II.4.5 Process Informatics Model (PrIMe): A Systematic Approach to Building Combustion Chemistry Models

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Introduction

Development of new energy-efficient low-emitting combustion technologies requires models for the combustion process that combine sub-models for combustion chemistry, heat and mass transfer, and fluid mechanics. A major limitation in developing these process models is the availability of accurate, validated, and computational tractable combustion chemistry models. This research is aimed at the development of a new approach for constructing and reducing models of complex chemical reactions. It has been termed *Process Informatics.* This endeavor is made possible by recent advances in computer science that allow assembly and manipulation of large amounts of data that may be scattered over different sources using Web-based computer networks. The goal is to convert combustion chemistry model building into science, to automate the methodology, and to make the information available in a prompt and convenient form on the Internet for researchers and designers of combustion equipment.

Background

A good deal of the effort in this project is in essence political. That is, it involves community organization in the combustion research community and it requires the acceptance of a somewhat different paradigm than the standard in the community. External developments in the field in the past year involve several workshops and symposia in which the PrIMe idea has been gaining currency. Presentations by the PI, Professor Golden, as well as American collaborators at UC Berkeley, SRI International and international collaborators from the UK and the Continent and other such developments are discussed below in the "Results" section of this report.

In addition, the National Institute of Standards and Technology (NIST) has agreed to be the permanent host for the PrIMe Library and eventually for the computer based tools required for model development. Some of these tools are being developed in a Sandia National laboratory led effort called, Collaboratory for Multi-scale Chemical Science (CMCS). Initially PrIMe will be available at Sandia as well. Professor Golden is a member of the Advisory Board of CMCS. Interest in industry is picking up with the attached endorsement from a major engine manufacturer. (Final company approvals are still pending, so the company name is omitted here.)

Results

The first goal of the PrIMe project is the creation of a database or library, sometimes even referred to as a warehouse for combustion data. The goal is an agreed upon, evaluated by the community, updated in a timely fashion, data library. The library is open, accessible to all and contains, beside the agreed upon values, all data and all

dissents from the consensus evaluation. There are some models for this type of activity, Professor Golden has been a member of the NASA/JPL Panel that evaluates rate data for atmospheric modeling, but the goal here is more far-reaching. All background information used in the evaluations will be available.

This program requires bringing a large community together and it has been somewhat slower than hoped. Professor Golden, Professor Michael Frenklach of the University of California, Berkeley and Professor Michael Pilling of Leeds University have acted as a "troika" in engaging the community. Prominent additions to the active team include Dr. Wing Tsang of NIST, Professor William Green of MIT and Dr. Jeremy Frey of The University of Southampton, UK. Many other workers have expressed their willingness to participate. In addition to the normal human factors, there has been a good deal of effort spent on understanding intellectual property matters.

The first informal gathering of possible PrIMe participants took place during the International symposium on Combustion in Sapporo, Japan in August 2002.

Professor Frenklach made a presentation at the DOE Basic Energy Sciences Contractor's Meeting in Lake Tahoe, CA in May 2003 that outlined possibilities associated with this project. He and colleagues have published an article[1] in December 2003 that points out the large amount of information available from extant experiments that is not being accessed as result of lack of familiarity with many statistical procedures that can now be accomplished with relative ease.

A meeting at NIST in September 2003 aimed at establishing a data base for "Real Fuels" served as a venue for discussions that resulted in NIST becoming the home for PrIMe. At that meeting Professor Golden explained the procedures used to develop the widely used Natural Gas combustion mechanism, known as GRI-Mech. He pointed out all the ways this could be better accomplished once PrIMe is underway. Professor Frenklach, once again described the future of process modeling.

In March 2004 there was a symposium in the Fuel Section of the National American Chemical Society Meeting in Annaheim, CA. Two days of speakers discussed combustion modeling and PrIMe was a central focus in several presentations. (The agenda is attached and those presentations directly involving PrIMe related activities are highlighted.) A presentation based on collaboration with Professor William Lester, Professor Frenklach and students at UC Berkeley, includes Professor Golden and is listed below.

At this time all the background data used in developing the GRI-Mech model has been cast into XML format and the very large amount of data available at Leeds University will be translated and made available for PrIMe.

Dr. Gregory P. Smith of SRI International, Menlo Park, CA has together with Professor Frenklach and colleagues at Berkeley, applied the tools of process informatics

to understanding a dichotomy in the understanding of OH chemistry in the upper stratosphere and the lower mesosphere. A paper is being prepared.[2]

Progress

In the instructions for this report we were asked to provide a discussion of the progress achieved to date toward the goal of developing the basis for technology options that could lead to substantial reductions in emissions of greenhouse gases that result from energy use. In other words, describe the potential impact of the research, if successful, on greenhouse gas emissions at a global scale.

This is a far-reaching goal. The best illustration of the future use of PrIMe for this purpose is found in the engine manufacturer letter of support. The goal is to make modeling and design of combustion driven devices easier and accurate, with the goal of energy efficiency and minimal pollution of all kinds.

Future Plans

This research project is really the tip of an iceberg. There will be ongoing work in codification of data in XML format and I putting together the evaluation teams. There will be an ongoing attempt to secure funding for a large scale collaborative effort. Colleagues at NIST are spearheading an effort to secure NSF support. Hopefully the modest support for Professor Golden will allow his continued participation.

Publications and Presentations

1. Evaluating and Codifying Data for Engineering Applications
   Presented by David M. Golden at NIST Workshop on Real Fuels, September 2003
2. Quantum Monte Carlo study of the thermochemistry of small hydrocarbons Alexander C. Kollias, Dominik Domin, Michael Frenklach, David M. Golden, William A. Lester Jr.
   Presented by Alexander C. Kollias at the American Chemical Society National Meeting, March 2004

References

1. Collaborative data processing in developing predictive models of complex reaction systems
   Michael Frenklach*, Andrew Packard, Pete Seiler, Ryan Feeley; Int. J. Chem . Kinetics 36, 2004, Pages: 57-66
2. A System Analysis Approach for Atmospheric Observations and Models: the Mesospheric HOx Dilemma
   Gregory P. Smith, Michael Frenklach, Ryan Feeley, Andrew Packard, and Peter Seiler

Contact

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Attachments

I: Engine Manufacturing Company Support for PrIMe
II: NIST Announcement of PrIMe Involvement
III: Agenda from Fuel Chemistry Symposium at ACS National Meeting March 2004

Attachment I: Engine Manufacturing Company Support for PrIMe

To whom it may concern: (This should be changed to the specific individuals that we need to target. We have not determined who they are yet.)

There is a proposed project, called PrIMe, with NIST and a few other individuals from universities and national laboratories that will be of utmost importance to us at this company. The importance is due to our efforts to meet the 2010 emission regulations. This is a very short time frame for technology that is highly new and innovative. It has to be highly innovative and new because of the super low levels of regulation required. In recent years, the levels for exhaust emissions required by law have been dropping at a rapid rate. This is going to require some extreme changes, and we need your help.

This company, like all manufacturers of heavy-duty engines, makes extensive use of computer simulations; but we need much more than just new and more capable computers. There are fundamental areas of science in which we are desperate for better definition. One of the areas is the chemical process that controls the generation of the emission species. We need a much better definition of the reaction paths from diesel fuel to products of combustion, including nitrogen oxides and particulates (soot). We recently attended a meeting at NIST where we discussed this problem, and were concerned with the lack of support received by scientists working in this area. However, we were able to put together a program that we feel is excellent and will go a long way to help us in this endeavor. Now we must ensure that this program receives the funding and support that it needs. We wish we had this 15 years ago, but we did not.

The fact that NIST has joined PrIMe is one of the essential steps necessary to insure that we obtain accurate models, so we endorse this action by NIST.

We understand that our competitors overseas are ahead of us in the US in these areas. We do not mind competing with them on an equal basis, but it is unnerving to compete while our science is behind.

The people that we consider to be essential to this project include:

Michael Frenklach, U. C. Berkley and Lawrence Berkley Laboratory
David Golden, Stanford U.
Wing Tsang, NIST

There may be others, but the people listed above are best at answering whom they should be. We are prepared to cooperate with them in anyway we can.

Thank you for your consideration,

Attachment II: NIST Announcement of PrIMe Involvement

NIST joins the PrIMe Initiative within the combustion research community

The PrIMe 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. NIST has recently joined the PrIMe initiative. In its initial focus NIST will seek to enable achievement of PrIMe's first objective, i.e. the creation of the PrIMe Data Warehouse. This warehouse is visualized as a comprehensive repository of all data relevant to modeling combustion processes. Development of this library is a community project involving submission and evaluation of the data, often presented in the form of a "mechanism", describing various combustion scenarios. Evaluation at this stage is concerned with the data required for quantitatively describing the chemical reactions within the mechanism 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.

NIST's commitment to the PrIMe initiative envisions creating new paradigms for scientific collaboration. This new paradigm relies on an information technology infrastructure which is currently under development in the Collaboratory for Multiscale Chemical Science (CMCS) and our efforts will rely on CMCS infrastructure and use their facilities. As a first step, the NIST Gas Phase Chemical Kinetics Database and the GRI-Mech 3.0 dataset, a consensus mechanism for combustion of C1 and C2 hydrocarbons, will be incorporated into the PrIMe/NIST Data Warehouse. Harmonization of data schema and XML data exchange standards and development of selected IT tools will be required in this first step. A data submission and a data query interface also will be developed to facilitate population of the Warehouse and open access to these data by the research community. Although the PrIMe/NIST Data Warehouse currently is focused on the combustion of hydrocarbon fuels, the Warehouse could logically extend to include other areas such as atmospheric chemistry. The new collaborative paradigm envisioned for combustion research may well benefit other research areas and increased information exchange amongst many diverse communities should benefit all.

It is planned to have an alpha version of the PrIMe/NIST Data Warehouse operational by the end of March 2004.

Attachment III:
Agenda from Fuel Chemistry Symposium at ACS National Meeting March 2004

Molecular Modeling and Reaction Chemistry

Organizer:		Hai Wang
Organizer, Presiding:		Tim Barckholtz
8:00 AM		Introductory Remarks
8:10 AM	115	Detailed chemical kinetic modeling: Is there life after GRI-Mech 3.0? Henry J. Curran
9:00 AM	116	Efficient lumping technique for the automatic generation of n-heptane and iso-octane oxidation mechanism Syed Sayeed Ahmed, Gladys Moréc, Thomas Zeuch, Fabian Mauss
9:25 AM	117	Automatic optimization of detailed kinetic mechanism for HCCI-engine simulation Raffaella Bellanca, Fabian Mauss, Hai Wang
9:50 AM	118	Development and use of rate-constrained chemical equilibrium with HCCI combustion modeling Scott B. Fiveland, Chris Rutland WITHDRAWN
10:15 AM		Intermission
10:25 AM	119	Surface reactivity as a many body multiscale problem Ashish B Mhadeshwar, Jeff Ludwig, Abhijit Chatterjee, Dionisios G Vlachos
11:05 AM	120	Importance of gas phase kinetics within the anode channel of a solid oxide fuel cell Chad Sheng, Anthony M. Dean
11:45 AM	121	Computational studies of boron/nitrogen and aluminum/nitrogen compounds for chemical hydrogen storage Maciej Gutowski, Tom Autrey
Presiding:		Michael Frenklach
1:30 PM	139	Developing and using mechanisms for the oxidation of organic compounds in the atmosphere Michael J. Pilling
2:20 PM	140	Ab initio study of the oxidation of NCN by O_2 R. S. Zhu, M. C. Lin
2:45 PM	141	The molecular origins of NO selectivity in the thermal reduction of NO_x by NH_3 Donghai Sun, W. F. Schneider, J. B. Adams, D Sengupta
3:05 PM		Intermission
3:20 PM	142	Computer aided design of complex chemical mechanisms for combustion applications Fabian Mauss
4:10 PM	143	New methods for predictive chemical kinetics William H Green Jr., Binita Bhattacharjee, Oluwayemisi Oluwole, Jing Song, R. Sumathi, Catherina D Wijaya, Hsi-Wu Wong, Paul E. Yelvington, Joanna Yu
4:35 PM	144	Pressure-dependent automated mechanism generation: Systematic models for difficult systems David M. Matheu, Anthony M. Dean, Jeffrey M. Grenda
5:00 PM	145	Simulation of light petroleum fractions Tareq A. Albahri
Presiding:		Anthony M. Dean
8:00 AM	168	Optimization and consistency of a reaction dataset Michael Frenklach, Ryan Feeley, Andrew Packard, Pete Seiler

8:40 AM	169	Reactivity extrapolation from small to large molecular systems via isodesmic reactions for transition states (RESLIR) Vadim D. Knyazev
9:05 AM	170	Methodology for the modeling of chemical reactions on accurate potential energy surfaces Michael R. Salazar
9:30 AM		Intermission
9:40 AM	171	The high temperature decomposition of hexyl radicals
		Wing Tsang
10:05 AM	172	Multi-channel chemically activated reactions: Comparison of Troe's weak collision model and solution of collisional energy transfer by Monte Carlo method Ameya V. Joshi, Scott G. Davis, Hai Wang
10:30 AM	173	A study on the initial product channels of cyclohexane pyrolysis Marina Braun-Unkhoff, C. Naumann, Peter Frank
10:55 AM	174	Quantum Monte Carlo study of the thermochemistry of small hydrocarbons Alexander C. Kollias, Dominik Domin, Michael Frenklach, David M. Golden, William A. Lester Jr.
11:20 AM	175	Thermodynamics of Jahn-Teller molecules Timothy A. Barckholtz
Organizer, Presiding:		Hai Wang
1:00 PM	192	Reaction paths, kinetics and thermochemical properties in the dimethylsulfide radical reaction with O2: CH3SC·H2 + O2 Joseph W. Bozzelli, Fei Jin
1:25 PM	193	Modeling the reaction of C2H5 + O2 Chitralkumar V. Naik, Hans-Heinrich Carstensen, Anthony M. Dean
1:50 PM	194	Thermochemical and kinetic analysis of the allyl radical with O2 reaction system Joseph W. Bozzelli, Jongwoo Lee
2:15 PM	195	Computational study of the oxygen initiated decomposition of 2-oxepinoxy radical John K. Merle, Christopher M. Hadad
2:40 PM	196	Hydrogen atom catalyzed isomerization of aromatic compounds Mark Nimlos, Jonathan Filley, J. Thomas Mckinnon
3:05 PM		Intermission
3:15 PM	197	Combination and disproportionation reactions of alkyl radicals: An ab initio kinetics study for $CH_3 + C_2H_5$R. S. Zhu, Z. F. Xu, M. C. Lin
3:40 PM	198	Ab initio quantum chemical studies of hydrogen abstraction reactions of hydrocarbons David W. Ewing, Michael J. Manka
4:05 PM	199	Methyl radical and shift reactions with aliphatic and aromatic hydrocarbons: Thermochemical properties, reaction paths, and kinetic parameters Leonhard K. Rutz, Henning Bockhorn, Joseph W. Bozzelli
4:30 PM	200	Theoretical study on the mechanism of Ni(d10 1S)+CO2+3H2→NiO+CH4+H2O reaction Changwei Hu, Song Qin, Anmin Tian