignition engines operating on ethanol/gasoline blends ranging from 0-85% ethanol. Neither of these options provides the most efficient use of ethanol, because the engines are limited by the ignition and combustion characteristics of gasoline. Because of ethonol's high octane number, there is considerable potential for enhancing the fuel efficiency of engines operating on ethanol—offering the possibility of overcoming the 30% energy density disadvantage of ethanol relative to gasoline. To make use of this potential, additional research is needed to support the development of engines optimized for ethanol-based fuels that overcome challenges such as the poor cold start characteristics of ethanol.

Science-Based Test Metrics for Fuel Characterization

The current metrics for characterizing fuels were developed for gasoline and diesel fuel. Their relevance to fuels from diversified sources is unknown, especially for fuels for use in engines employing LTC. For example, octane and cetane numbers, which are used to characterize the ignition properties of gasoline and diesel fuels, are inadequate for describing the fuel ignition properties necessary for reliable operation in an LTC engine. Science-based test metrics for characterizing ignition quality, chemical stability, volatility, viscosity, lubricity, coking characteristics, etc., that are applicable to a wide range of fuels, would be invaluable to fuel and engine producers.

CONCLUSION

The U.S. energy picture is evolving for the first time in many decades. The traditional sources of oil are becoming more expensive, are less plentiful, and are subject to geopolitical tensions as well as significant environmental impacts. New competitive fuel sources are emerging, but they are not identical to the fuels they may replace. These new fuels pose challenges for existing engine technologies and opportunities for new technologies. At the same time, an evolution of engine designs promises greater efficiency and lower environmental impact. These new technologies may benefit from the chance to tailor these new fuels to their needs. A comprehensive scientific understanding of the combustion of new fuels under conditions relevant to novel engines will enable their optimal co-development and application.

REFERENCE

Mongia, H. C. 2006. "GE Aviation Low Emissions Combustion Technology Evolution," *LTTG Technology Review*, London, March 20-24, 2006.

APPENDIX 2 – WORKSHOP PARTICIPANTS

WORKSHOP CO-CHAIRS

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APPENDIX 3 – WORKSHOP PROGRAM

Workshop on Basic Research Needs For Clean & Efficient Combustion of
21st Century Transportation Fuels
October 29 – November 1, 2006
Sheraton National Hotel, 900 S. Orme Street, Arlington, Virginia 22204

Agenda for Plenary Sessions

Pre-Meeting– Monday, October 29, 2006		
6:00 am – 8:00 am	Strategy discussion over working dinner	Co-chairs, panel leads, core writers, BES program managers

Plenary Opening Session – Monday, October 30, 2006		
7:30 am – 8:30 am	Registration & Continental Breakfast	
8:30 am – 8:45 am	Welcoming remarks	Pat Dehmer, DOE BES
8:45 am – 9:00 am	Workshop Charge	Eric Rohlfing/Andy McIlroy/Greg McRae
9:00 am – 9:30 am	US/ DOE Technology Perspective	James Eberhardt, DOE EE/RE
9:30 am – 10:00 am	Industry Perspective	Hukam Mongia, GE
10:00 am – 10:30 am	Break	
10:30 am – 11:00 am	Science Challenges	Charlie Westbrook, LLNL
11:00 am – 11:20 am	Review agenda/process/output for the workshop	Greg Mc Rae/Andy McIlroy
11:20 am – 11:40 am	Breakout group introduction/coordination	Panel Leads
11:40 am – 12:00 noon	Break for working buffet lunch for all	
12:00 noon – 1:00 pm	Working Lunch Talk - Energy Policy Issues	David Greene, ORNL

WORKSHOP ON

BASIC RESEARCH NEEDS FOR CLEAN & EFFICIENT COMBUSTION OF 21ST CENTURY TRANSPORTATION FUELS

October 30 – November 1, 2006

Monday, October 30, 2006

Breakout Panels Start (***AFTERNOON SESSION***)

Time	Fuels Utilization	Cross-Cutting Science	Novel Combustion
1:00-3:00	Full Fuels Panel Plenary Session - Five "invited" speaker presentations **EAST #1**	Full Cross-cut Panel Plenary Session - Topic: Overview/discussion **NORTH #1**	Three subpanels - each with overview followed by initial discussion topic of Mixture Preparation
	Smith - Intro, fuel geography, breakout expectations	Three 20-30 min presentations, with discussions encouraged	Novel Subpanel 1 – HCCI/GDI with overview by Sick followed by session discussion topic **SOUTH BALLROOM**
	TBD - Oil shale specifics, profiles, special features	Leone - Emerging Techniques for Fundamental Chemical Physics	Novel Subpanel 2 - LTC with overview by Reitz followed by session discussion topic **MEZZ #2**
	Fairbridge - Oil sands specifics, profiles, special features	Klippenstein - New Challenges in Combustion Kinetics & thermo chemistry	Novel Subpanel 3 – GT/μComb with overview by Dunn-Rankin followed by session discussion topic **MEZZ #3**
	Boehman - Biodiesel fuels, profiles, special features	Rutland - Computation and Simulation for Advanced Combustion	
	TBD - How fuels can be important, some experience		
3:00 - 3:30	**Break**		
	Subpanel Breakouts		
3:30 - 5:00	Fuels Subpanel 1 - Theory & modeling **EAST #1**	Cross-cut Subpanel 1 Chemistry - Topic: Mixing and ignition **NORTH #1**	Novel Subpanel 1 – HCCI/GDI- Topic: Ignition, combustion, pollutant formation, reacting flows **SOUTH BALLROOM**
	Fuels Subpanel 2 - Laboratory & scaling experiments **EAST #2**	Cross-cut Subpanel 2 Diagnostics - Topic: Mixing and ignition **NORTH #2**	Novel Subpanel 2 – LTC - Topic: Ignition, combustion, pollutant formation, reacting flows **MEZZ #2**
		Cross-cut Subpanel 3 Modeling - Topic: Mixing and ignition **NORTH #3**	Novel Subpanel 3 – GT/μComb - Topic: Ignition, combustion, pollutant formation, reacting flows **MEZZ #3**

Breakout Panels Continue ***(EVENING SESSION)***

Time	Fuels Utilization	Cross-Cutting Science	Novel Combustion
6:00 - 7:00	**Working Dinner for all participants and panel leads, executive committee meeting**		
	Subpanel Breakouts Continue		
7:00 - 9:00	Fuels Subpanel 1 - Theory & modeling **EAST #1**	Cross-cut Subpanel 1 Chemistry - Topic: Fully-developed turbulent combustion **NORTH #1**	Novel Subpanel 1 **CHEMISTRY** - Topic: LTR, ignition, pollutants **SOUTH BALLROOM**
	Fuels Subpanel 2 - Laboratory & scaling experiments **EAST #2**	Cross-cut Subpanel 2 Diagnostics - Topic: Fully-developed turbulent combustion **NORTH #2**	Novel Subpanel 2 **SCALAR MIXING & REACTING FLOW** - Topic: Sprays/Mixture prep., lean-limit combustion stability, ignition stability **MEZZ #2**
		Cross-cut Subpanel 3 Modeling - Topic: Fully-developed turbulent combustion **NORTH #3**	Novel Subpanel 3 **TOOLS** - Topic: Diagnostics, modeling closely coupled to experiments, comprehensive, first principles design capable models **MEZZ #3**
	Panel leads construct brief report for Tuesday morning	Panel leads construct brief report for Tuesday morning	Panel leads construct brief report for Tuesday morning

Tuesday, October 31, 2006

Interim Reports and Breakout Panels Continue ***(MORNING SESSION)***

Time	Event		
7:00 – 8:00	***Continental Breakfast***		
	Fuels Utilization	**Cross-Cutting Science**	**Novel Combustion**
8:00 - 8:20	**Interim report plenary session: Brief report from Fuels Utilization**		
8:20 - 8:40	**Interim report plenary session: Brief report from Novel Combustion**		
8:40 – 9.00	**Interim report plenary session: Brief report from Cross-cutting Science**		
9:00 -10:00	**Subpanel Breakouts Continue**		
	Fuels subpanel 1: Theory and modeling. Discussions and formulation of PRD topics **EAST #1**	Cross-cut Subpanel 1 Chemistry - Topic: Burnout & pollutant formation **NORTH #1**	Novel Subpanel 1 Chemistry - Topic : LTR, ignition, pollutants **SOUTH BALLROOM**
	Fuels subpanel 2: Laboratory and scaling experiments. Discussions and formulation of PRD topics **EAST #2**	Cross-cut Subpanel 2 Diagnostics - Topic: Burnout & pollutant formation **CONCOURSE #1**	Novel Subpanel 2 Scalar mixing & reacting flow – Topic: Sprays/mixture prep, lean-limit combustion stability, ignition stability **MEZZ #2**
		Cross-cut Subpanel 3 Modeling - Topic: Burnout & pollutant formation **CONCOURSE #2**	Novel Subpanel 3 Tools – Diagnostics, modeling closely coupled to experiments, comprehensive, first principles design capable models **MEZZ #3**
10:00-10:30	**Break**		
10:30-12:00	Fuels subpanel 1: Theory and modeling. Discussions and formulation of PRD topics **EAST #1** Fuels subpanel 2: Laboratory and scaling experiments. Discussions and formulation of PRD topics **EAST #2**	Full Panel - Topic: Reporting/discussions, interactions with other panels **NORTH #1**	Full panel - Topic: Discussions and fill out PRD and other document templates for out brief **SOUTH BALLROOM**
12:00-1:00	**Working Lunch (buffet for all provided)**		

Fill out document templates ***(AFTERNOON SESSION)***

Time	Fuels Utilization	Cross-Cutting Science	Novel Combustion
1:00-2:30	Full panel - Topic: Discussions and fill out PRD and other document templates **EAST #1**	Full panel - Topic: Discussions and preparation of PRDs **NORTH #1**	Full panel - Topic: Discussions and fill out PRD and other document templates **SOUTH BALLROOM**
2:30 - 2:45	**Break**		
2:45-4:00	Full panel - Topic: Discussions and fill out PRD and other document templates **EAST #1**	Full panel - Topic: Discussions and preparation of PRDs **NORTH #1**	Full panel - Topic: Discussions and fill out PRD and other document templates **SOUTH BALLROOM**
4:00- 5:00	Panel leads/co-chairs meet		

Working Dinner ***(EVENING SESSION)***

Time	Event
6:00 – 7:30	***Working dinner (chairs, panel leads, BES management only)***
	REMAINING PARTICIPANTS - ON OWN FOR DINNER

Wednesday, November 1, 2006

Report outs from breakout panels ***GENERAL SESSION***

Time	Event
7:00 - 8:00	**Continental Breakfast**
8:00 - 8:15	Chairs intro
8:15 - 8:35	Report out of PRDs from Fuels Panel
8:35 - 8:55	Discussion of Fuels PRDs
8:55 - 9:15	Report out of PRDs from Novel Combustion Panel
9:15 - 9:35	Discussion of Novel Combustion PRDs
9:35 - 9:55	Report out of PRDs from Cross-cutting Science Panel
9:55 - 10:15	Discussion of Cross-cutting PRDs
10:15 -10:30	**Break**
10:30 - 11:30	Overall discussion of PRDs
11:30 - 12:00	General wrap up by chairs
12:00 - 1:00	***Working Lunch (co-chairs, panel leads, core writers, BES program managers only)***

Report writing (co-chairs, panel leads, and core writers only) ***(AFTERNOON SESSION)***

Time	Event
1:00 - 6:00	Report Drafting **Mezz #3**

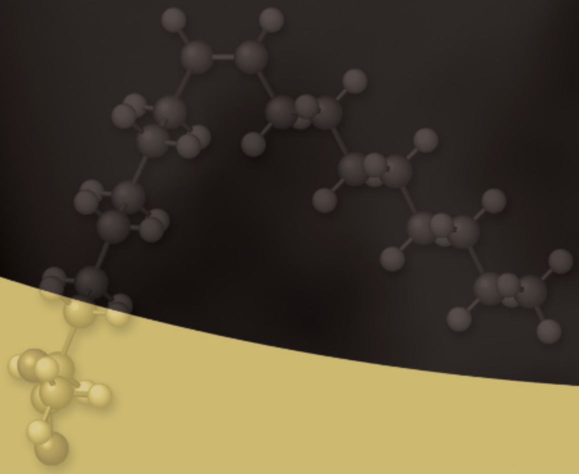
Report writing continues (co-chairs, panel leads, and core writers only)

Time	Event
6:00-7:30	***Working Dinner (co-chairs, panel leads, core writers, BES program managers only)***
7:30-10:00	Report Drafting **Mezz #3**

Thursday, November 2, 2006

Post Meeting

Time	Event	
7:00–8:00	***Continental Breakfast***	
8:00-12:00	Report Drafting and Confirmation of Writing Assignments/Deadlines	**Mezz #3**
12:00	**BOXED LUNCH**	



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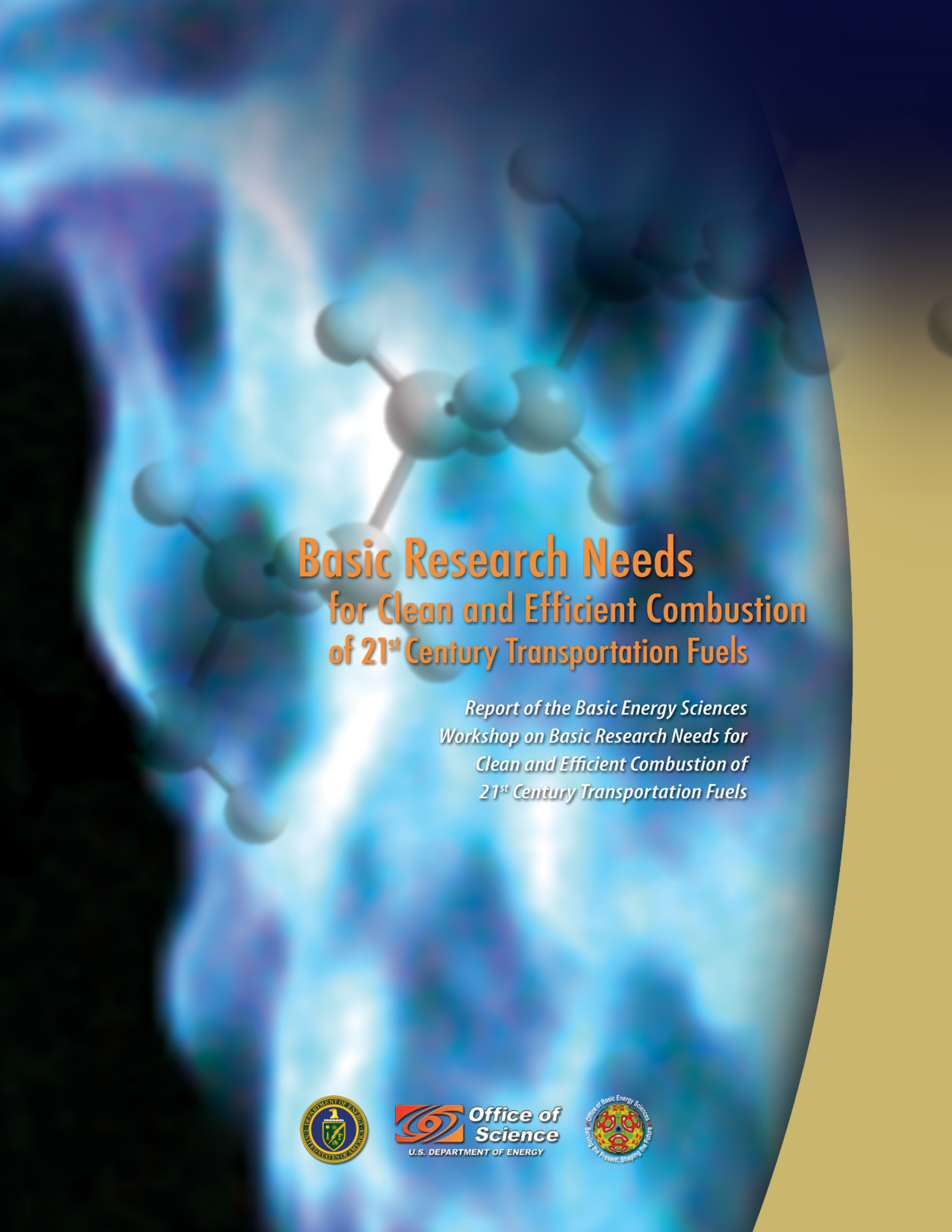

Basic Research Needs
for Clean and Efficient Combustion of 21st Century Transportation Fuels

Report of the Basic Energy Sciences
Workshop on Basic Research Needs for
Clean and Efficient Combustion of
21st Century Transportation Fuels

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