Workshop on Combustion Simulation Databases for Real Transportation Fuels
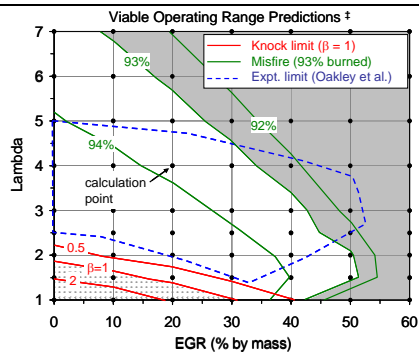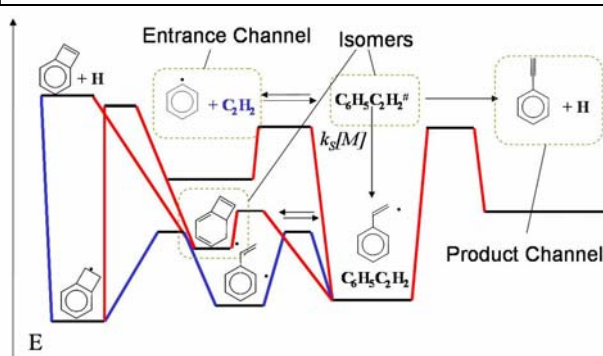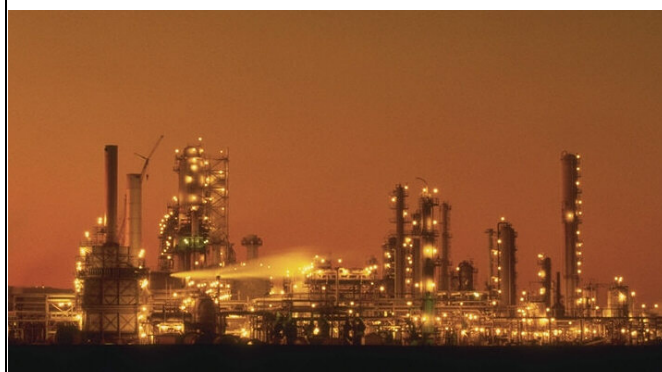

September 4-5, 2003
National Institute of Standards and Technology
Gaithersburg, Maryland

Cover Page Figures:

- <u>Upper left:</u> Civilian aircraft flying over a city.
- <u>Upper right:</u> Night time view of a refinery that produces transportation fuels.
- <u>Lower Left:</u> Potential energy surface for addition of phenyl radical to acetylene, showing some isomerization reactions and product channels. *Adapted from H. Richter, MIT.*
- <u>Lower right:</u> Graph plotting the predicted and experimental knock and misfire limits for a homogeneous charge compression ignition (HCCI) test engine. *Adapted from W. Green and P. Yelvington, MIT.*

Workshop on Combustion Simulation Databases for Real Transportation Fuels

Report of the workshop conducted at the National Institute of Standards and Technology, Gaithersburg, MD, September 4-5, 2003

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

Overview

A workshop entitled *"Workshop on Combustion Simulation Databases for Real Transportation Fuels"* was held on September 4-5, 2003 at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. The workshop was organized in response to the recognized overwhelming importance of energy to the United States economy, the increasing need to optimize combustion processes for efficiency and pollution minimization, and to address the increasing role of computer simulations in all areas of design. Approximately sixty scientists and engineers from industry, academia, and government (civilian and military) attended the workshop.

The economic, environmental, and health benefits accruing to the nation from improved combustion processes for transportation are enormous and well-recognized. Technologically-feasible advanced engine technologies would operate more efficiently, saving the nation at least $50B/year in fuel costs, and reducing substantially the global warming load associated with CO_2 production. Health and environmental benefits estimated at ~ $62B/year would accrue through reductions of health problems (*e.g.*, pollution-induced asthma and heart disease), crop damage, and visibility enhancements, due to the lower chemical and particulate emissions from advanced engines.

For these benefits to be realized, it is necessary to efficiently translate our underlying scientific understanding to technological development. Future engines will require stringent control of the combustion environment, which is determined by complex interactions of the combustion chamber with the chemical composition, physical properties, and combustion properties of fuel. The overall aim of the present workshop was to create a forum that would help NIST and the combustion community to assess the data needs of studies involving transportation fuels and to recommend plans for developing reference databases and chemical kinetic models. These databases and models will enable the combined application of chemical kinetics and computational fluid dynamics (CFD) programs to simulate combustion processes realistically. The target applications were envisioned to be real liquid transportation fuels, which we refer to hereafter as "real fuels," and include aviation, diesel, and gasoline fuels.

Some specific objectives were 1) to evaluate the benefits and feasibility of a cooperative program that focuses upon the combustion of real fuels; 2) to evaluate the benefits and feasibility of using surrogate mixtures and modeling thereof to realistically describe the important characteristics and behavior of real fuels; 3) to broadly assess the data needs; 4) to assess the community's willingness to work together to address the data and information needs for model-based design and; 5) to assess how to make better use of knowledge management structures to facilitate information exchange and more rapid progression from the laboratory to applications.

The following section outlines the findings of the Workshop as perceived by NIST.

Key Conclusions

- Simulations are poised to benefit the design of real combustion devices.
- The set of evaluated fundamental data for use in these simulations is incomplete.
- Major gaps exist in the understanding of combustion chemistry specific to real fuels.
- Mixtures comprised of compounds from six chemical classes can be used to formulate a spectrum of useful surrogate fuels.
- A complete description of the combustion chemistry for real fuels would be prohibitively large and, thus, reduced chemical kinetic models must be developed.
- The lack of information exchange standards is a major barrier to advancement.
- Strong collaboration is imperative and requires a suitable infrastructure.
- The combustion community wishes to develop a research roadmap that focuses its efforts for advancing combustion research.

Workshop Findings

In broad terms the outcomes may be grouped as those related to the existence and quality of relevant data and models (items 1-5) and those related to the need for a better infrastructure for sharing, analyzing, and comparing data and models (items 6-8).

1) Computational simulations incorporating realistic fluid dynamics and chemistry are poised to be of great benefit in the design of real combustion devices (*e.g.*, internal combustion engines) that are vital to the nation's energy and environmental goals. This new simulation capability may also accelerate the development of novel energy technologies, *e.g.*, hydrocarbon reforming for hydrogen fuel production.

2) The dearth of critically evaluated thermochemical, kinetic, and transport data severely hampers the development of predictive chemical models and simulations for combustion as well as other technologies. The published literature contains a proliferation of chemical kinetic models for combustion at different conditions. Although they may fit a set of results, they are a reflection of the science at that time; hence, they may now be incorrect, inconsistent, or in conflict with other established models and are definitely not extensible.

   i.   Much of the thermochemical, thermophysical, and reaction rate data used in chemical kinetic modeling has not been compared to evaluated data, nor systematically checked for self-consistency.

   ii.   There is no generally-accepted set of results on experimental systems that can be used to inter-compare and refine chemical kinetic models.

   iii. Essentially no generic software tools are available for comparison and evaluation of combustion models.

iv.   Evaluation of the data should be a collaborative project among a wide range of experts in the area of chemical kinetics.

3) There are major gaps in our knowledge of the combustion chemistry of real liquid transportation fuels. This is because real fuels involve large, complex molecules, and because real fuels can contain hundreds of constituents.

i.   Because large molecules undergo a sequential reduction in size during combustion, simulations of real fuels must include and will be built around existing chemical kinetic models that detail the chemistry of small (C1 to C3) hydrocarbons.

ii.   "Small molecule" chemistry must be extended to include the relevant chemistry of the larger species present in transportation fuels. These include pyrolytic cracking and oxidation reactions that convert large molecules to small, and several classes of condensation reactions that govern the growth of polycyclic aromatic hydrocarbons (PAHs) and soot. Although some reasonable estimations of the chemistry are possible with the currently available knowledge, benchmark experiments are needed to validate these estimations, to provide insight into chemistry not yet accessible by theory, and to provide high accuracy values for the most crucial reactions.

iii.   An understanding of the kinetics and chemical kinetic models of fuel combustion is crucial to the continued development and improvement of key emerging technologies (*e.g.*, homogeneous charge compression ignition (HCCI) engines).

4) There is some consensus on how to formulate surrogates for real fuels that will aid experiments and computational simulations:

i.   Six chemical classes were identified that are presumed to encompass the minimal set of constituent types necessary to describe the hydrocarbon chemistry of real transportation fuels. For the six classes there is a (reasonable) consensus as to specific model compounds whose combustion chemistry, if reliably determined, would advance the simulation of the combustion of real fuels.

ii.   There is no one surrogate mixture that will address all the testing and research needs for diesel, gasoline, and jet fuels or apply to all of the numerous different combustors of interest, but surrogates for all fuels could reasonably consist of distinct formulations of the six model compounds.

> **Workshop Consensus for Chemical Constituents of Surrogate Fuels**
>
> - **Iso-paraffins:** Iso-octane
> - **Normal paraffins:** Heptane, Hexadecane, Decane
> - **Single ring aromatics:** Toluene, Xylenes
> - **Cyclo-paraffins:** Methylcyclohexane
> - **Olefinic species:** 1-Pentene
> - **Multi-ring aromatics:** 1-methylnapthalene

iii.   The cost of pure-compound-based surrogate fuels remains a serious concern to researchers and engine developers who require large quantities of fuel. Nonetheless, it was generally believed that surrogate fuels would be useful for testing and modeling purposes and would aid in our understanding of the related "reference fuels" commonly used in engine design and specification.

iv.   In addition to the hydrocarbon surrogates, surrogates for sulfur containing impurities, oxygenate additives, and anti-knock agents may be needed.

5)   The combustion problem is multi-scale, ranging from atoms and molecules to particulates and devices (*e.g.*, engines and turbines). Successful treatment of combustion problems is necessarily multi-disciplinary.

i.   Accurate chemical kinetics models that reproduce the combustion characteristics of real devices need to be quite complex and this requirement makes them more costly to compute.

ii.   To produce accurate results, CFD simulations need to incorporate accurate kinetic rate coefficients; however, current CFD codes can only incorporate a small subset of the total reaction set.

iii.   The current best practice is to create reduced chemical kinetic models that capture the essential features of the combustion problem being studied. Each reduced chemical kinetic model needs to be derived from a larger chemical kinetic model that is validated against experimental data sets collected over a broad range of conditions.

iv.   Producing a chemical kinetic model for combustion requires access to accurate thermodynamic and chemical kinetic data for many chemical species. It is a practical impossibility to measure or compute all of the fundamental data required. Clearly an approach that focuses the greatest effort on the most important chemical species and their reactions is appropriate. Likewise, model parameters shown by mathematical analysis to be less important are permitted to have larger uncertainties and may be estimated.

Chemical Kinetic Models of Combustion Become Complex as "Real Fuels" are Approached

Model	# Species	# Reactions
$O_2 + H_2$	8	27
O_2 + Methane	34	210
O_2 + iso-Octane	860	3600

6)   The absence of a commonly understood and accepted terminology for describing and quantitatively specifying combustion chemistry is a significant barrier to realizing the benefits of computer-aided design and inhibits the sharing of information among researchers.

i.   Even in areas for which there is little dispute as to the physical or chemical meaning of the information, there are no accepted standards for the exchange of the required information.

ii.   At present there are no commonly understood and agreed upon descriptors for the information required to quantitatively represent a chemical kinetic model and no information exchange standards that would allow facile and reliable exchange and widespread use of combustion simulation models.

7) The current absence of strong and effective collaboration, limited at least partly by the lack of an appropriate infrastructure for collaboration, is a major impediment to reaching the goal of simulation-based combustor design. This collaboration will require full access to a common set of data, models, benchmark test information, and a wide variety of tools.

i.   There was general agreement that internet-based collaboration would be valuable and widely used. The goal of the Collaboratory for Multi-Scale Chemical Science (CMCS) to develop an adaptive informatics infrastructure to enhance data management, data sharing, and scientific collaboration was broadly supported.

ii.   There was also general agreement that the establishment of a commonly accessible repository of data validated by consensus of the community would be beneficial.

iii.   NIST was cited as a logical center for such operations, and the attendees were very interested in NIST playing a central role in facilitating the provision of data required for the collaboration.

8) There is need for the creation of a carefully planned roadmap by the combustion community. The roadmap should establish well-defined goals and a means to achieve those goals as a community.

WORKSHOP REPORT

I. Introduction

On September 4th and 5th the NIST Chemical Science and Technology Laboratory hosted the *"Workshop on Combustion Simulation Databases for Real Transportation Fuels"* at its Gaithersburg, MD campus. Approximately sixty expert scientists and engineers, drawn evenly from industry, academia, and government (including military), attended the meeting. The objective of the workshop was to assist NIST and the combustion community in formulating a plan for developing databases and chemical kinetic models for simulating the combustion of real liquid fuels. The workshop was organized in response to the recognized overwhelming importance of energy to the United States economy, the increasing need to optimize combustion processes for efficiency and pollution minimization, and to address the increasing role of computer simulations in all areas of design. Modern computational fluid dynamics (CFD) codes are of great potential value because they may accelerate research and engineering projects that will design novel, efficient, less polluting combustion devices and improve older ones.

Statistics provided by the Energy Information Administration[1] (EIA) indicate that the United States consumed 29 trillion kilowatt-hours (29×10^{12} kW-h) of energy during 2002. Of this total, 86 % was derived from fossil fuels, 8 % from nuclear electric sources, and 6 % was classified as renewable energy. The EIA predicts that combustion of fossil fuels will remain the primary source of energy in the U.S. for decades to come. Domestic fossil fuel sources of energy are petroleum products (45 %), natural gas (28 %), and coal (27 %). The NIST workshop concentrated on technology that can improve the combustion of liquid petroleum fuels in turbines and engines, which are used mainly by the transportation sector of the economy. These power sources are also used in construction and stationary power equipment.

Since energy consumption is a local on-demand activity, the associated consequences of fuel combustion cannot be exported. The related economic, environmental, and health effects impact the entire population of the United States. In 2000 industry and consumers spent $272B for transportation fuels.[2-4]

Liquid Transportation Fuel Usage (2000)		
Sector	10^9 liter/yr[a]	Cost[b]
Gasoline	488	$191.7B
Diesel	141	56.8B
Jet Fuel	101	23.6B
Aviation Gas	1	0.4B

Source:
Derived using DOE source data from:
[a] Ref. 2.
[b] Ref. 3.
NOTE: Ave. 2000 domestic crude oil price: $26.73/barrel (Ref. 4).

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[1] Energy Information Administration, *Table 1.3 Energy Consumption by Source*, <u>Monthly Energy Review</u>, available on-line: http://www.eia.doe.gov/emeu/mer/overview.html.

[2] Energy Information Administration, <u>Annual Energy Review</u>, *Table 5.12c Petroleum Consumption: Transportation Sector and End-Use Total, 1949-2002,* available on-line: http://www.eia.doe.gov/emeu/aer/txt/stb0512c.xls and http://www.eia.doe.gov/emeu/aer/petro.html.

In industry, energy costs are a major concern in production processes. Increased efficiency translates directly to greater economic competitiveness in the global marketplace. Even very small improvements in efficiency will result in vast savings. For example, the homogeneous charge compression ignition (HCCI) engine, which is one of several advanced concepts under development, offers a 33 % improvement in peak combustion efficiency over current spark-ignition engines.[5-6] Calculated with 2000 average fuel prices,[4] the emergence of such engines, enabled by a thorough understanding their combustion chemistry,[6] could potentially reduce annual domestic automobile fuel costs by $50B/year.

Improved efficiency would lower CO_2 emissions, which are strongly linked with global climate change and may be expected to see increasing national and international scrutiny and regulation. For example, the current voluntary reporting[7] of greenhouse gases (GHG) under section 1605(b) of the Energy Policy Act of 1992[8] is widely expected to lead to mandatory regulations and international trading of GHG credits.

The costs to the nation associated with environmental effects related to combustion are large. In its recent report to congress on the benefits and costs of the clean air act, EPA analysis suggests a net benefit to the nation of approximately $62B/year resulting from air quality improvement, largely through the reduction of pollutants associated with the combustion of fossil fuels.[9]

Particulate matter produced by transportation engines is a major concern due to its possible health and environmental consequences. Several studies that have established[10-14] a link between particulate matter and asthma and cardiovascular disease. These adverse health effects result

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[3] Energy Information Administration, *Table 5. Transportation Sector Energy Price and Expenditure Estimates, Selected Years 1970-2000, United States*, State Energy Statistics, available on-line: http://www.eia.doe.gov/emeu/states/sep_prices/tra/pr_tra_us.html.

[4] The average domestic crude oil price during 2000 was $26.73/barrel: Energy Information Administration, *Table 9.1 Crude Oil Price Summary*, Monthly Energy Review, Mar 2001 (http://tonto.eia.doe.gov/FTPROOT/multifuel/mer/00350103.pdf and http://www.eia.doe.gov/mer).

[5] K. Epping, S. Aceves, R. Bechtold, J. Dec, *The Potential of HCCI Combustion for High Efficiency and Low Emissions*, Society of Automotive Engineers, Inc. (Warrendale, PA), SAE Paper 2002-01-1923.

[6] Science & Technology Review, Apr 2004, (http://www.llnl.gov/str/April04/April04.html).

[7] See for example: Energy Information Administration, *Voluntary Reporting of Greenhouse Gases 2002*, DOE/EIA-0608(2002), (Washington, DC, January 2004), (http://www.eia.doe.gov/oiaf/1605/vrrpt/index.html).

[8] *Energy Policy Act of 1992, Section 1605, National Inventory and Voluntary Reporting of Greenhouse Gases*, Voluntary Reporting of Greenhouse Gases Communication Center (http://www.eia.doe.gov/oiaf/1605/policy.html).

[9] *The Benefits and Costs of the Clean Air Act 1990 to 2010: EPA Report to Congress*, Table ES-1 (EPA central value converted to year 2000 dollars), EPA-410-R-99-001, U.S.EPA, 1999 (http://www.epa.gov/oar/sect812/).

[10] M. Lipsett, S. Campleman, *Occupational Exposure to Diesel Exhaust and Lung Cancer: A Meta-Analysis*, American Journal of Public Health **89**, 1009-1017 (1999).

[11] W. Stober, U. R. Abel, *Lung Cancer Due to Diesel Soot Particles in Ambient Air? A Critical Appraisal of Epidemiological Studies Addressing This Question*, International Archives of Occupational and Environmental Health **68**, S3-S61 Suppl. S (1996).

[12] A. Peters, D.W. Dockery, J. E. Muller, and M. A. Mittleman, *Increased Particle Air Pollution and Triggering of Mycardial Infarction*, Circulation **103**, 2810-2815 (2001).

[13] S. Boland, A. Baeza-Squiban, F. Marano, *Respiratory Toxicity of Diesel Exhaust Particles: Cellular and Molecular Mechanisms*, M S-Medecine Sciences **17**, 596-603 (2001).

[14] Environmental Protection Agency 40 CFR Part 50 [AD–FRL–5725–2] RIN 2060–AE66, *National Ambient Air Quality Standards for Particulate Matter*, Federal Register **62** (No. 138), Jul 18, 1997, 38652-38760 (http://homer.ornl.gov/oepa/rules/62/62fr38652.pdf).

from deposition and subsequent actions of particles in the thoracic (tracheo-bronchial and alveolar) portions of the lower respiratory tract. Particulates and associated subsequent chemistry also have deleterious effects[15] on vegetation and eco-systems, visibility, and man-made materials used in construction.

Acting on these find-ings, the United States Environmental Protec-tion Agency (EPA) has issued National Ambient Air Quality Standards (NAAQS) for
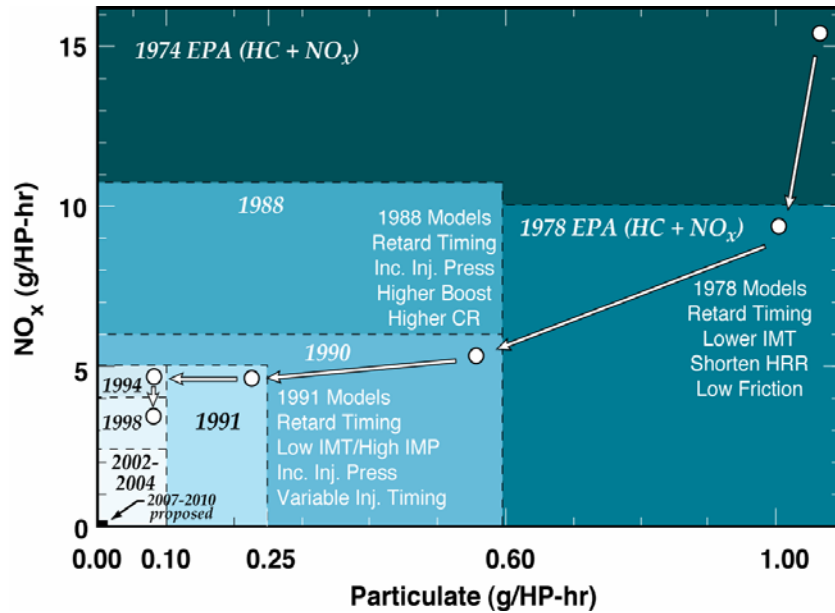

Figure 1. Progress in reducing particulate emissions from engines as improvements were incorporated (right to left). Blocks outline the past and future EPA emission regulations governing engines. *Adapted from J. Dec, Sandia Combustion Research Facility.*

Particulate Matter (PM) [14]. The air quality standards, known as PM_{10} and $PM_{2.5}$, set maximum allowable ambient concentrations permitted for particle sizes ≤ 10 µm diameter (10 microns) and particle sizes ≤ 2.5 µm diameter, respectively. Every five years the PM_{10} and $PM_{2.5}$ standards are reviewed and may be revised under the U.S. Clean Air Act. In addition to standards for particulate matter, the EPA continues to set standards for regulation of other combustion-produced pollutants such as NO_x and SO_2.

Figure 1 charts the stepwise reductions of allowable NO_x and particulate matter emission from engines permitted under EPA regulation since 1978. Hollow circles and arrows plot the reduction in emissions from research engines as mechanical and operational improvements have been incorporated over the past 24 years. The tiny black box at the X-Y origin depicts the EPA stipulated NO_x and PM emission levels that new engines must meet for the 2007-2010+ model years.[16]

As engineers try to design engines that comply with increasingly stringent (EPA or international) emission regulations, they must confront, in more detail, the components of an enormous multivariate problem that spans mechanics, fluid dynamics, and chemistry. Research has revealed that engine efficiency, NO_x generation, and particulate matter production are largely governed by complex interactions between the fluid dynamics and the fundamental combustion

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[15] L. Yang, I. Stulen, L. J. De Kok, Y. Zheng, *SO₂, NOₓ and Acid Deposition Problems in China Impact on Agriculture,* Phyton-Annales Rei Botanicae **42**, 255-264 (2002).

[16] *Control of Air Pollution from New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements*, Federal Register: Jan 18, 2001 (Vol. 66, No. 12), [Rules and Regulations, Pages 5001-5050] (http://www.epa.gov/fedrgstr/EPA-AIR/2001/January/Day-18/a01a.htm).

chemistry of fuel oxidation. Therefore, scientists believe that computer simulations that account for these interactions explicitly will become an important tool for designing more efficient, less polluting combustion devices. Since studies also indicate that the microscopic details of the combustion chemistry govern emissions, simulations of engine performance will require CFD codes that incorporate sophisticated chemical kinetic models in order to reproduce the important features of real fuel combustion.

The formulation of chemical kinetic models of fuel combustion is a fundamental research topic for which the state-of-the-art is constantly evolving. Chemical kinetic models are living entities that improve in accuracy and usefulness as additional chemistry is added. The complexity of real fuels will require the construction of models that are vastly larger in size than models devised previously for the combustion of simple fuels. While it was possible for one person to compile a satisfactory model for hydrogen combustion and a small group to compile the model for methane combustion, it will require a community to build models for real fuels. The previous construction of the GRI-Mech[17] and stratospheric ozone[18] databases have demonstrated that a large committee of scientists can work together in support of large models for important problems. This workshop found consensus that modern experimental capabilities, recent theoretical developments, and novel web-based infrastructure concepts can make the construction of comprehensive models for real fuel combustion feasible.

II. Session Presentations

The following summarizes the presentations and discussions presented at the meeting. The presentations spanned four broad headings: Physical and Chemical Property Data, Fuels and Surrogates, Simulations and Chemical Kinetics, and Community Collaboration. The topics and order of this report reflect the workshop program schedule during a two-day meeting. Each section presents an overview of the presentations and summaries the consensus of the participants. Individual talks are also summarized and reflect the individual opinions of each presenter.

It became clear from the presentations and discussion at the meeting that many commonly used terms have slightly or even very different meanings to various researchers in the field. This in itself is a good illustration of some of the current difficulties in sharing information within the community. The Glossary at the end of this text provides definitions of terms as used in this document.

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[17] GRI-Mech Home Page (http://www.me.berkeley.edu/gri_mech).
[18] S. P. Sander, R. R. Friedl, A. R. Ravishankara, D. M. Golden, C. E. Kolb, M. J. Kurylo, R. E. Huie, V. L. Orkin, M. J. Molina, G. K. Moortgat, B. J. Finlayson-Pitts, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 14 of the NASA Panel for Data Evaluation*, JPL Publication No. 02-25, Feb 2003 (http://jpldataeval.jpl.nasa.gov).

A. Physical and Chemical Property Data

1. Overview

Correct models of combustion systems require access to an enormous volume of physical and chemical information. The workshop examined the current state-of-the-art of the supporting databases and discussed the features of future databases that will facilitate simulations involving real fuels. Workshop discussions were posed with the postulate that future databases will be accessible through an Internet interface.

The physical property data needed for combustion modeling of liquid fuels includes thermal conductivity, viscosity, surface tension, vapor pressure curve, heat capacity, density (P-V-T), and speed of sound over a range of temperature, composition, and pressure. The chemical data includes thermochemical data ($\Delta_f H^o, S^o, C_p^o$, etc.) for fuel components and reaction intermediates as functions of temperature and pressure. In addition to the numeric values listed for these properties, these data must be traceable, *i.e.*, the data source and property uncertainties are provided. Many participants indicated a strong preference for databases of critically evaluated (recommended) data, due to their reliability and self-consistency. Several speakers also expressed a need for increased integration among databases.

As combustion simulations have considered more complex fuels, the number of chemical constituents and number of reactions have increased dramatically. The accompanying table shows the number of species and reactions required to describe the combustion of simple fuels, hydrogen and methane[17], and smaller real fuels, heptane[19] and iso-octane[20]. Models increase rapidly in complexity as the molecular weight of the fuel increases. The model size is further increased by accounting for additional combustion features such as polycyclic aromatic hydrocarbon (PAH) production.

Chemical Kinetic Models of Combustion Become Complex as "Real Fuels" are Approached

Model	# Species	# Reactions
$O_2 + H_2$	8	27
$O_2 + $ Methane	34	210
Real Fuels[a]:		
$O_2 + $ Heptane	540	2450
$O_2 + $ Heptane/PAH[b]	625	2700
$O_2 + $ iso-Octane	860	3600
$O_2 + $ iso-Octane/PAH[b]	935	3850

[a]*Refs. 19, 20.*
[b]*Includes production of PAH soot precursors.*

For larger chemical species, a simple assemblage of elementary chemical reactions and rate coefficients will be no longer possible because direct measurements are unavailable. There is,

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[19] H. J. Curran, P. Gaffuri, W. J. Pitz, and C. K. Westbrook, *A Comprehensive Modeling Study of n-Heptane Oxidation*, Combustion and Flame **114**, 149-177 (1998).

[20] H. J. Curran, P. Gaffuri, W. J. Pitz, and C. K. Westbrook, *A Comprehensive Modeling Study of iso-Octane Oxidation*, Combustion and Flame **129**, 253-280 (2002).

however, a great deal of understanding in terms of algorithms with predictive or extrapolative properties. The conversion of this "understanding" to rate expressions and thermodynamic properties with known uncertainties is not a trivial task, but it is being actively addressed by the research community.

Constructing combustion models of large hydrocarbons reveals major gaps in our knowledge of the reaction chemistry of real liquid transportation fuels. These gaps exist because real fuels involve large, complex molecules and because common real fuels contain hundreds of constituents. Because large molecules undergo a sequential reduction in size during combustion, simulations of real fuels must also include chemical kinetic models that detail the chemistry of small hydrocarbons. Some of these data are available for C1 to C3 species, but this "small molecule" chemistry must be extended to include the relevant chemistry of the larger species present in transportation fuels, particularly reactions that convert large molecules to small. The needed chemistry may be categorized in terms of pyrolytic cracking, oxidation, and condensation reactions that govern the growth of polycyclic aromatic hydrocarbons and soot.

One of the most important aspects of creating these databases is the increasing reliance on theory to generate the necessary information. This reflects our increasing fundamental understanding of the physical and chemical interactions. The demonstrated utility and reliability of theoretical methods is a fortunate recent development, since it is impractical to directly determine experimentally all the data that are needed. New methods for estimating unmeasured elementary rate coefficient data continue to be actively pursued research topics. Although the predictive capabilities of many of the existing algorithms are impressive, experiments are still needed to validate particular estimations, to provide insight into chemistry not yet accessible by theory, and to provide high accuracy values for the most crucial reactions.

Participants noted that the dearth of critically evaluated thermochemical, kinetic, and transport data severely hampers the development of predictive chemical models and simulations for combustion. The combustion literature contains many chemical kinetic models, many of which are internally inconsistent, are in conflict with other established models, or contain chemical kinetic rate coefficients that can be easily shown to be incorrect. A large fraction of the thermochemical, thermophysical, and reaction rate data used in chemical kinetic modeling has not been compared to evaluated data, nor systematically checked for self-consistency. There is no generally accepted set of results on experimental systems that can be used to inter-compare and refine chemical kinetic models.

2. Individual Talks[21]

John Farrell (Exxon Mobil Corp.) presented at talk entitled *"Gasoline Composition."* He described the classes of compounds contained in gasoline, the predominant individual components, how the proportions can vary significantly due to many factors, and how the exact composition of gasoline is driven by both performances needs and regulatory criteria. He provided an overview of gasoline derived from crude oil.

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[21] Speakers usually addressed two or more subtopics. To avoid fragmentation, this report summarizes each presentation completely under the dominant report subheading addressed by the talk.

Although the nascent composition of crude oil is peaked toward the high boiling point diesel and lubricating oils, the commercial demand is peaked towards gasoline. The exact composition of gasoline is driven by both performance needs and regulatory criteria. Emission driven requirements include physical properties such as volatility and stability, limits on levels of carcinogens, aromatics, and olefins, and the addition of oxygenates. Performance driven criteria include octane number, easy startup, and low tendency to vapor lock.

The composition of gasoline is extremely dependent upon the origin/location of the crude, the specific refinery, and other factors including seasonal needs (*e.g.*, relative volatility) and streams extracted for the chemical industry. Crude contains largely paraffins, naphthalenes, and aromatics. Gasoline is a blend from many different refinery streams containing different percentages of the types of major components.
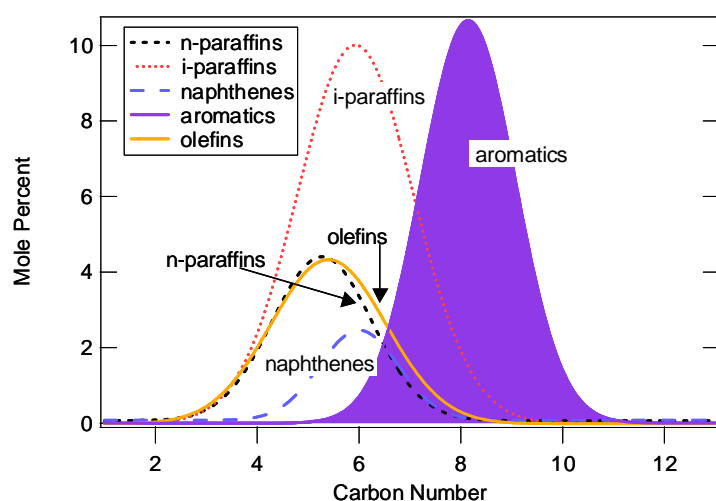

Figure 2. The composition of gasoline showing the relative amounts of each chemical class and the distribution of carbon numbers within each class. *Adapted from J. Farrell, Exxon Mobil Corp.*

The composition of real fuels is tailored to minimize refinery costs and to comply with regulatory restrictions. Real fuels contain olefins simply because they are by-products of the refinery process. Due to the carcinogenic properties of benzene, streams of aromatics are processed to maintain low levels of benzene (< 1 %). To meet requirements of the Clean Air Act of 1990,[22] reformulated gasoline contains added oxygenates, either ethanol or methyl tert-butyl ether (MTBE).

Although the exact composition of gasoline is complex and varies considerably, one can provide a list of representative molecules for each type of component based upon abundance: aromatics (toluene, m-xylene), normal paraffins (n-butane, n-pentane), isoparaffins (methyl butane, methyl pentane, isooctane), naphthalenes or cycloparaffins (methyl cyclopentane, cyclohexane), olefins (methyl butene, methyl pentene), and oxygenates (ethanol).

Daniel Friend (National Institute of Standards and Technology) presented the talk, co-authored by M. Huber, E. Lemmon, R. Perkins, and J. Magee, entitled *"Thermophysical Properties of Real Fuels."* His talk presented an overview of past and present work and capabilities at NIST with regard to measurements, calculations, modeling, and databases for thermophysical properties of fluids with a particular emphasis on those related to hydrocarbon fuels.

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[22] *Clean Air Act as amended in 1990,* U.S. Environmental Protection Agency (http://www.epa.gov/air/oaq_caa.html).

NIST has developed and maintains of a number of relevant thermophysical databases; these include the NIST Standard Reference Databases NIST-4 (SUPERTRAPP - Thermophysical Properties of Hydrocarbon Mixtures), NIST-12 (Thermodynamic and Transport Properties of Pure Fluids), NIST-14 (Mixture Property), and NIST-23 (REFPROP - Reference Fluid Thermodynamic and Transport Properties), as well as the TRC Thermodynamic Tables. NIST has capabilities for high precision measurements of thermophysical properties over a wide range of pressures and temperatures for single component and mixtures in liquid, vapor, and supercritical phases. This includes the ability to prepare well-defined and well-characterized mixtures. NIST has apparatus for high precision measurements of properties such as thermal conductivity, viscosity, surface tension, heat capacity, density (P-V-T), and speed of sound. Implicit to these thermophysical databases at NIST is the ability to accurately model the properties of fluids over a wide range of pressures and temperatures. Relevant data span mixtures consisting of different components and mixtures of more than one phase.

This talk discussed some of the requirements for accurately modeling the thermophysical properties of complex fluids such as real fuels and some of the advances needed in this area. A database connecting physical and chemical properties would be a significant breakthrough. One of the conclusions was that a strong coordinated program could achieve major impact in design, development, and optimization of combustion systems. To achieve this goal, Friend suggested that it would be necessary to develop extensive collaborations among industry, academia, and governmental agencies. Industry can help this process by defining the scope of data needs with regard to systems, ranges, and uncertainties. NIST can take a lead in areas where data standards are required.

M.C. Lin (Emory University) presented a talk, co-authored by R. Zhu, entitled *"Ab Initio Studies of NCN Reactions with O, OH and O_2."* He described recent work on the oxidation of NCN. This represents a new interpretation of the mechanism for prompt NO formation and demonstrates the power of modern computational techniques. The *ab initio* calculations and RRKM rate predictions presented in this talk highlighted the issue of "what is an elementary reaction?" The examples given in the talk showed how the rate of reaction of an apparently straightforward A+B=C+D bimolecular reaction can arise from the sum of several different channels that contain multiple short-lived intermediates and several nearly iso-energetic transition states. The overall reaction can be influenced by association steps and operate simultaneously on potential energy surfaces of differing spin multiplicity.

Wing Tsang (National Institute of Standards and Technology) presented the talk entitled *"Combustion Simulation Databases for Real Transportation Fuels."* His talk presented a review of the chemical database needs for real fuels with explicit consideration given to the presence of larger alkanes. The general picture involves four general reaction types: a) pyrolytic cracking forming smaller species, b) oxidative cracking forming smaller species, c) soot formation from unsaturated compounds, and d) oxidation of the species formed by cracking processes.

Without making judgments on their quality, kinetic databases for soot formation and oxidation of the smaller species can be found in the literature. Chemical kinetics databases also exist for the oxidative cracking of fuels up to decane. This highlights the need for information on pyrolytic

cracking of smaller fuels and, in general, the breaking down of the larger fuels to smaller fragments by pyrolysis or oxidation.

Some problems and solutions for building cracking databases for the larger fuels were discussed in the talk. It was pointed out that for large alkanes, the resulting database must contain reactions for the decomposition of all of the smaller linear alkyl and 1-olefinyl radicals. An experimental methodology for building a chemical kinetic model for the pyrolytic cracking of n-alkanes and n-alkyl radicals was presented. This takes advantage of the availability of the n-alkyl iodides and large normal alkanes as sources for the generation of appropriate precursors. The situation is more unfavorable for branched alkyl radicals due to the possible need for numerous custom syntheses. In terms of elementary reactions, the key missing elements are the isomerization reactions involving radicals.

B. **Fuels and Surrogates**

1. Overview

Transportation fuels, gasoline, jet fuel, and diesel, are refined products from the processing of crude oil. The composition of each fuel is driven by performance needs (*e.g.*, octane/cetane numbers), regulatory-driven criteria for physical properties (*e.g.*, vapor pressure, flash point), and economic factors imposed by the refining process and feedstock. These circumstances produce fuels that contain hundreds of chemical compounds in amounts that vary considerably.

To attain consistent test results, industry uses reference fuels to assess engine-operating parameters, both for design purposes and for demonstration of performance related to regulatory requirements. Reference fuels may be specified by domestic or international governmental regulating agencies. These specifications vary by region. Reference fuels are usually needed in very large quantities, making it impractical to replace them with pure component mixtures.

Although reference fuels will always be needed at some stage in the engine design and testing process, workshop participants felt that laboratory studies and simulations based on surrogate fuels would be more reproducible and facilitate deeper insights into combustion processes. The participants believe that data derived with surrogate fuels could significantly reduce some of the current needs for expensive, large-scale testing.

The community defines surrogates as a set of compounds whose relative concentrations can be adjusted so that the chemical and physical properties pertinent to combustion approximate those of a real fuel. A properly composed surrogate fuel should share nearly the same chemical kinetics and thermodynamic properties as the real fuel it simulates. The physical properties that surrogates should match include vapor-liquid-equilibrium, viscosity, surface tension, ignition delay, smoke points, and thermal stability. In this context, it is likely that absolute matches of all physical properties may not be achieved, but nonetheless, the consensus is that surrogates can serve as a useful proxy for reference fuels.

The workshop presentations gave evidence for the feasibility of surrogates that match the combustion properties of real fuels. Although each fuel type contains hundreds of chemical compounds, these compounds are members of only a few chemical classes: alkanes, cycloalkanes, aromatics and olefins. Each of these compounds does not itself make a unique contribution to the combustion properties of a fuel. Experience has shown that despite the wide variations in the composition of fuel mixtures, fuel combustion properties, such as octane numbers (for gasoline) and cetane numbers (for diesels) are relatively invariant. However, some work remains in defining surrogate fuel specifications. For example, data that define the soot and PAH characteristics of real fuels and surrogate candidates are needed.

The workshop outlined some steps toward filling the major information gaps for real fuels. The six chemical classes identified at the workshop are presumed to constitute the minimal set of constituent types necessary to describe the chemical composition of real fuels used by the trucking, construction, aviation, and personal transportation sectors. No one surrogate mixture is expected to address all the testing and research needs for diesel, gasoline, and jet fuels or for the many different

> **Workshop Proposal for Chemical Constituents of Surrogate Fuels**
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> - **Iso-paraffins:** Isooctane
> - **Normal paraffins:** Heptane, Hexadecane, Decane
> - **Single ring aromatics:** Toluene, Xylenes
> - **Cyclo-paraffins:** Methylcyclohexane
> - **Olefinic species:** 1-Pentene
> - **Multi-ring aromatics:** 1-methylnapthalene

combustors of interest. But surrogates for all fuels could reasonably consist of different compositional mixtures of the six model compounds. There is an initial working consensus as to the specific model compounds whose combustion chemistry, if reliably determined, would allow simulation of the combustion of real fuels. These choices should be further reviewed as relevant data become available and may well see refinement.

The cost of pure-compound-based surrogate fuels remains a serious concern to researchers and engine developers who require large quantities of fuel. Nonetheless, it was generally believed that surrogate fuels would be useful for testing and modeling purposes and would aid in our understanding of the related "reference fuels" commonly used in engine design and specification. In addition to the hydrocarbon surrogates, surrogates for sulfur-containing impurities, oxygenate additives, and anti-knock agents may be needed.

Surrogates for aviation fuels are already being tested. The degree to which they truly represent the properties of a real fuel is beginning to appear in the literature. Some results were reported at this workshop.

In summary, the consensus of the workshop is that applying the concept of surrogate fuels is enabling. Mixtures of surrogate compounds can reproduce the combustion behavior of transportation fuels. Simulations that begin with a limited set of surrogate components will be more quickly computed. Finally, a limited set of surrogate compounds would allow a single database of chemical and kinetics properties to support combustion simulations relevant to all sectors of the transportation industry.

2. Individual Talks[21]

William L. Brown (Caterpillar) presented a talk entitled *"'Real' Diesel Fuel - Caterpillar's Story."* He gave a brief overview of the specifications of diesel fuels. Although diesel engines operate on fuels of widely different composition, all fuels share high Cetane numbers. Customers and applications use many different diesel certification fuels. Each foreign national government also stipulates tests with specific certification fuels.

Although 2-D is the most common commercial diesel fuel, Caterpillar uses many different certification fuels with tight specifications when developing engines. The talk also discussed in detail the development of HCCI engines and the inability of current chemical kinetic models to accurately simulate this low temperature system that contains slow reaction kinetics. Current simulations of sprays lack sufficient resolution in the CFD simulations. To achieve better simulations, full chemical kinetic models are needed that include the reactions describing NO_x and soot formation processes.

Meredith B. Colket (United Technology Research Center) presented a talk, co-authored by Steve Zeppieri, entitled *"Jet-A Surrogate Blends."* His talk focused on the properties of surrogate mixtures used at UTRC and the important kinetics, physical, and chemical features that simulations should reproduce. Surrogate fuels should be formulated to match the physical and structural chemical properties of surrogate fuel. These properties should include the H/C ratio, molecular weight, vaporization temperature, viscosity, surface tension, aromatic content, and normal and branched and unbranched hydrocarbon fraction.

For surrogate fuels chemical kinetic models should enable simulations to reproduce important combustion properties. These macroscopic kinetic properties include the light-off (ignition), auto-ignition, extinction, pyrolysis rates, soot production, conversion rate to CO, initial heat release rates and super-equilibrium radical concentrations. Data were presented on the equilibrium temperatures of a number of fuel mixtures.

Tim Edwards (Air Force Research Laboratory) presented a talk entitled *"Jet Fuel Composition."* He detailed the composition of jet fuel, the range of variations possible due to broad specifications, and the differences among various jet fuels with regard to required physical properties such as flash point and freezing point, as well as with regard to additives.

This talk gave a significant amount of information about the characteristics of jet fuel. Jet fuels are kerosenes. Even for specific jet fuels, batch-to-batch variations can be significant due to broad specifications. Commercial jet fuels are Jet A, Jet A-1, and Jet B. Jet B is a wide cut kerosene-gasoline (naphtha) mix that is highly flammable and has limited use in very cold climates having a very low freezing point compared to Jet A. Jet A and Jet A-1 are very similar with Jet A available only in the U.S. and Jet A-1 outside the U.S. They have the same flash point characteristics, but the international Jet A-1 has lower freezing point specifications. The most common military jet fuel is JP-8, which is the equivalent of commercial Jet A-1 but with additives. JP-4 is the wide cut military equivalent of commercial Jet B. JP-5 is very similar in characteristics and composition to JP-8, but has a much higher flash point and is used

predominantly by the Navy on aircraft carriers, due to its reduced flammability. Jet fuels are composed of a distribution of hydrocarbons that peak and center about C11-C12. For comparison, gasoline/naphtha distillates are composed of hydrocarbons that range up to C10-C11.

Specialty jet fuels such as JP-7, RP-1, and RG-1 are highly processed, clean kerosenes with high flash points. Compared to JP-8, these specialty jet fuels have very low aromatic and sulfur content and slightly higher hydrogen content. The composition of these fuels is typically restricted to C11-C14, as compared to JP-8, which ranges between C9-C15. Specifications for jet fuels are combinations of physical and chemical properties. For example, JP-8 hydrogen content must be > 13.4 % (H/C > 1.84), and is typically 13.8 ± 0.26 %; aromatics must be < 25 %, total sulfur < 0.3 % with < 0.002 % mercaptan sulfur; naphthalenes must be < 3 %; flash point > 100 °F (> 38 °C); and freezing point < -53 °F (< -47 °C).

This talk also addressed the issues of surrogates and their composition compared to typical jet fuels, indicating that surrogate mixtures for jet fuels are practicable. The talk provided an overview of progress to-date and broad-reaching future plans to perform detailed gas-chromatography mass spectrometry (GC-MS) chemical analyses of 57 jet fuel samples from sources worldwide; and current and future plans to store standard or typical jet fuels for use by others.

David Lenhert (Drexel University) presented a talk, co-authored by D. Miller and N. Cernansky, entitled *"Development and Evaluation of Fuel Surrogates in the Low and Intermediate Temperature Regime."* He presented experimental results on the results of studies with surrogate gasoline and JP-8 mixtures using their pressurized flow reactor. The studies covered reactions in the low and intermediate temperature region. In this work they present reactivity maps (CO production versus temperature) for individual components, surrogate mixtures, and reference fuels. They developed a surrogate that matched reactivity maps for JP-8 over a range of conditions.

Adel Sarofim (Reaction Engineering and University of Utah) presented a talk entitled *"Surrogates for Complex Fuels,"* that outlined criteria for the selection of surrogates. The talk outlined technical metrics for selection of surrogates including physical properties (*e.g.*, boiling point) and fuel validation (*e.g.*, burning rate). Sarofim also emphasized that the choice of each surrogate component should be directed to minimize the overall cost, as expensive surrogate fuels would not be widely used or accepted.

Sarofim also presented overviews of work in the areas of measurements and modeling of surrogate fuels. Much of the past work on surrogates has to do with matching one or more properties. He reported that matching real fuel ignition properties is relatively easy by formulating mixtures composed of few compounds. However, formulating surrogates that match all desired physical and combustion properties simultaneously is very difficult. Sarofim described a new strategy for determining useful formulations. This method, structure oriented lumping, considers explicitly the chemical groups that comprise real fuels. In this approach, hydrocarbons in petroleum are characterized by sixteen chemical groups. Rules govern the

construction of the chemical reaction networks and group additivity rules account for the structural property relations.

Very little data are available in the literature that compares the sooting properties of surrogate mixtures to those of real fuels. Sarofim reported observations on the GC patterns derived from soot fractions collected from JP-8. These patterns were compared with a surrogate mixture that matched the smoke point of JP-8.

<u>Mitchell D. Smooke (Yale University)</u> presented a talk, co-authored by James Cooke, Matteo Bellucci, and Alessandro Gomez, entitled *"JP-8 Surrogate Counterflow Diffusion Flames."* He described recent results from experimental and modeling studies on counterflow diffusion flames using individual components, surrogate mixtures and JP-8. Detailed chemical kinetic models involving 220-260 species with 5000-7000 reactions were used. A six-component JP-8 surrogate (dodecane, isooctane, methylcyclohexane, tetradecane, tetralin and m-xylene) was used. Good agreement between predicted and measured temperature profiles (within about 100 K) and rich extinction limits (within about 10-20%) were observed. The differences are believed to reflect that experimental uncertainty and inaccurate specification of plug flow boundary conditions.

C. **Simulations and Kinetics**

1. Overview

The Simulations and Kinetics presentations focused on the problems of simulating combustion systems with particular reference to the selection and use of surrogates. Computer simulations of real combustion devices span many length scales, ranging from atoms and molecules up to particulates and devices (*e.g.*, engines and turbines). Accurate simulations require evaluated data formulated by experts from the chemical kinetics, thermodynamics, and fluid dynamics properties communities.

The presentations demonstrated that computational fluid dynamics (CFD) simulations incorporating realistic fluid dynamics and chemistry are poised to be of great benefit in the design of real combustion devices, including diesel, HCCI, and jet engines. Presentations also showed promise that such simulations may accelerate the development of novel energy technologies, *e.g.*, solid-oxide fuel cells and hydrocarbon reforming for hydrogen fuel technologies.

Presentations showed that the development of new methods for deducing useful reduced chemical kinetic models is an actively pursued research topic. Such reduced models are needed so that the highly complex CFD simulations may fit within the resources available on supercomputers. Even if it were known, the complete reaction set describing the combustion of a real fuel would be too large for practical use in any simulation model. Likewise, most detailed initial reaction sets that describe the combustion of real fuels are also impractical. To remedy this resource conflict, research teams usually trim down the initial reaction set by deleting reactions that contribute little to the overall chemistry and/or by consolidating several elementary reactions into a smaller group of lumped reactions. Good practice includes validating each reduced model

against experimental data. Having detailed results of validated, well-defined, reference experiments available in a public database would be particularly helpful to the combustion community in its effort to validate new reduced models.

Presentations pointed out the need for models that can predict simultaneously NO_x and particulate matter production from diesel and HCCI engines. The simultaneous requirements for NO_x and particulate matter minimization are in conflict since the high temperatures that are advantageous for particulate removal can lead to NO_x formation, while the lower temperatures that reduce NO_x production enhance particulate production. The need is to locate an optimum "window" where the most favorable tradeoffs occur. The HCCI engine, which promises to satisfy future emission standards and to give large energy savings, is a particularly interesting case. Because these engines operate under very lean conditions and lower temperatures than other engines, the chemical reaction rates of combustion are slower than for other engines. Thus, models must account for the chemical reaction process with greater detail. Models and measures developed for spark ignition engines (at much richer conditions and higher temperatures) have proved inadequate for predicting HCCI engine performance.

The workshop identified a strong need for the creation of a database of chemical kinetic models and simulation models that have been validated for at least one set of combustion conditions. This database would help standardize model nomenclature, traceability, and data exchange protocols. The current lack of information exchange standards for communicating chemical kinetic models and validation data are slowing the development of chemical kinetic models for real fuels. At present, there are no agreed upon descriptors for the representation of information within models. Even in areas for which there is little dispute as to the physical or chemical meaning of the information, no accepted standards exist. These deficiencies impede the sharing of information among researchers and diminish the ability of the community to validate models. These deficiencies may also lead to the inadvertent proliferation of inaccurate mechanisms.

2. Individual Talks[21]

C. Thomas Avedisian (Cornell University) presented a talk entitled *"Toward a Standard for Evaluating Jet Fuel Kinetics."* He discussed the use of a spherically symmetric droplet burning flame as a means of carrying out benchmark experiments for surrogate development. He also raised the interesting issue of determining the relative composition of a surrogate mixture that fits the particular application. Avedisian discussed some of the issues with regard to validation. He recommended the use of flow reactors, counter-flow diffusion flames, and shock tubes as benchmark configurations. He noted that ignition and extinction are the most sensitive features in combustion chemistry, but are strongly impacted by multi-dimensional transport phenomena. Thus, systems with 1-D transport are most important for validation studies. Avedisian discussed a burning droplet as an idealized one-dimensional system because droplets are spherically symmetric. He presented examples that showed measuring droplet diameter as a function of time as a useful metric for characterizing combustion systems.

Anthony M. Dean (Colorado School of Mines) presented a talk entitled *"Coupling Detailed Kinetics and Transport."* The talk was co-authored by H. Carstensen, R. Kee, C. Sheng, K. Walters, and H. Zhu. He described the use of a fundamental hydrocarbon chemical kinetic

model (~ 400 species, ~ 2000 reactions) for simulating the direct electrochemical oxidation (DECO) of hydrocarbons in a solid-oxide fuel cell (SOFC) in a combined experimental and simulation study using butane as the fuel.

The operational principles of the SOFC are complex, involving electron transport processes, electrochemical kinetics, heterogeneous chemistry, and hydrocarbon deposit formation. Since a SOFC typically operates at 700-1000 °C, one would expect that homogeneous cracking would also make a contribution. The kinetic model captured the strong temperature dependence of the butane conversion and correctly predicted the effects of dilution by N_2 and H_2O. Sensitivity analysis was used to determine a small subset of reactions that had the largest impact on butane conversion and other observables.

The chemical kinetic model is in the process of being refined to include heterogeneous chemistry and electrochemical kinetics, as well as being coupled to an anode transport model. Although the application described is for direct combustion of hydrocarbons, this type of database will be invaluable for simulating the effect of additives on combustion, hydrocarbon cracking (the basic process for producing chemical feedstock) and indeed in any combustion based process. In all cases the proposed chemical kinetic model will describe the underlying process and thus form the basis for investigating what are essentially perturbations on the system.

Frederick L. Dryer (Princeton University) presented a talk entitled *"Some Remarks on Large Hydrocarbon Models and Surrogate Fuel Issues."* He described the serious barriers to the construction of chemical kinetic databases suitable for the simulation of real fuels. These barriers include the absence of elementary data on the larger chemical reactants and intermediates and the absence of experimental data pertinent to the validation of chemical kinetic models of surrogate mixtures and real fuels. Dryer emphasized that detailed chemical kinetic models are never mathematically complete; therefore, the existing models are neither static nor unique. Instead, they are dynamic constructs that must be continually refined, optimized, and constrained as new data become available. Dryer noted that the very large size of typical chemical kinetic models makes simulations possible for only simple one-dimensional situations.

Dryer presented a methodology for and examples of reaction set minimization and constraining procedures. He elaborated on the severe disconnects caused by the complexity of chemical kinetic models and the limited number of constraints available from validation data. From a statistical and parametric model point of view, this leads to a poorly posed minimization problem. This problem arises because initial chemical kinetic models contain many more free variables (usually 100's of species and 1000's of reactions) than can be constrained by a small number of experimental observables. Dryer recommended that the reduction processes should begin by selecting the validation data and then iteratively optimizing the reaction set through minimization of its dimensionality.

Dryer expressed optimism regarding the use of surrogates and illustrated results based on three-component mixtures that are currently being used for engine testing. He recommended the use of primary reference fuel mixtures with an added aromatic (toluene) as a starting point for surrogate development. However, Dryer noted that the sub-models for toluene combustion have some

problems. This can have serious implications for soot/PAH simulations, since the standard employed databases for combustion have reactions that can be found in the former.

Graham Goldin (Fluent, Inc.) presented a talk entitled *"Chemical Kinetics in Multi-dimensional CFD,"* which summarized the present capabilities of CFD codes from Fluent, Inc. Combustion chemistry and modeling are important in different areas including internal combustion engines for automotive applications and gas turbines for power generation. Combustion modeling is particularly complex, because good models comprise complex chemistry, complex fluid dynamics, complex numerics (*e.g.*, stiff differential equations, numerical errors, and convergence problems).

Current computational methods attempt to strike a balance between simplified chemistry and simplified transport equations. CFD codes have been developed with the capability of handling the complex geometries found in real systems. This is, however, only realized with much simpler chemistry. Examples were presented that contained 15-20 species and 50-100 reactions. Examples were given with reduced reaction sets for a laminar diffusion methane-air flame, a methane-air rapid compression machine, a piloted turbulent jet methane/air flame, a lean premixed pre-vaporized propane/air flame, a combustor methane/air flame measured in an industrial combustor at Sandia's Burner Engineering Research Laboratory, and a trapped vortex combustor methane/air flame.

The developing computational technology of *in situ* adaptive simulations (ISAT) was discussed. ISAT may shorten computation time by an estimated 100-fold. During typical simulations, the stiff reaction rate equations are integrated millions of times. By building a table of mappings for the composition space, ISAT eliminates the need for repeating similar integrations. As a simulation approaches convergence, fewer new integration procedure calls are necessary because solutions are interpolated from mappings previously computed. Although ISAT and other developing numerical methods show promise for handling complex chemistry and transport, it is clear that in the near future, that there will still be a need for reduced chemical kinetic models. However, the general trend is clearly toward more species with a corresponding increasing number of reactions.

Viswanath Katta (Innovative Scientific Solutions, Inc.) presented a talk entitled *"CFD/large Chemistry Models: Unicorn 3.0 Code"* that described a CFD code, UNICORN, that is being used at Wright Patterson Air Force Base in conjunction with an experimental program. Using only a conventional personal computer, they have been able to simulate two-dimensional complex flames with full chemistry, although with very long running times. Results for an impressive range of combustion situations were presented. The capabilities demonstrated by this modeling code suggest that combustion systems with reduced dimensionality can be completely described without the need for reduced chemical kinetic models.

Chung K. Law (Princeton University) presented a talk entitled *"Some Thoughts and Action Items on Mechanism Development for Combustion Applications."* He described chemical kinetic model development in terms of the urgent need to have a realistic description of the events in combustion. In particular, Law was concerned with the proliferation and indiscriminate use of inadequate chemical kinetic models. He was also concerned with the enormous long-lasting

impact of training students to develop and utilize inadequate models, which propagates the problem. He emphasized that many of the individual elements necessary to achieve a realistic description of good models are in place, which he stated highlights the need for a detailed road map for combustion research.

In addition to the need for further development of both detailed and reduced chemical kinetic models, Law emphasized the need for the development of a rigorous methodology for the semi-automatic generation and reduction of models. Such algorithms would be immune to changes in the reaction set, and thus, can provide a way of standardizing chemical kinetic models and assist in screening inadequacies in models. Law emphasized that the complexity of the chemistry and transport processes in combustion requires an integrated, comprehensive, multidisciplinary approach requiring significant broad-based education of students in this area.

Gregory J. McRae (Massachusetts Institute of Technology) presented a talk, co-authored by Bill Green, entitled *"Next Generation Reaction Modeling"* that evaluated the state of the art in simulations and provided a detailed set of necessary next steps providing significant guidance to the community. He considered the aims of the present workshop in the context of the need for multi-scale integration. He (and others in the course of the workshop) pointed to the success of the biological community in successfully integrating individual data elements into large data sets that can be used for final applications.

The talk provided an overview of current problems in practical applications covering a wide range of technology including hydrocarbon reformers, fuel cell technology, CVD, catalytic combustion for NO_x reduction, and an overview of current databases used in reaction modeling. He highlighted the inadequacies in the current state of the art. These inadequacies include a lack of integration among databases, poor or no practical uncertainty estimates for the observed properties, poor documentation and traceability of data, and the absence of evaluated databases.

McRae outlined many different advances needed in reaction modeling. Advances are needed in the identification and prioritization of research directions, rigorous statistical uncertainty analysis, rigorous determinations of the range of conditions over which models are valid, user friendly graphical interfaces for chemical kinetic model development, reduced model libraries, integration and exploitation of thermochemical and chemical kinetic data from quantum calculations and systematic benchmarking with experimental data. There is a strong need to semi-automatically generate chemical kinetic models by using rules for reaction types that are based on functional groups. Methods that use rate-based testing to determine relative importance are needed in order to constrain the number of species and reactions included in these chemical kinetic models. This approach would also help researchers determine when additional species and reactions must be added to a reaction set.

The need for an organized effort by the entire community was stressed. The diversity of the combustion community makes organization with clearly stated goals in the form of road maps particularly important. The need is not only for data sets with clearly stated uncertainties, but also the tools to generate and manipulate data sets and libraries of reduced data sets that can be used directly. Success with regard to the next generation of reaction modeling will require a multi-disciplinary community providing a range of resources, knowledge, and views. Leveraging

input from each sub-community will require multi-scale integration among the private and public databases. To achieve this integration, robust standards for adequate representation of necessary physical and chemical data will need to be established.

William J. Pitz (Lawrence Livermore National Laboratory) presented a talk entitled *"Barriers to Developing Surrogate Mechanisms,"* which presented a summary of the practical problems with developing chemical kinetic models for the combustion of surrogate mixtures. Because such models are very large, Pitz believes that model reduction procedures must be used in order to make simulations feasible. Such reductions are difficult due to the scarcity of experimental thermodynamic and kinetic data for the chemical compounds that are likely to comprise surrogate mixtures. Although theory is becoming a more important tool, its actual use is time consuming and requires considerable judgment. The traditional way, based on a single investigator, of generating a reaction set is no longer a viable procedure given the enormous potential size and complexity of the models necessary to describe the pyrolysis and oxidation of large hydrocarbons, as well as PAH formation/destruction.

Pitz pointed out that although combustion largely occurs on low-dimensional manifolds and is thus amenable to chemical kinetic model reduction, ignition and extinction are inherently multi-dimensional. This difference presents a fundamental problem for model reduction that may limit its application. Pitz also brought up an important question regarding model validation: when are disagreements between models and observables simply because small details in the boundary conditions have a large impact on the chemistry? When this situation arises, tweaking the chemistry to fit the observables is an incorrect procedure. In many cases, it is difficult to model or characterize the boundary conditions. Pitz provided an overview of some elements of the "bag of tricks" necessary for iterative model development

Charles K. Westbrook (Lawrence Livermore National Laboratory) presented a talk, co-authored by Bill Pitz, entitled *"Detailed Chemical Kinetic Modeling of Large Hydrocarbon Fuels."* The objective of his current work is to provide validated chemistry models for combustion applications, including spark ignition engines, diesel engines, gas turbines, and the newest technology, HCCI.

The presentation comprised a general discussion of the fuels (natural gas, gasoline, diesel, jet fuels) and the important chemistry for different temperature regimes. These represent important considerations for the selection of a surrogate. Westbrook detailed the complexity of the different fuels with regard to differing composition from fuel type to fuel type and even the wide range of compositions for individual fuels. He discussed the general issue of surrogates in the context of the differing chemical classes contained in the different fuel types. Westbrook summarized the problems and challenges involved in matching traditional measures of combustion properties, the Research Octane Number, with experimental results on ignition delays from the Rapid Compression Machine (RCM) and simulations. Generally, simulations match experimental results from the RCM. However, for the HCCI engine agreement between experiment and model predictions is very poor. This suggests that existing chemical kinetic models are incomplete in the very lean region.

D. Community Collaboration

1. Overview

Although the optimization of a specific geometry and design for a combustion device may represent an individual or even proprietary activity of a sponsoring organization, simulations of this device will incorporate a chemical kinetic model and other data that is not proprietary. For real fuels, most of this nonproprietary knowledge remains to be defined and optimized. Several speakers stressed the value of and need for increased community collaboration to solve the complex combustion problems involving real fuels. They noted that the current absence of effective mechanisms for developing multidisciplinary collaborations has impeded the improvement of simulation-based combustor designs. Most proposed that an effective mechanism would give access to a common set of data, chemical kinetic models, benchmark test information, and a wide variety of tools.

Several web-based mechanisms for facilitating effective collaborations were presented, including the process informatics model (PrIMe) initiative and the Collaboratory for Multi-Scale Chemical Science (CMCS). Attendees generally supported the idea that these mechanisms would include a central repository for data that is validated through testing and discussions among the community. NIST was cited as a logical center for such operations, and the attendees were very interested in NIST playing an enabling role by facilitating the provision of data. The mechanisms and interactions of these central clearing houses and data operations across NIST, CMCS, and PrIMe would require integration by information technology experts and NIST scientists. The workshop attendees generally agreed that this comprehensive internet-based repository would be valuable and widely used.

2. Individual Talks[21]

Michael Frenklach (Berkeley) presented a talk entitled *"Development of Predictive Reactions Models."* He outlined an approach for collaboration termed the Process Informatics Model (PrIMe). The aim of the project is to develop a community activity for development of reaction models of combustion. The initiative is a community effort to generate data libraries, analysis software, and the supporting information technology infrastructure that will enable a collaborative approach to development of predictive models of combustion. This information would be warehoused in a comprehensive repository containing all data relevant to modeling combustion processes. Development of this library is a community project involving submission and evaluation of the relevant data, often presented in the form of a "model" describing a particular combustion scenario. Evaluation at this stage is concerned with the data required for quantitatively describing the chemical reactions within the model and a measure of the uncertainty of the data. In addition, the evaluation will seek to discern a clear documentation as to the sources of the data and associated uncertainties; this documentation is often termed the traceability or pedigree of the data.

David M. Golden (Stanford University) presented the talk entitled *"Evaluating and Codifying Data for Engineering Applications: Atmospheric Chemistry and Combustion."* He summarized his experiences with multi-institutional collaborations that generated the NASA Chemical

Kinetics and Photochemical Database for Stratospheric Modeling[23] and produced the GRI-Mech database, which is the optimized detailed chemical kinetic model that represents natural gas flames and ignition during simulations. He characterized the former as a good 19th century-like effort towards database development and the latter as a good 20th century-like effort. Encouraged by the current advanced state-of-the-art of measurement, computational, and information technologies, he called for a 21st century approach to chemical kinetic model database development. Continued use of 20th century-like paradigms would be very ineffective, given the complexities of the problems that need to be addressed today.

He emphasized that kinetics data evaluation is a hard and tedious job that can only be successfully carried out by expert practitioners in the field. At the present time good measurements remain the basis for all evaluations. Theory is playing an increasingly important role. Currently, this involves the extension of the measurements to ranges that are not covered by the measurements and to set limits on possible rate constants and expressions.

William H. Green (Massachusetts Institute of Technology) presented a talk entitled *"The Future of our Field: Predictive Chemical Kinetics."* He first noted that a great many chemical processes of importance to industry and society, as wide-ranging as combustion, soot formation, kerogen maturation, and consumer product aging, proceed via complex sets of reaction pathways. The ultimate goal of chemical kinetic modeling for these systems must be to make predictions that can guide process design, business, and policy decisions. That goal demands that we be able to *i*) predict the vast array of needed thermochemical and rate parameters, since these cannot all be taken from literature data; *ii*) build models that contain the correct chemistry for the conditions of interest; *iii*) solve the large kinetic models we build to address concrete, useful questions; and *iv*) develop, as a community, standards for the interchange and evaluation of data, standard software tools for using and manipulating chemical kinetic models, and institutional incentives that will promote collaboration.

Green gave examples of how to address the first three challenges, but stressed that much more work is needed for the fourth, including the formulation of roadmap by the community, and the collective development of data standards and tools.

Larry Rahn (Sandia National Laboratories) presented a talk entitled *"Enabling Collaborative Science for Real Fuels Combustion."* He gave a report of the present status of the Collaboratory for Multi-Scale Chemical Science (CMCS).

Attacking the problem of real fuels combustion requires a multi-scale approach. Multi-scale in this context refers to the fact that information from physical scales ranging from the atomistic level up to large-scale reaction processes are required to fully address the problem. It is difficult to deal with multi-scale information due to the difficulty of propagating the data pedigree (including uncertainty, methods, data dependencies, etc.) across scales and the fact that annotation and validation of data often occurs after publication of the data. Additional barriers

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[23] W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, R. E. Huie, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. J. Kolb, and M. J. Molina, *Chemical Kinetic and Photochemical Data for Use in Stratospheric Modeling: Evaluation No. 12 of the NASA Panel for Data Evaluation*, JPL Publication 97-4 (April, 1997).

arise, due to the time involved in traditional means of scientific publication, incompatible and undocumented data formats, geographic distribution of researchers, and the multi-disciplinary nature of collaborators. These difficulties tend to hinder progress.

CMCS will enhance chemical science research by breaking down the barriers to rapid sharing of validated information and by opening new paradigms for multi-scale science. In the longer term, new forms of collaborative data sharing and pedigree annotation that complement scientific peer review and publication will be created. The CMCS will also enable the creation of radically new types of collaborative multi-disciplinary chemical science projects and dramatically increase accessibility of state-of-the-art research studies to industry and the public.

The objectives of the CMCS project are to build an adaptive informatics infrastructure that facilitates multi-scale science ventures, to pilot a project within the combustion research community, to demonstrate the power of adaptive infrastructure to existing and new areas, to gain adoption and continued support via community participation, to document success, and to map a continuation path. Current capabilities of the CMCS infrastructure include data sharing, collaboration, data and metadata management, annotation, translation, visualization, notification, searching and security.

III. Breakout Session Reports

On the afternoon of the second day, each participant selected to participate in one (or more) of five topical focus sessions: Reference Fuels, Surrogate Fuel Selection, Essential Databases, Experimental Validation Data Sets, and Creation of a Roadmap for Combustion Science. Each breakout group has formulated recommendations designed to advance combustion science though community improvements within the focus topic.

A. Reference Fuels

Reporter: Tim Edwards (WPAFB).

Participants: William L. Brown (Caterpillar); Frederick L. Dryer (Princeton U.), briefly; Kenneth Erdman (Caterpillar); Daniel Friend (NIST); Jeffrey Manion (NIST); Christopher Montgomery (Reaction Engineering); Adel Sarofim (Reaction Engineering & U. Utah).

This section summarizes discussions of the above group regarding the scientific and engineering community needs for databases related to reference fuels. The conclusions of this breakout group were presented to the full workshop attendance.

Reference fuels are used by industry to assess engine-operating parameters, both for design purposes and for demonstration of performance related to regulatory requirements. Reference fuels may be specified by national [*e.g.*, the U.S. Environmental Protection Agency (EPA)] or state regulating agencies [*e.g.*, the California Air Resources Board (CARB)]. Additional agencies and specifications are involved for international regulations and vary by region. Regardless of

regulatory specifications, reference fuels are often needed in very large quantities, making it impractical to replace them with pure component mixtures.

For the foreseeable future, reference fuels will always be needed at some stage in the engine design and testing process. However, for purposes of computer simulations and lab-scale device testing, it may be possible to develop surrogate fuels that mimic the important characteristics of the reference fuels. If successful, this could significantly reduce some of the current needs for expensive large-scale testing.

Various types of information related to reference fuels would be a useful resource to the combustion community. This would include information not only on the specific reference fuels themselves, but also, for comparison, on real fuels (*i.e.*, commercial products) and some commercial hydrocarbons solvents (used as fuels in certain tests). Some of the suggested resource data to be made available are summarized below.

Fuels and Fuel Substitutes Pertinent to Database:

1) Real fuels.

   a) Commercial gasoline fuels from major refiners.
   b) Commercial diesel fuels from major refiners.
   c) Civilian jet fuels: Jet A, Jet A1, Jet B
   d) Military jet fuels: JP-4, JP-5, JP-7, JP-8 (Jet Propellants), RP-1 (Rocket Propellant-1 or "rocket kerosene")

2) Reference fuels.

   a) Diesel: EPA F173 certification fuel. This is a full-boiling, tight specification diesel fuel. Note it will change to lower sulfur version in 2007.
   b) Gasoline: to be determined.
   c) Jet fuel: There is presently no generally-accepted reference jet fuel. The Society of Automotive Engineers (SAE) has defined a "Jet Reference Fluid" (JRF) that is used to evaluate fuel tank sealants. The current composition (SAE AMS 2629B) is 28 % toluene, 34 % cyclohexane, and 38 % iso-octane, with t-dibutyl disulfide and t-butyl mercaptan added to achieve 0.42 wt % sulfur and 0.005 wt % mercaptan sulfur, respectively. The composition is in the process of being updated to be more reflective of kerosene jet fuels.

3) Industrial reference solvents. Industrial solvents are relatively cheap hydrocarbon fractions, simpler than real fuels. They include aliphatics, olefins, and aromatics and have potential use as test fuels or in test fuel mixtures. A relevant, but incomplete listing is given below (all are products of Exxon Mobil Corp. Chemical).

   a) Aliphatics: Norpar, Isopar, Exxsol (all have various grades)
   b) Aromatics: Aromatic 100, Aromatic 150, Aromatic 200
   c) Olefinic: Nonenes, Tetramer K, Tetramer L, Tetramer M

4) Specific surrogate mixtures: as they are developed. Some preliminary suggestions are given later.

Properties of Interest: A preliminary list of properties defining the important characteristics of reference fuels is given below. The possibly incomplete list is intended to be inclusive – that is, not all properties will necessarily be needed for all purposes or for all reference fuels or fuel substitutes.

1) Physical and Chemical properties

   a) Chemical composition and range of variation thereof
   b) Cetane number/Octane number
   c) H/C ratio (or heat of combustion)
   d) Chemical class breakdown (paraffins, aromatics, etc.)
   e) Volatility, boiling range, molecular weight
   f) Spray-related properties (viscosity, surface tension) + density
   g) Low temperature kinetics for HCCI (*i.e.* "cool flames" region)

2) Other important characteristics:

   a) Cost
   b) Availability/storage life

Potential Surrogates for Reference Fuels: The following lists initial suggestions by breakout session participants of surrogate mixtures that may be shown to mimic reference fuels.

1) Diesel Fuel (William L. Brown)
   a) Approximately 70 % aliphatics. A mixture of cetane and hexamethyl nonane to match the Cetane number.
   b) Approximately 30 % aromatics. Initial suggestion is to use α-methylnaphthalene as the single surrogate for aromatics. Based on the most prevalent aromatic species in diesel fuels additional possible components are biphenyl, naphthalene, and diethylbenzenes.
2) Jet Fuel:
   a) Violi – two mixtures consisting of different compositions of iso-octane/methylcyclohexane/ *meta*-xylene/dodecane/tetralin/tetradecane/decane/toluene.
   b) Dryer (based on available chemical kinetic models) – A mixture of n-heptane/iso-octane/toluene/naphthalene/methylcyclohexane
3) Gasoline:
   a) Cernansky: A mixture of iso-octane/n-heptane/1-pentene/toluene.

Target Applications: In general it was felt that any central data center for the community should also include discussion of and links to target applications of the data.

B. Surrogate Fuel Selection

Reporter: Frederick L. Dryer (Princeton U.).

Participants: Thomas Allison (NIST); David Lenhert (Drexel U.); Charles K. Westbrook (LLNL).

This document summarizes the presentation to the full workshop attendance, which reports the breakout session discussions regarding the selection of surrogate fuel candidates for emulating gasoline, diesel, and JP-8 conventional fuels. Of particular interest throughout the workshop was the recent paper of Violi *et al.*[24] in which the development of a surrogate for JP-8 was described. The basic procedural strategy used for JP-8 development involved the following issues, with the specific constraints:

1. **Feasibility** – Candidates in the formula must have known detailed kinetic mechanisms.
2. **Simplicity** – Initially limited for computational capabilities to normal paraffins with less than 12 carbons, monocyclic paraffins with less than 8 carbons, and simple aromatics such as benzene, alkyl-benzenes, and naphthalene.
3. **Similarity** – The surrogate is required to match practical fuels on both physical and chemical properties:
   a. **Volatility** – boiling range and flash point;
   b. **Sooting Tendency** – smoking point and luminous number;
   c. **Gross Combustion Property Similarity** – heat of combustion, flammability limits, and laminar premixed flame mass burning rate
4. **Cost**

The specific issues itemized under each of the listed categories are those utilized by Violi et al., and generalization to other fuels require some re-working perhaps of the specific itemizations, particularly under Item 3. For example, Item **3a** might use 10 %, 50 %, and 90 % volatility issues in characterizing a gasoline surrogate mixture "boiling range" rather than a more detailed distillation curve. Similarly, gasoline surrogate octane characteristics, and cetane diesel surrogate characteristics need to be included in Item **3c** in these respective cases. Following the discussions of this workshop, there may also be a need for an Item **3d** to include similarity issues and conventional fuel responses to additives used in commercial products.   Finally, smoke point might also be replaced by other sooting characterizations in Item **3b**, derived from other standardized ASTM test procedures as well as more fundamental soot characterization methods. As further elaborated by Prof. Sarofim in his workshop discussions, the cost of pure surrogate species candidates can become prohibitive in terms of large scale testing, and so surrogate species must be chosen with an eye to both fundamental and prototype testing characterization against practical fuels

For the short term, the feasibility and simplicity issues relate to the presently available mechanistic information upon which to build more robust models for each candidate and their mixtures.   Considerations should include not only modeling elements (*i.e.*, the mechanistic

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[24] A. Violi, S. Yan, E.G. Eddings, F. Sarofim, S. Granata, T. Faravelli, E. Ranzi, *Experimental Formulation and Kinetic Model for JP-8 Surrogate Mixtures*, <u>Combustion Science And Technology</u> **174**, 399-417 (2002).

knowledge base and the thermochemical and elementary rate parameter base) but also the existing experimental database upon which to validate component and mixture physical and chemical kinetic behavior. These matters are sometimes related to the properties of the actual fuel, but may also relate to standard reference mixtures used to characterize conventional fuel behavior. For example, as mentioned by Pitz during the presentations, real gasoline does not contain n-heptane, and therefore at first appearance one might not consider it as one of the surrogate components for a gasoline surrogate. However, as it is one of the two species used in defining the octane reference scale (n-heptane and iso-octane) and as a considerable experimental database exists for its combustion and physical properties as well as for its thermochemical and kinetic parameters, it appears that n-heptane should be included as a surrogate fuel candidate.

A number of experimental/modeling studies have utilized n-heptane as a fuel to emulate diesel and gas turbine fuel combustion behavior, but the lubricity of n-heptane is insufficient for more practically oriented experimental characterizations in, for example, diesel engines. Normal decane and n-dodecane both appear as reasonable species on this basis; with more mechanistic studies presently emerging using both of these components. Neither of these larger carbon number normal paraffins have experimental or modeling databases of similar size to those available for the smaller normal and branched paraffins.

Cetane (n-hexadecane) is a normal paraffin utilized in the cetane reference fuel scale for diesel applications, but this species has received very little attention kinetically. It is also worth including it as a surrogate fuel species candidate.

Olefinic species have become more common in processed fuel organic compositions over the past decade as refining practices have progressed. Better matching some of the organic characteristics of conventional fuels may include a surrogate olefinic component, for example, in gasoline surrogate mixtures. Fewer mechanistic and experimental studies of olefinic species have been published in comparison to those on alkanes. As an example, however, Drexel University (Cernansky and co-workers) presented research that utilized 1-pentene as an olefinic component in developing a gasoline surrogate blend of reference components, toluene, and 1-pentene that would match low temperature and negative temperature coefficient kinetic behavior of gasoline. Sufficient small-fragment kinetics information exists for those species expected in 1-pentene oxidation. Therefore, the mechanistic and fundamental parameter specifications for its oxidation would be straightforward.

Whereas Violi *et al*. considered only normal paraffins in representing JP-8, the composition of surrogate gasoline mixtures must also include branched paraffins. Iso-octane, the other octane reference fuel component, may serve as the representative for this class of compounds. Additionally, Westbrook and co-workers have recently considered the varied combustion and kinetic behavior of isomers of n-heptane. These species are also reasonable candidates for investigating branching effects in gasoline surrogate mixtures. This research shows that these species can be used for building a large number of surrogate mixture characteristics that involve octane-blending effects and fuel characteristics related to disparate Research and Motor Octane.

Aromatic species must necessarily be included in surrogate candidates to represent the aromatic

character effects on auto ignition and, especially, sooting behavior. By regulation, benzene is not present in significant quantities in raw conventional fuels, but benzene and phenyl radical kinetics need to be considered because benzene and phenyl radicals are formed by various kinetic paths in the oxidation of both other aromatic components and non- aromatic components. Clearly toluene should be included as a surrogate in developing gasoline surrogate fuels, as this species is a very significant component in gasoline and a substantial (but incomplete) mechanistic database presently exists. Di-methylated single ring aromatics (xylenes) are not present in large quantities in conventional fuels, and it appears from existing experimental observations that the emission of these hydrocarbon species is primarily from raw fuel component emission, not *in situ* formation during combustion. Consideration of these compounds is likely unnecessary.

In the case of diesel and JP-8 surrogate species candidates, larger carbon number species and at least double-ring aromatics appear to be necessary surrogate components, particularly in matching volatility and sooting properties. Cetane (n-hexadecane), methyl cyclohexane, and 1-methyl naphthalene should likely all be selected as surrogate component candidates, as they are again species utilized in formulating cetane reference fuel mixtures. Violi *et al.* also considered tetralin as a surrogate candidate. Finally, Dryer noted in his workshop presentation that in a combination of engine and fundamental studies on diesel combustion and the effects of common cetane improvers, a mixture of n-hexadecane, decahydronaphthalene (decalin), and 1-methylnaphthalene was shown to closely emulate the behavior of full blend diesel fuel under the same test conditions. It appears that decalin may also be an interesting surrogate candidate to consider.

Summarizing, a first selection of surrogate candidates for covering all of the above classes of conventional fuels should include olefinic species, *e.g.*, 1-pentene; normal paraffins; *e.g.*, n-heptane, decane, dodecane, n-hexadecane; iso-paraffins, *e.g.*, heptane isomers, iso-octane; single ring aromatics, *e.g.*, toluene; multi-ring aromatics, *e.g.*, 1-methyl naphthalene, tetralin, and decalin; and cyclo-paraffins, *e.g.*, methyl cyclo hexane.

In the short term, developing chemical kinetic models on similarity and grouping methods such as those used in Violi *et al.* is a methodology to circumvent the present lack of mechanistic information and fundamental thermochemical and chemical kinetic parameters. Comprehensive, hierarchical mechanism development combined with these methods can produce initial chemical kinetic models. Automatic mechanism generation with accompanying estimation methods for the needed thermochemical and rate data can also produce the needed starting mechanism. In each case, it is beneficial to minimize the chemical kinetic model through detailed reduction methods applied over the range of parameters and conditions for which the model prediction will be constrained by comparison with experimental targets. Minimization is essential to achieving a computational efficiency required for parametric studies and the application of formal numerical analyses using sensitivity studies and other methods to study and optimize model predictive behavior. Additionally, reduction methodologies will be required to produce models that can be utilized in multidimensional applications.

In all of the above, experimental observations are required to validate the model behavior and to assist in identifying the relative significance of individual surrogate species upon various

combustion issues. Westbrook favored developing chemical kinetic models and performing analyses principally using predictions of experimental targets produced using prototype energy conversion situations, such as engines, model combustors, and rapid compression machines. While not discounting the utility of such targets, Dryer suggested that that model comparisons at this level of complexity can fail to decouple the uncertainties in the respective sub-models such that the source(s) of inadequacy in the various sub-models can be identified and mitigated. Chemical kinetic sub-model development and validation can be significantly improved by using experimental targets that essentially do not involve transport effects such as shock tubes, flow reactors, and stirred reactors, and fundamental configurations that are strongly affected by transport such as laminar premixed flames (flat flame burner studies, flame velocity determination), and laminar diffusion flame (opposed jet, stagnation, and isolated droplet configurations, including those that characterize extinction). The database of fundamental experimental targets should include results on individual surrogate components, surrogate mixtures, and conventional fuels. Experimental uncertainties of targets need to be carefully assessed and defined.

C. Essential Databases

Reporter: Jeffrey Hudgens (NIST).

Participants: Timothy Barckholtz (Exxon Mobil Corp.); Donald Burgess (NIST); Robert Huie (NIST); M. C. Lin (Emory U.); William J. Pitz (LLNL); Graham Westmacott (Reaction Design, Inc.).

This section summarizes the discussions among the above regarding the scientific and engineering community needs for databases that will enable accurate modeling of combustion processes involving real fuels, *i.e.*, gasoline, diesel, and aviation fuels. The conclusions of this breakout group were presented to the full workshop.

The goal of the combustion community is to develop computational models that can simulate the performance and emissions of engines and burners. Since state-of-the-art chemical kinetic models are constructed from reaction sets, elementary rate coefficients, and thermochemical data, the group recommended that effective service to the combustion community would be accomplished by a unified website containing the following databases:

1. **Thermochemical property data** ($\Delta_f H^o$, S^o, C_p^o, etc.) for fuel components and reaction intermediates.
   a) **Extensive compilation** of all available data**.**
   b) **Critically evaluated (recommended) data.**

2. **Elementary rate coefficients** (*k*) of reactions relevant to combustion.
   a) **Extensive compilation** of all available data**.**
   b) **Critically evaluated (recommended) data.**

3. **Chemical Kinetic Models** used within the community for combustion simulations.

a) **Tools** enabling comparisons among the chemical kinetic models.
b) **Translators** that relate the acronym labels within each database record (which, itself, contains a chemical kinetic model) to the chemical structure of each species.

In a computer simulation program the complete reaction set is the algebraic list of all stepwise chemical changes that may occur during a combustion process. The elementary rate coefficients are numbers describing the rates with which each reaction step proceeds. The thermochemical data are numbers associated with each species that are used to compute the energy release by reaction steps. Thermochemical data also assure thermodynamic consistency between forward and reverse reaction rate coefficients in thermalized systems and facilitate estimations of rate coefficients for which direct measurements are unavailable.

Currently, NIST provides substantial service to the combustion community by publishing items **1a** and **2a** through the NIST Chemical Kinetic Database[25] and the NIST Chemistry WebBook.[26] Within these databases each record provides the information needed by the user to trace the origin of the data and to evaluate the quality of each number and uncertainty. The breakout group emphatically agreed that NIST should continue to maintain these databases and add new data, as they become available.

The group identified a strong need for "critically evaluated" databases of thermochemical properties and elementary rate coefficients. The existing evaluated databases addressing combustion needs are not continually updated and do not reflect current, accepted "best values." A critically evaluated database would span a group of important combustion species. For each species a critically evaluated database would list "recommended" numbers found by identifying the best data and re-adjusting numbers (within their uncertainties) to optimize agreement among the observed and calculated exothermicities and relative reaction rates. Ideally, the existence of critically evaluated databases would greatly reduce the extensive effort required of researchers when they need to trace and ascertain the quality and uncertainty of rate coefficients and thermochemical values. The widely-used NIST databases are compilations, not evaluations, nor recommendations. It was suggested that NIST could accelerate the creation of critically evaluated databases by organizing committees drawn from the academic and other experts and facilitating communication by hosting websites and workshops. This will require the development of standardized formats or templates for reporting kinetic and modeling data.

The breakout group identified a strong need for a compilation of complete and reduced chemical kinetic models. No database devoted to chemical kinetic models is available, nor is any organization known to be assembling such a database. The need for a chemical kinetic model database is driven by the emergence of computational codes that more accurately simulate macroscopic flames by accounting for the effects of fluid dynamics and chemical reactions. Industry is increasingly adopting these codes to accelerate product development and optimization through accurate simulation of macroscopic flame behavior.

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[25] Chemical Kinetics Database on the Web, NIST, 2000 (http://kinetics.nist.gov).
[26] H.Y. Afeefy, J.F. Liebman, and S.E. Stein, "Neutral Thermochemical Data" in **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, Eds. P.J. Linstrom and W.G. Mallard, March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

The breakout group concluded that the creation of a chemical kinetic model database would benefit industry through rapid dissemination of improved models. The database would also accelerate research directed to model optimization by bringing about standards for nomenclature, notation, traceability, and communication. The present absence of such standards and the absence of a central data repository prevent facile comparison of models developed by different researchers. These absences hamper efforts to determine why two models may predict the same results under one set of conditions yet diverge as conditions change. Such comparisons are essential for identifying the absence of important elementary reactions and presence of inaccurate rate coefficients. It was suggested that NIST create this web-based database and host a workshop that will discuss and define 1) the database organization, 2) flexible reporting protocols that can accommodate the dissonant nomenclature in the community, 3) translation tools for relating acronyms to chemical structures, and 4) software tools that enable visualization of the differences among chemical kinetic models.

D. Experimental Validation Data Sets

Reporter: Nicholas Cernansky (Drexel U.).

Participants: Thomas Avedesian (Cornell U.); Kenneth Brezinsky (U. Illinois, Chicago); John Farrell (Exxon Mobil); David Leahy (Sandia); Balu Sekar (AFRL/PRTC); Mitchell D. Smooke (Yale U.).

The group not only looked at the specific issues assigned to the group, but it also looked at the big picture, as seen in the overall context of the workshop. A few key points and positions emerged from the discussions.

> 1. The underlying and driving force behind this workshop on Real Fuels and Simulation of Realistic Combustion Systems is the overarching need for energy independence and a cleaner environment. Members of the breakout group indicated that they would be willing to do their part in this pursuit and felt that this enthusiasm can be used to generate support for the activity.

> 2. There is a critical need for reference fuels (gasoline, diesel, gas turbine) and for appropriate surrogates (which may be application specific) that can be used for development and validation purposes. Addressing this need will require the active involvement and support of government agencies—particularly from the Department of Defense (DOD) and the Department of Energy (DOE)—to develop such fuels and surrogates.

> 3. DOD and DOE should begin a program to support development/creation of appropriate reference fuels and surrogates. NIST should spearhead this effort and serve as a central repository for the associated data and information, including kinetic rates, thermochemistry, transport phenomena, chemical kinetic models, and experimental validations.

4. The community knows how to evaluate fuel properties and to generate the data necessary for validation of surrogate mixtures with reference to these fuels. Depending on the specific questions/hypotheses being posed, a sequence of highly directed experiments can be conducted to provide the necessary validation data.

5. There is a suite of canonical experiments (well developed and used for many years) that can be employed to address issues associated with the behavior of realistic combustion systems and their models. Experiments using shock tubes, flow reactors, premixed flames, counter flow flames, and droplet/spray systems (to name just a few) can be conducted over appropriate ranges of T, P, equivalence ratio, etc. (even approaching practical conditions) to generate data germane to the modeling and prediction of auto-ignition, flame behavior, ignition/extinction, emissions (*e.g.*, NO_x & soot), and other phenomena in realistic combustion systems.

E. Creation of a Roadmap for Combustion Science

Reporter: Wing Tsang (NIST).

Participants: Meredith B. Colket (United Technologies Res. Ctr.), William H. Green (MIT), William Kirchhoff (DOE); Thomas Sloane (GM Res. & Dev.), M. C. Lin (Emory U.)

The goal of the breakout session was to help NIST devise a roadmap for building databases and chemical kinetic models for the combustion of real fuels, so that they may be used for CFD modeling of realistic systems. The target was transportation fuels. The elements for such an effort were outlined with general agreement that this was a desirable and achievable goal. There was general agreement that this must include the construction of detailed chemical kinetics models for transportation fuels that will permit the simulation of the combustion of gasoline, aircraft and transportation fuels. These models should be capable of reproducing chemical kinetics related issues bearing on operation, performance and emissions. It should be reducible for use in CFD codes and a target date of 2007 was suggested when the work will become available for general use.

A listing of specific tasks was given. These include the selection of surrogate fuels and the range of composition to be used and the particular combustion kinetics features that models should seek to reproduce. The nature of the data to be generated in the context of surrogates and actual fuels (reference fuels) must be defined. The effort should include programs for fundamental measurements, theoretical modeling, validation, informatics, tool development and chemical kinetic model reduction. Although it was agreed the that a NIST derived database will be a valuable contribution to combustion technology, the full benefits of the technology can only be achieved in the context of a combustion kinetics information center to serve as a clearing house for all aspects of work tied to the use of fundamental physico-chemical data in combustion applications.

It is proposed that the various components for the information center have designated team

leaders and that individual research plans and schedules should be identified and formulated. NIST, drawing upon the expertise of the community should articulate and communicate a high level plan. There is a need to sort out the mechanisms and interactions for the central clearing house and NIST/CMCS/PrIMe.

It also became apparent that the combustion community was badly in need of a roadmap in a more general sense. In particular there is the need to identify and agree on longer-term objectives and the strategies to focus the community activities in this direction. It was agreed that this was a remarkable deficiency of the combustion community since practically all successful larger scale projects have well defined goals and roadmaps on how to get there. Examples cited include the human genome project, the astrophysics community, the stratospheric ozone program and the high-energy physics community. These plans should be carried out in the context of no extra funding. It is an activity that should draw upon the expertise of the entire combustion community. As with the case for the NIST database efforts, a key motivation is the development of CFD codes that have the potential of projecting laboratory results directly into the real world. The HCCI engine was cited as an example where a combination of laboratory experiments and CFD simulations may lead to large savings in energy without offsetting increases in undesirable emissions.

GLOSSARY

The following glossary contains definitions of terms as used in this document. Where possible, the International Union of Pure and Applied Chemistry (IUPAC) definition is used.[27]

Emissions:
- **NO_x** – A short-hand term used to denote collectively all oxides of nitrogen.
- **Polycyclic aromatic hydrocarbon** or **PAH** – Large molecular weight hydrocarbon molecules, composed mainly of carbon and hydrogen, which have chemical structures containing many aromatic and non-aromatic carbon ring groups.
- **Particulate Matter** or **PM** (both terms are used in atmospheric chemistry) – A general term used to describe airborne solid or liquid particles of all sizes.
- **PM_{10}** – An acronym for particles $\leq$ 10 μm (10 microns) diameter. The National Ambient Air Quality Standards (NAAQS) for Particulate Matter (PM) regulation[14] sets the ambient air PM_{10} concentration to less than 150 μg/m^3 over a 24 hour period and an annual average of 50 μg/m^3 annual average.
- **$PM_{2.5}$** – An acronym for particles $\leq$ 2.5 μm (2.5 microns) diameter. The National Ambient Air Quality Standards (NAAQS) for Particulate Matter (PM) regulation[14] sets the ambient air PM_{10} concentration to less than 65 μg/m^3 over a 24 hour period and an annual average of 15 μg/m^3 annual average.
- **Soot** – A generic term for particulate matter composed mainly of carbon. Current data indicate that soot is formed from reactions involving PAH species.
- **SO_x** – A short-hand term used to denote collectively all oxides of sulfur including SO_2.

Fuels:
- **Cetane Number** – A value derived from the measured ignition delay observed for a diesel fuel. This is the time period between the start of injection and start of combustion (ignition) of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. (Cetane number is often mistaken as a measure of fuel quality.)
- **Octane Number** – A value used to indicate the resistance of a motor fuel to knock. Octane numbers are based on a scale on which isooctane is 100 (minimal knock) and heptane is 0 (bad knock).

Model:
- **Simulation Model** – A collection of algebraic equations and associated coefficients that describes the transport properties of the chemical species, the fluid dynamic boundary conditions, the system geometry, and the chemical kinetic model.
- **Chemical Kinetic Model** – A collection of symbolic equations and numbers comprising the reaction set, the associated rate coefficients, and the thermochemical properties of species.
- **Reduced Chemical Kinetic Model** – A collection of symbolic equations and numbers comprising the reduced reaction set, the associated rate coefficients, and the thermochemical properties of species. The reduced chemical kinetic model may contain lumped reactions and lumped rate coefficients.

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[27] International Union of Pure and Applied Chemistry, *IUPAC Compendium of Chemical Terminology,* Oct 2003 (http://www.iupac.org/publications/compendium/index.html).

Organizations:

- **CMCS** – Collaboratory for Multi-Scale Chemical Science.
- **DOD** – Department of Defense.
- **DOE** – Department of Energy.
- **NIST** – National Institute of Standards and Technology.

Rate Coefficient:

- **Elementary Rate Coefficient** – A number describing the rate at which an elementary reaction step proceeds.
- **Lumped Rate Coefficient** – A number describing the rate at which a lumped reaction proceeds.

Reaction:

- **Chemical Reaction** – A chemical reaction is a process that results in the interconversion of chemical species. Chemical reactions may be elementary reactions or stepwise reactions.
- **Elementary Reaction** – An algebraic representation of a chemical transformation for which no *reaction intermediates* have been detected or need to be postulated in order to describe the chemical reaction on a molecular scale. An elementary reaction is assumed to occur in a single step and to pass through (at most) a single *transition state*.
- **Isomerization Reaction** – A chemical reaction, the principal product of which is isomeric with the principal reactant. Isomeric species are molecular entities that have the same stoichiometric molecular formula, but differ with respect to the connectivities of the atoms, their respective bond orders, or the spatial arrangement of the atoms.
- **Lumped Reaction** – A collection of elementary reactions expressed as an "equivalent" apparent single-step reaction. A lumped reaction may be a stepwise reaction, involving a consecutive set of elementary reactions, the simplest example being $A \rightarrow I \rightarrow B$, where I is a steady state intermediate. A lumped reaction may also be a set of related, but dissimilar reactions, operating as alternative or parallel pathways, or $A \rightarrow \{I_n\} \rightarrow B$, where $\{I_n\}$ represents the set of parallel pathways. A lumped reaction may also be a set of similar reactions, operating collectively, on similar molecular species, or $\{A\} \rightarrow \{I\} \rightarrow \{B\}$ where $\{A\}$, $\{I\}$, and $\{B\}$ are sets of similar reactants, intermediates, and products, respectively.
- **Reaction Intermediate** – A reaction intermediate is a molecular entity with a lifetime appreciably longer than a molecular vibration (corresponding to a local potential energy minimum of depth greater than RT) that is formed from the reactants and reacts further to give the products of a chemical reaction.
- **Transition State** – A transition state is a state of more positive molar Gibbs energy between the reactants and the products through which an assembly of atoms must pass on going from reactants to products in either direction.

Reaction Set:

- **Complete Reaction Set (or Reaction Sequence)** – A list of elementary reactions comprising all conceivable combinations of reactants and products with no judgment of their importance. This is a theoretical construct that is probably never known for any complex system.
- **Initial Reaction Set** – An algebraic list of stepwise chemical changes believed important to a combustion process in the absence validation or testing.
- **Reduced Reaction Set** – An abridged algebraic list of stepwise chemical changes abstracted from the initial or complete reaction set that attempts to contain the minimal list of reactions required to capture the relevant chemistry for a particular problem and set of conditions. A reduced reaction set may contain lumped reactions; hence, the list of rate coefficients may include lumped rate coefficients.

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