3rd International Workshop On CHEMKIN In Combustion

proceedings

Sapporo, Japan

July 21, 2002

Sponsored by:
Department of Energy
Sandia National Laboratories/CA
and Reaction Design

Dear Friends,

As the Program Manager for combustion activities in the US Department of Energy's Office of Industrial Technologies, I was pleased to provide support for this third in the series of International Symposia on CHEMKIN in Combustion which took place in Sapporo, Japan

As indicated in past Symposia, I continue to believe that there is a need for the appropriate application of computational tools to the development of advanced combustion systems. The increasing competitive and regulatory pressures that industry faces require the rapid and cost-effective development of burners and related equipment with performance that could only have been imagined only a decade ago. Tools such as CHEMKIN have been central in moving combustion technologies into the 21st century.

But to continue to successfully apply tools like CHEMKIN, we must continually assess where we are and where we want to go. This is the reason behind Symposia like this. It was a *working* meeting, where all participants were encouraged to share their perspective. Only through the open exchange of views and the free exploration of possible new directions can we hope to continue to get the most from the application of our understanding.

I trust that you found the Symposium worthwhile.

Bob Gemmer

Robert Gemmer
Combustion Program Manager
Office of Industrial Technologies
US Department of Energy

Introduction

The Third International Workshop on CHEMKIN in Combustion was held at Hokkaido University in Sapporo, Japan, July 21, 2002. This was immediately prior to the 29th International Symposium on Combustion in the same city.

In the first 20 years of its existence, CHEMKIN has enabled significant advances in combustion modeling. Approximately seventy people attended the daylong Workshop. Their purpose was to exchange ideas related not only to combustion modeling but also to modeling chemical systems in general. It is hoped the Workshop helped participants expand the application of CHEMKIN-related modeling approaches in their own research and educational activities.

The Workshop featured ten invited talks and much lively discussion. These Proceedings record only the invited presentations; they divide into four groups. The first presentation reports the status and plans for the commercial version of CHEMKIN. This is the software distributed by Reaction Design under its exclusive license from Sandia National Laboratories. The second and third group of talks addresses fundamental issues in research and industrial applications. The final group of two talks focused on CHEMKIN in education

The Symposium was organized by Bob Gallagher from Sandia and Ellen Meeks from Reaction Design. Hokkaido University was a gracious and helpful host; particular thanks are due to Professor Osamu Fujita and Dr. Tsuyoshi Totani. The Combustion Institute and the organizers of the 29th Combustion Symposium shared their resources and lent valuable advice; thanks are due especially to Sue Terpack. The considerable preparation required for such a meeting would not have been possible without the dedicated assistance of the Workshop secretary, Deanna Agosta-Lazares.

The Workshop was sponsored by the United States Department of Energy's Office of Industrial Technology, by Sandia National Laboratories' Combustion Research Facility, and by Reaction Design.

It is anticipated a fourth Workshop will be held in conjunction with the 30th International Symposium on Combustion in Chicago in 2004.

Bob Gallagher

Bob Gallagher
Combustion Research Facility
Sandia National Laboratories

3rd International Workshop On CHEMKIN In Combustion

Agenda

9:00am	Opening Remarks	Bob Gallagher Sandia
9:15am	Recent CHEMKIN Developments and Future Plans	Ellen Meeks Reaction Design

Research and Industrial Applications, Session I, Chair: Steve Niksa, Niksa Energy Associates

10:00am	Modeling Needs and Directions for Solid-Oxide Fuel Cells	Professor Bob Kee Colorado School of Mines
10:30am	Probing Reaction Mechanisms with CHEMKIN III	Professor Ken Brezhinsky University of Illinois, Chicago
11:00am	CHEMKIN-Based Simulations of Large Scale Pulverized Fuel Flames	Steve Niksa Niksa Energy Associates
11:30	Investigation of Engine Knock by Zonal and In-Cylinder Modeling	Shahrokh Hajireza Saab
Noon	Lunch	

Research and Industrial Applications, Session II, Chair: Bill Pitz, LLNL

1:00pm	Mechanism Development Using RRKM Theory	Professor Miyoshi University of Tokyo
1:30pm	Dimethylether (DME) in HCCI Engines	Professor Tezaki University of Tokyo
2:00pm	Soot Modeling	Professor Arvind Atreya University of Michigan

CHEMKIN in Education, Chair: Professor Koshi, University of Tokyo

2:30pm	Recent Experience with CHEMKIN in Education	Professor Hong Im University of Michigan
3:00pm	Recent Experience with CHEMKIN in Education	Professor Bob Dibble UC Berkeley
3:30pm	General Discussion	
4:00pm	Brief Closing Remarks	

Status of CHEMKIN

Ellen Meeks

REACTION DESIGN

3rd International Workshop on CHEMKIN in Combustion
July 21, 2002

Outline

- What’s new at Reaction Design
- Status of the CHEMKIN Collection
- What’s new in CHEMKIN Release 3.7
- Status of the CHEMKIN Plug-in to STAR-CD
- Reaction Design academic programs

What’s New at Reaction Design

Reaction Design -- Objectives

- Reduce time & effort for reacting flow simulations
  - User interface & post-processing
  - Mechanism development / analysis tools
- Develop hierarchy of models for industrial applications
  - Link CFD to CHEMKIN technology
    - » STAR-CD
    - » CFD-ACE+
  - New reactor models to address different flow regimes
- Customize for application to today's industry problems
  - Internal combustion engine
  - Gas turbine
  - After-treatment
  - Catalytic conversion
- Assist customers in obtaining mechanism data

New People at Reaction Design

- Chen-Pang Chou, Application Engineer
  - Developing and expanding combustion capabilities
- Pauline Ho, Senior Scientist
  - Formerly at Sandia National Labs
  - Building RD’s mechanism development services business
- Steve Miller, Software Strategist
  - 20 yrs of experience in scientific software engineering
  - Developing long-term strategy for RD software architecture
- Herman De Meyer, Chief Engineer
  - Formerly at Bayer Chemical
  - Building RD’s Chemical Industry Services business
- Graham Westmacott, V.P., Sales & Marketing
  - Formerly at AEA
  - Building CHEMKIN’s global market
- Kevin de la Torre, Chief Financial Officer

Expanded global presence

- New Reaction Design office in Japan
  - Reaction Design Japan, KK opened 7-1-2002
  - Dr. Y. Watanabe, President of RDJ, KK
    - 5 years experience with CHEMKIN
    - 15+ years experience with computational chemistry methods
- Office in Belgium
  - Services business with focus on chemical industry
  - Dr. H. De Meyer, Chief Engineer
    - 20+ years experience with reactor process simulation
- CHEMKIN Distributors
  - Japan: CD adapco Japan
  - Korea: Reaction Engineering Korea
  - Europe: CD adapco Group

Continuous improvement of tech support

- Depth of team has increased dramatically with recent hires
- New corporate resource management (CRM) system for sales & support
  - Better tracking of customers and customer issues
- Web-based system allows tech support engineers to participate from around the world
- Searchable knowledgebase provides quick solutions to common problems

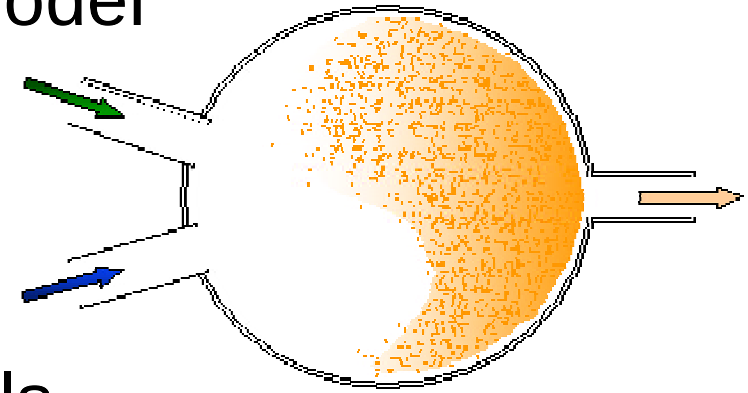
Highlights of CHEMKIN development over past few years

- Improved user friendliness
  - – Dynamic memory allocation (no need to compile)
  - – Built-in post-processing
- Expanded Applications
  - – Transient stirred reactor, HCCI Engine model, Plasma (AURORA)
  - – Plug-flow with packed-bed capability (PLUG)
  - – Opposed-flow diffusion flame (planar and axisymmetric) (OPPDIF)
- New kinetics options
  - – Surface-chemistry Applications (SPIN, CRESLAF, PLUG)
  - – Global reaction rate expressions
  - – Chebyshev polynomial fits
- New Capabilities and Flexibility
  - – Extensive heat-transfer options for all applications
  - – Specified time and distance profile options
- Improved Solvers and Algorithms

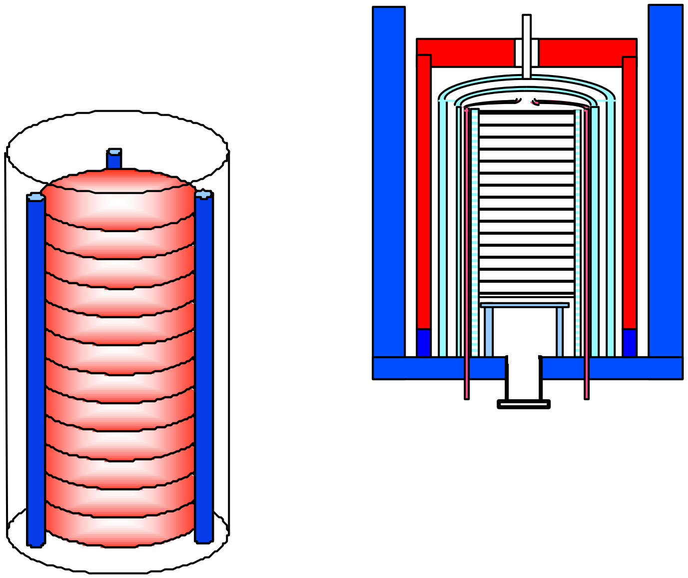
What’s New in CHEMKIN Collection 3.7

New Applications

- Partially Stirred Reactor Model
  - Mixing and kinetics
  - Turbulent flows

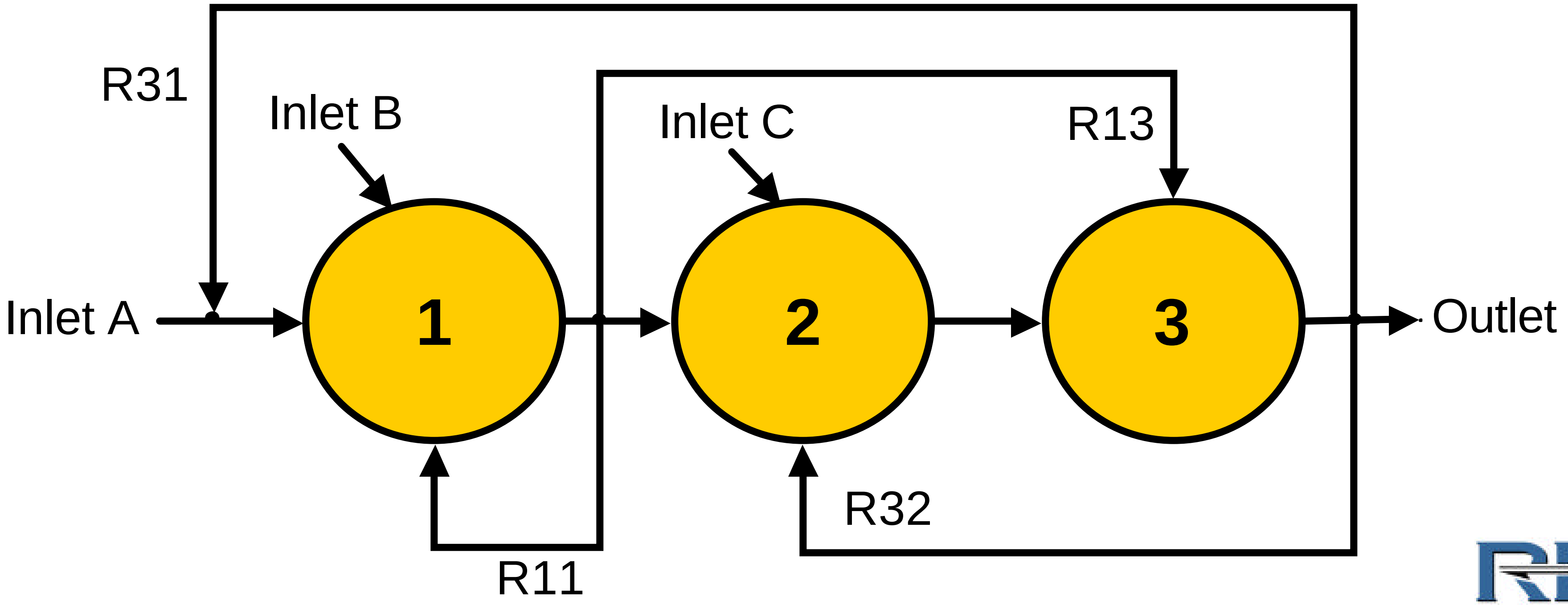


- Batch Furnace CVD Models
  - TWAFER: temperatures
  - OVEND: deposition

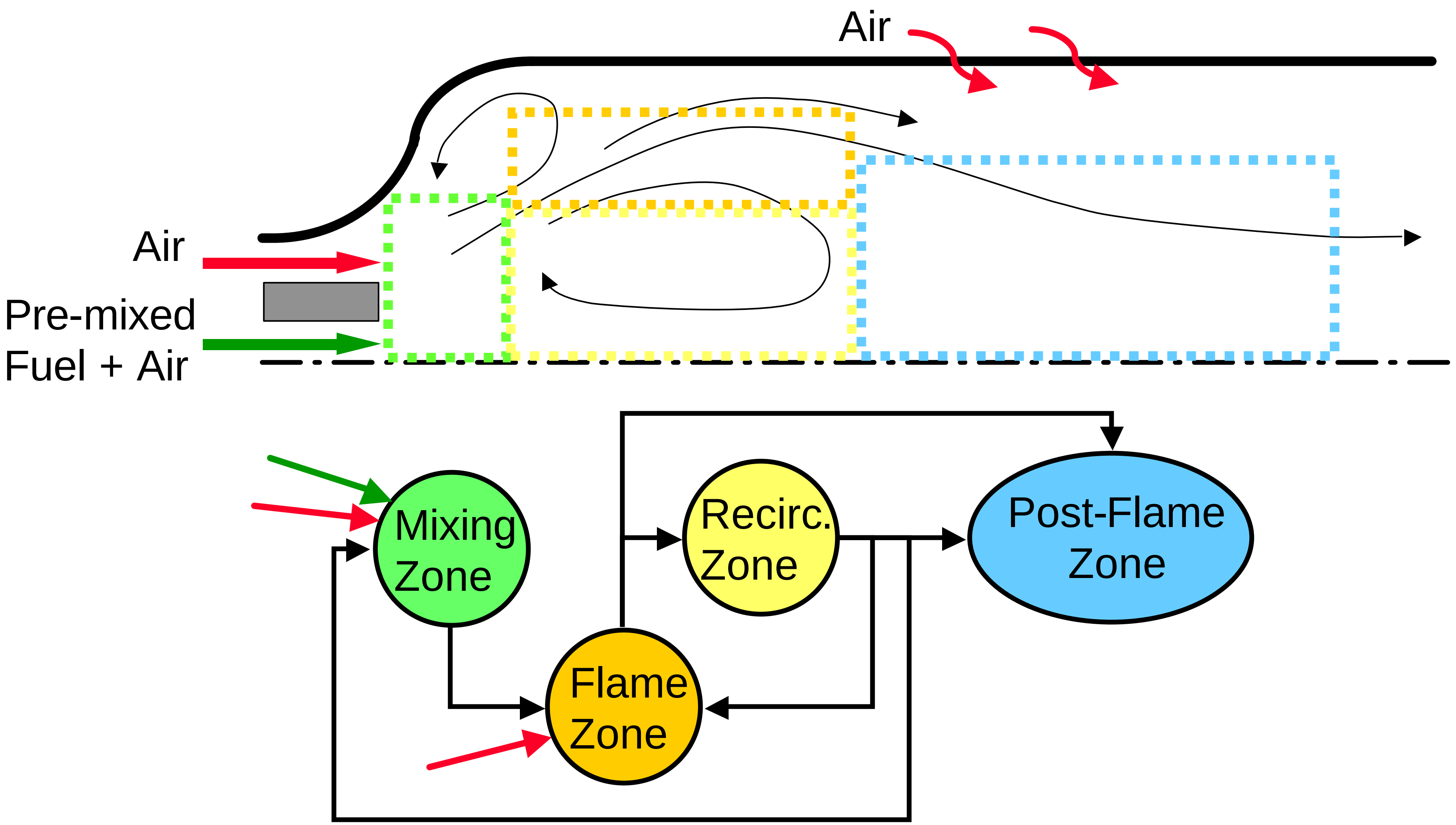


New Reactor Network Capability in AURORA

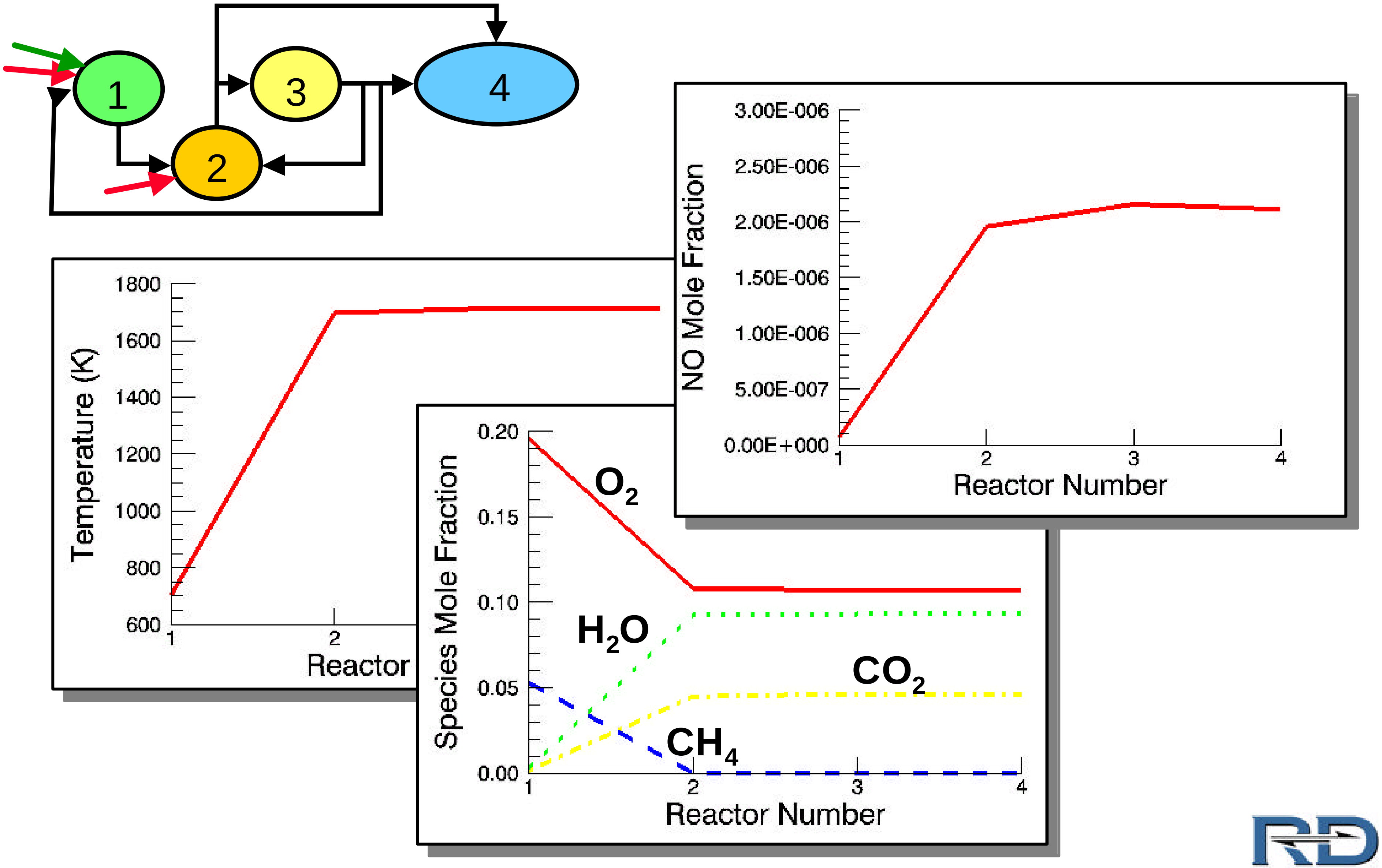
- Transient or Steady-state
- Multiple inlet streams
  - Different composition, Temperature, flow rate
- Recycle streams between reactors
  - User-specified recycle fractions & paths
- Perfectly stirred reactor elements



A gas turbine combustor may be modeled with a reactor network



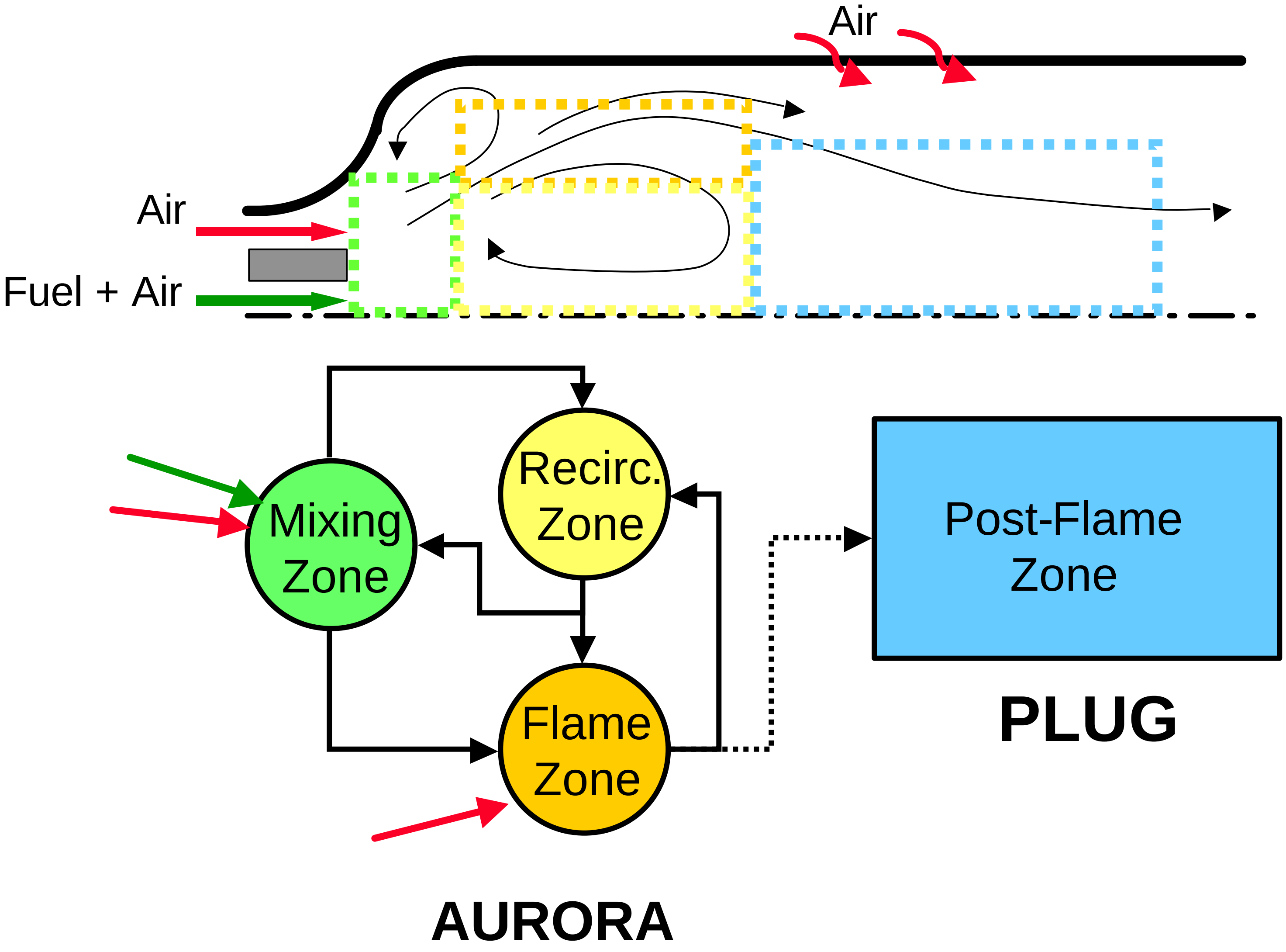
Results from 4-Reactor network



New XML-based Common Data Format

- Each Application can be initialized with a solution from any other Application
  - Like restart capability but more general
  - Facilitates external networking of Applications
- More options available for Post-processing
  - Units conversions
    - SI or cgs options
    - Extensive options for linear growth-rates
  - Derived calculations
    - Rates of production contributions
    - Emissions indices
- More robust processing of data
  - XML Parser technology
  - Improved consistency in data handling

A plug-flow reactor may be added to the end of a reactor network, using new initialization



Air

Air

Fuel + Air

Mixing Zone

Recirc. Zone

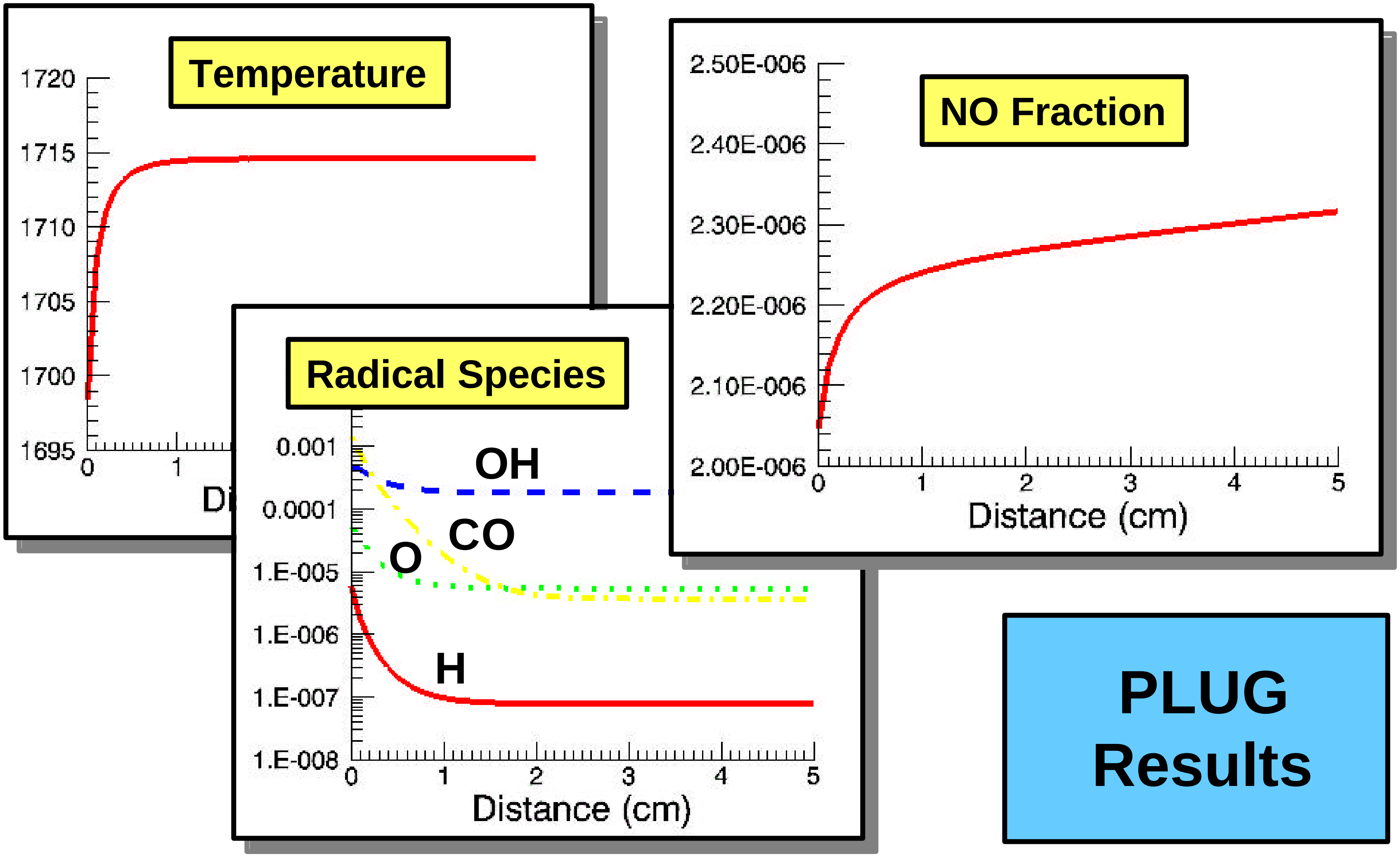
Flame Zone

Post-Flame Zone

PLUG

AURORA

Using PLUG for post-flame provides more accurate prediction of emissions



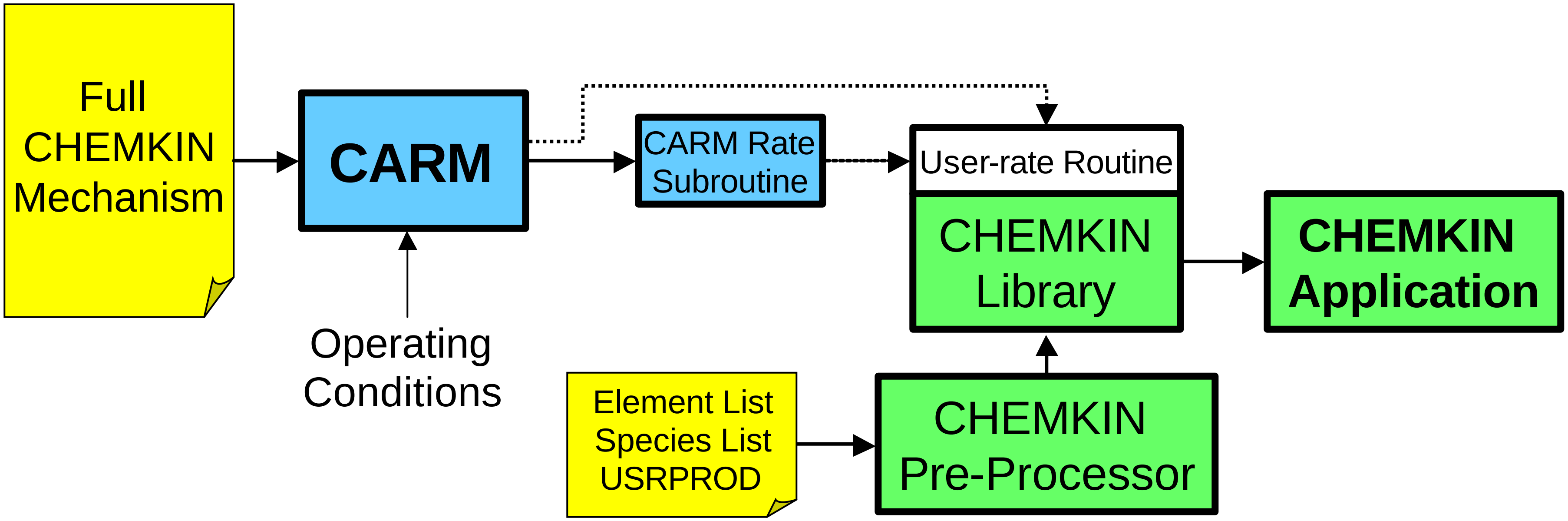
PLUG Results

Added flexibility in user-rate specifications

- Option for user programming to specify the rate-of-progress for an individual reaction (USRPROG)
  - Allows non-standard Langmuir-Hinshelwood expressions, for example
  - Global rate expressions with complex dependencies
- Option for user programming to replace all species net rates-of-production (USRPROD)
  - Facilitates links to mechanism reduction tools
  - Facilitates testing & comparison for use in CFD

Example of mechanism reduction tool

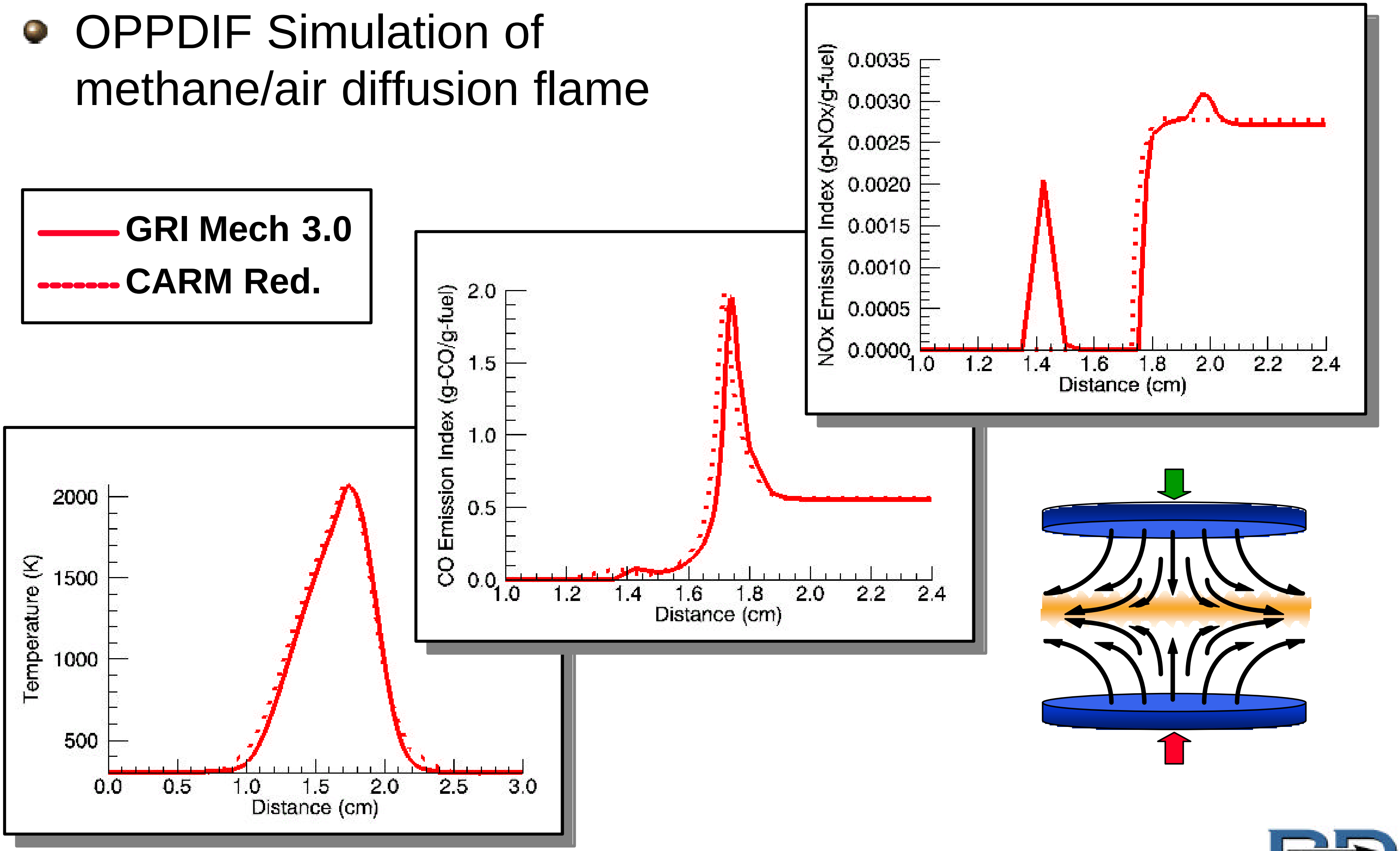
- Prof. J. Y. Chen at UC Berkeley developed Computer-Aided Reduced Mechanisms (CARM)*
- CARM output can be converted to use the new user-rate routine in CHEMKIN
- We are working with Prof. Chen to adapt CARM to output the use-rate routine directly



*Ref: Combustion & Flame, 125:906-919 (2001)

Example comparison between full mechanism and CARM reduction

- OPPDIF Simulation of methane/air diffusion flame

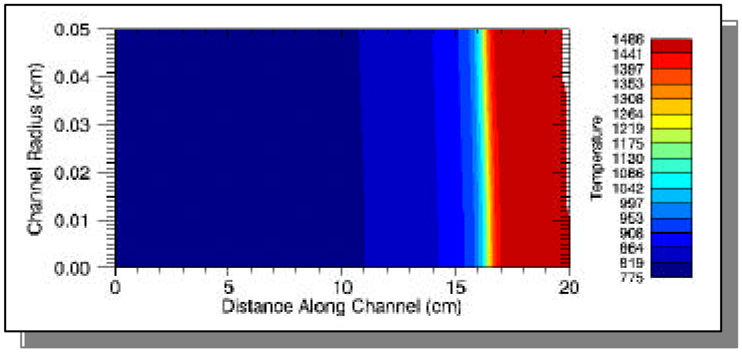


GRI Mech 3.0

CARM Red.

New contour plot option for 2-D data sets

- CRESLAF
  - – Contour plots for gas-phase species, temperature, flow
  - – Axial centerline and surface X-Y Plots
  - – Cross-flow “slices” for X-Y Plots



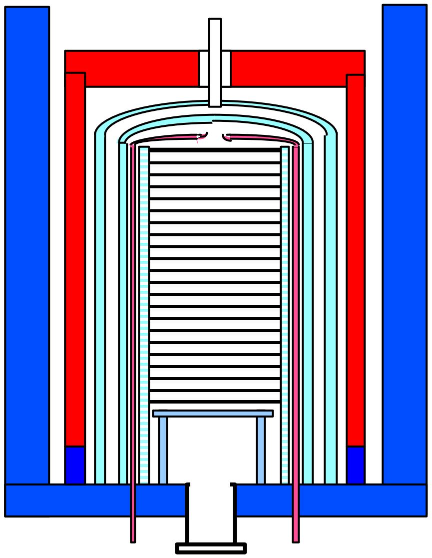
- TWAFER
  - – Contour plots for Temperature
  - – Cross-wafer uniformity X-Y Plot
  - – Axial uniformity along walls X-Y Plot
- OVEND
  - – Contour Plots of gas-phase species, temperature, flow
  - – Cross-wafer uniformity X-Y Plots
  - – Axial uniformity along walls X-Y Plots

Steamlined User Interface

- HELP menu on User Interface gives direct access to online user manuals
- More options for saving user preferences
  - Units preferences
  - Working directory history
- Improvement of multi-user environment
  - User’s can save their own preferences
  - User operation can be separated from root install

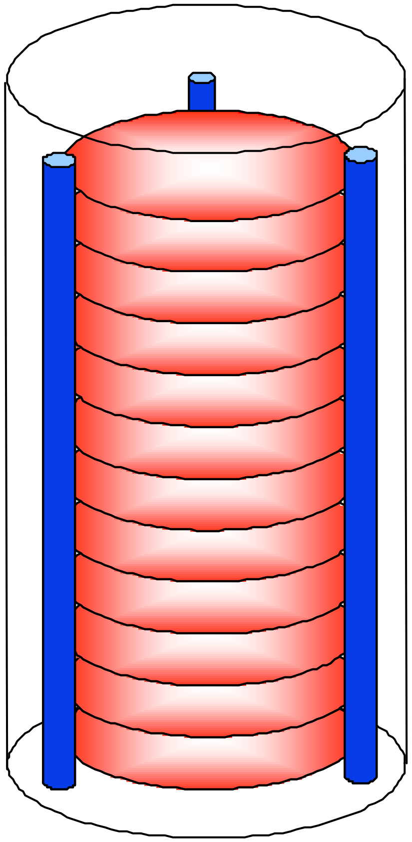
TWAFER predicts temperatures in a batch furnace heated by radiant lamps

- Wafer loading effects
- Transients during ramp-up
- Track difference between thermocouple locations and wafer
- Cross-wafer uniformity
- Cross-stack uniformity



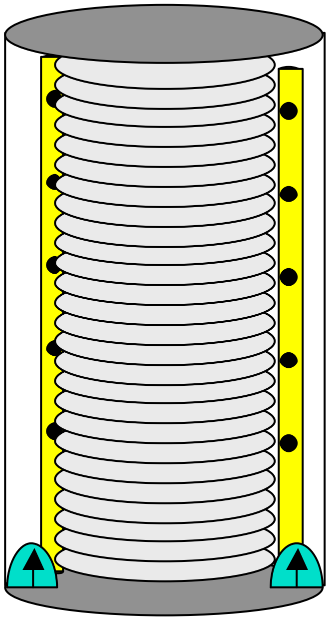
OVEND predicts deposition behavior in a batch furnace under low-pressure conditions

- Can take TWAFER results as input
- Wafer loading effects
  - Inter-wafer spacing
  - Use of “dummy” wafers at ends
- Reagent depletion
- Cross-wafer uniformity
- Cross-stack uniformity
- Transient ramp-up effects



Early version of TWAFER and OVEND applied to furnace optimization project

- Optimize furnace operation for Poly-Si CVD from SiH_4
  - Flow rates
  - Pressure
  - Reagent gas composition
- Identify design options to improve uniformity
- Develop controller to ensure robust, repeatable, and predictable process
  - Minimize ramp-up time
  - Maximize through-put

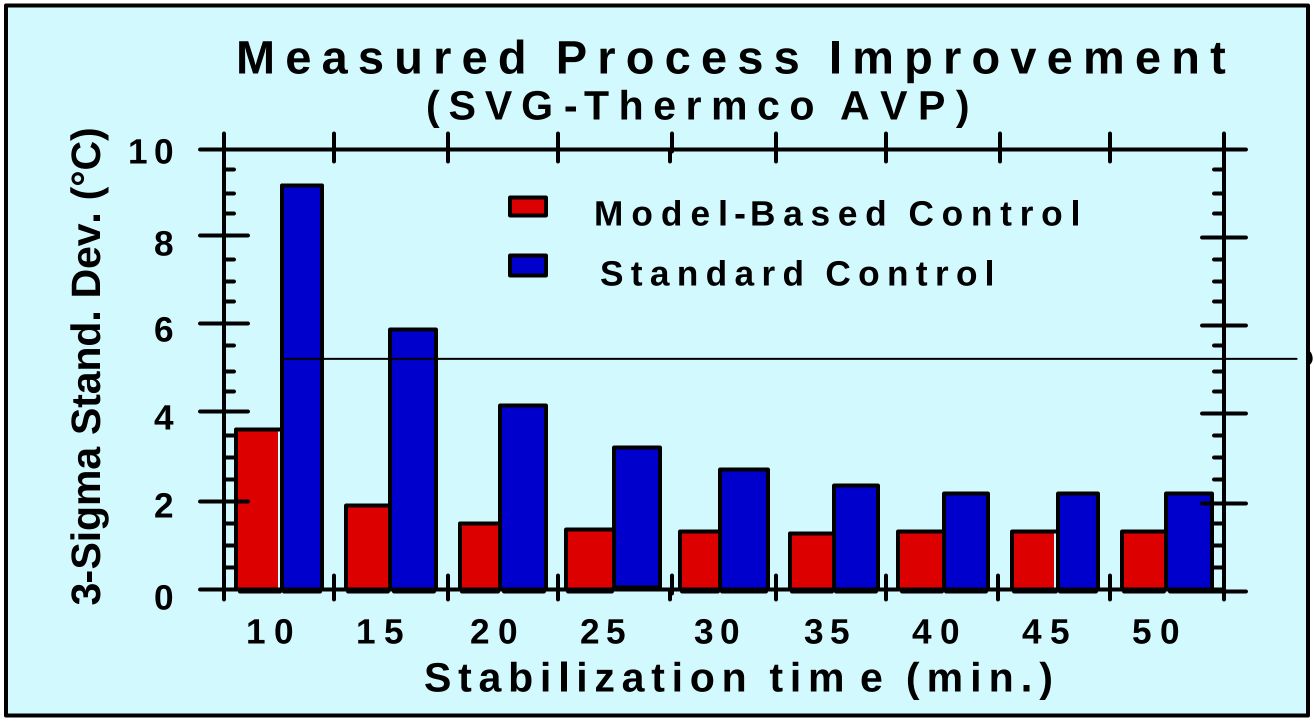


$SiH_4 + 2Si(s) \rightarrow 2SiH(s) + Si(b) + H_2$
$SiH(s) \rightarrow Si(s) + 1/2H_2$
$SiH_2 \rightarrow Si(b) + H_2$

Work performed at Sandia National Laboratories in cooperation with SEMATECH, Relman (Voyan), and SVG-Thermco (ASML-T)

Benefits of Chemical Process Modeling

- Costs per deposition reduced by 25%
- Process cycle time cut by 20%
- Reach stable operation 3 times faster
- 3σ uniformity exceeded goal of < 4%



PaSR is a computationally efficient means for studying turbulent-kinetic interactions

- Sequential Monte Carlo Simulation of Probability Density Functions for Species*:

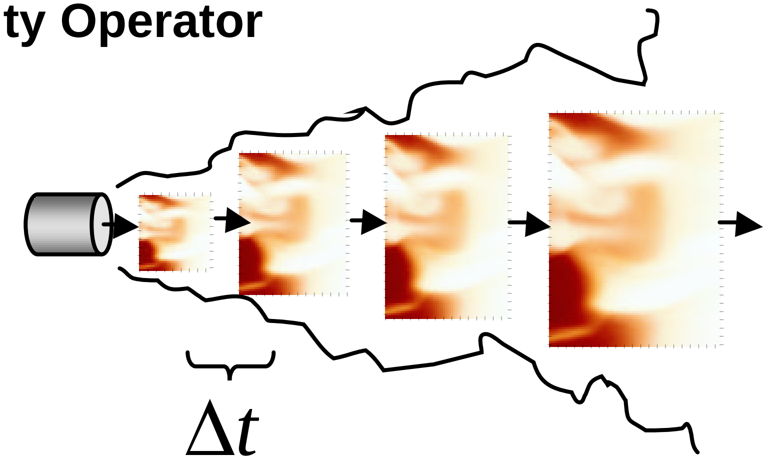
$$\tilde{P}(t+\Delta t)=[I+\Delta tC+\Delta tM+\Delta tK]\tilde{P}(t)+O(\Delta t)$$

Chemical Reaction

Molecular Mixing

Convection

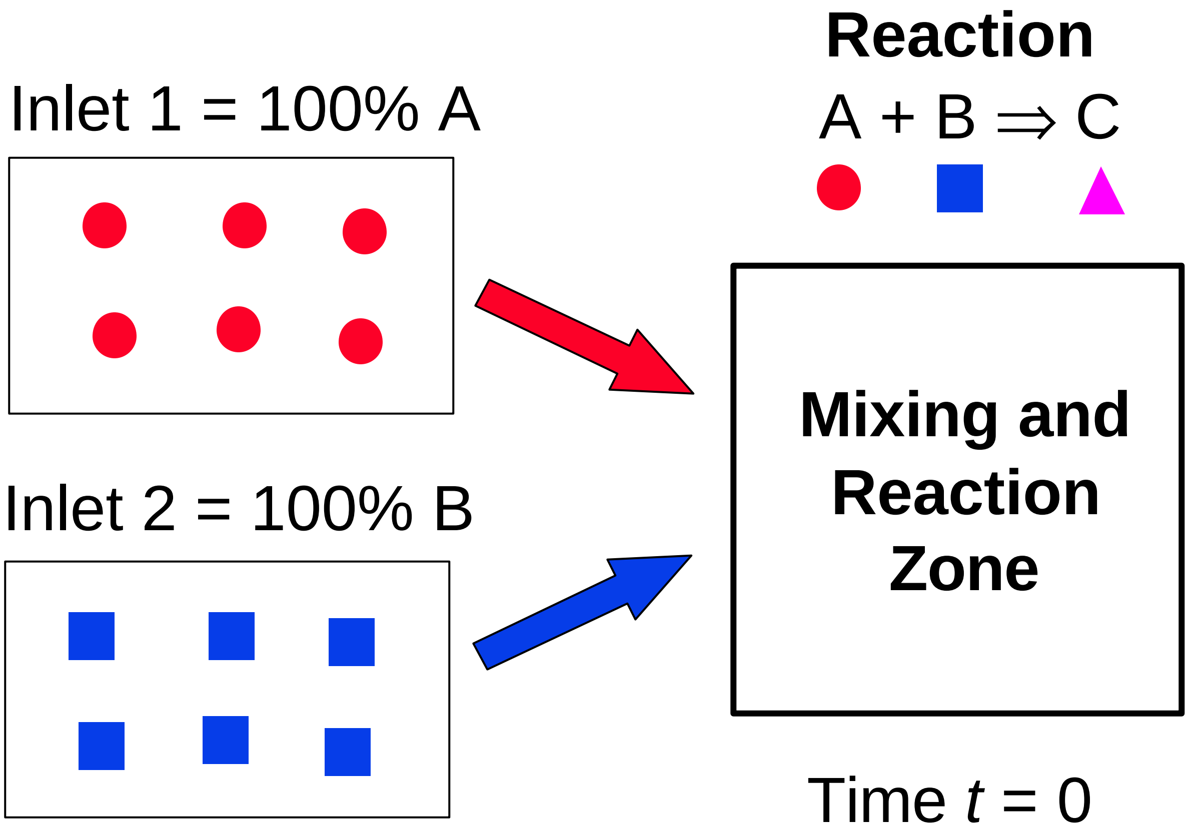
Identity Operator



**Ref: S.B. Pope, Combustion Science and Technology 25:159-174 (1981)*

The partially stirred reactor model tracks turbulent mixing and reaction in a zone

- Consider two reacting streams:



Inlet 1 = 100% A

Inlet 2 = 100% B

Reaction

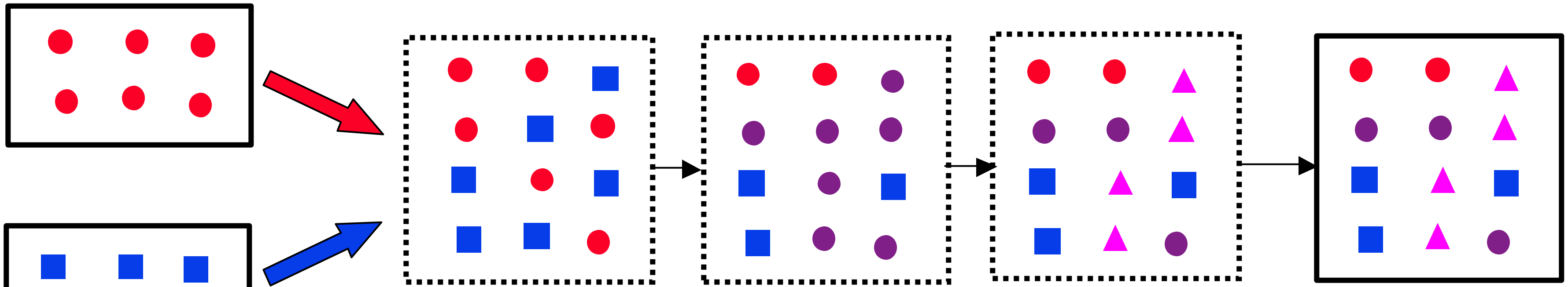
$A + B \Rightarrow C$

● ■ ▲

Mixing and Reaction Zone

Time $t = 0$

PaSR considers convection, molecular mixing, and kinetics in each time step



Convection

Molecular Mixing

Chemical Reaction

Time *t* = Dt

- Kinetics options:
  - No reactions
  - Equilibrium calculation
  - Full finite-rate CHEMKIN kinetics
- Molecular Mixing options :
  - Modified Curl’s Model
  - Interaction by Exchange with Mean (S. Correa)

Reaction

A + B ⇒ C

● ■ ▲

Input required to run PaSR

- Residence time of the mixing zone (based on flow rate)

- Characteristic Mixing time $t_{mix} = k/e$
  - Estimate based on flow (e.g. CFD calculation)
  - Range ~ μs to s

- Chemical reaction mechanism
  - CHEMKIN Input file
  - Thermodynamic data

PaSR provides important insight into turbulent kinetic interactions in combustors

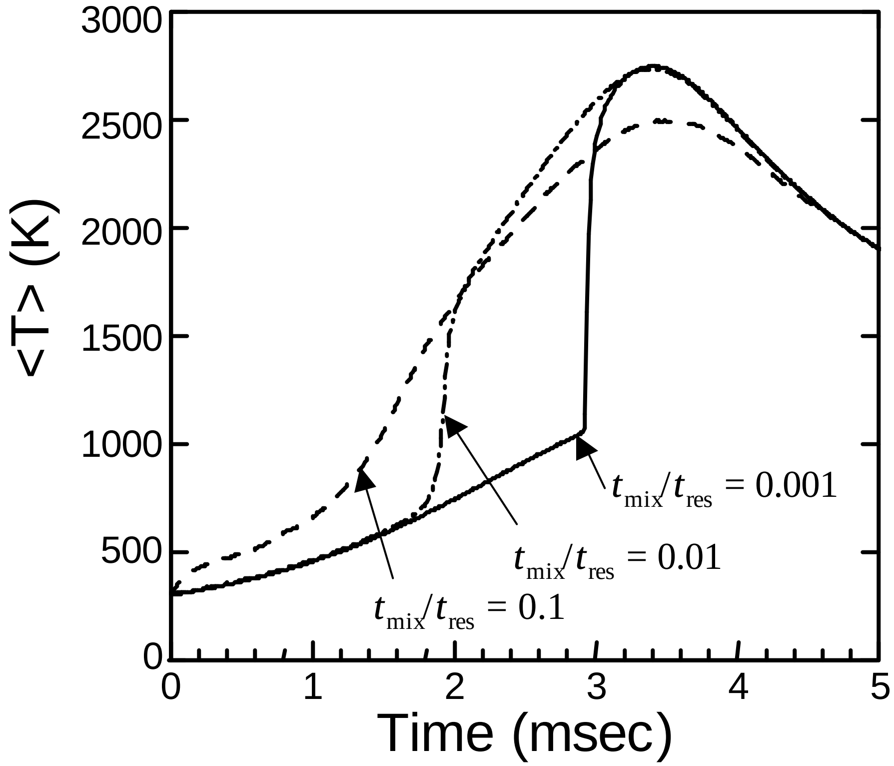
- Gas turbines*
  - Mixing zone with pre-mixed fuel and re-circulated burned products (ignition time delay)
  - Flame zone
  - Post-flame zone with cooling air addition
- Industrial burners
  - Jet entrance region
- Internal combustion engines
  - Single zone modeling
  - Effect of residual gas trapped on ignition time delay

**Ref: S.M. Correa, Combustion and Flame 93:41-60 (1993).*
J.-Y. Chen, Combustion Science and Technology 122:63-94 (1997)

Example of results from PaSR

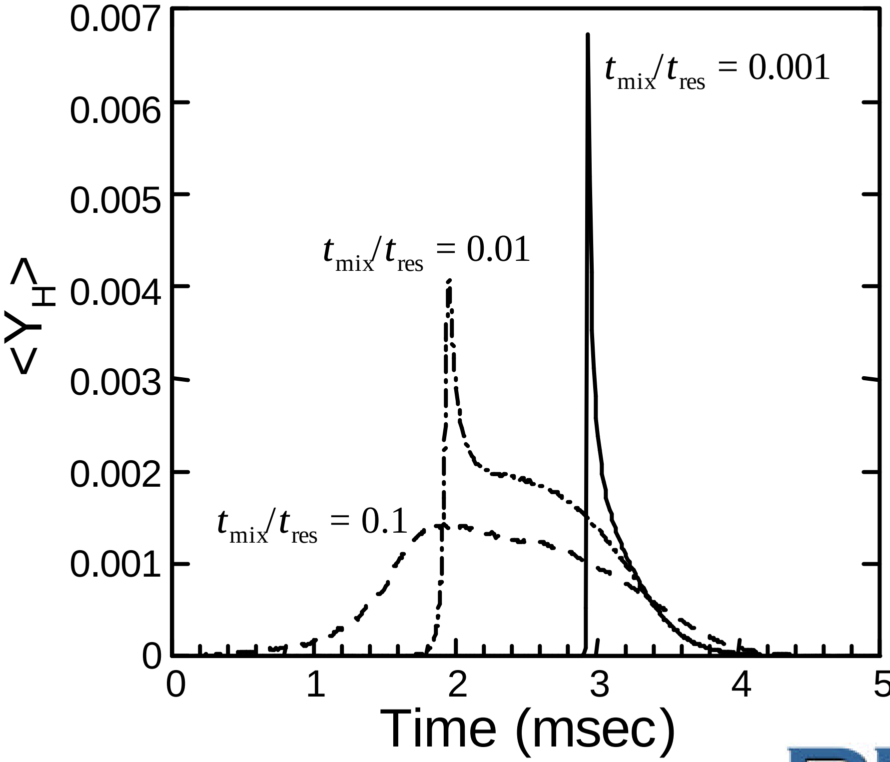
- H_2/Air Non-premixed Combustion
  - Hot air (1500 K) injected into cold H_2 (300 K)

Curl's Model
2000 particles



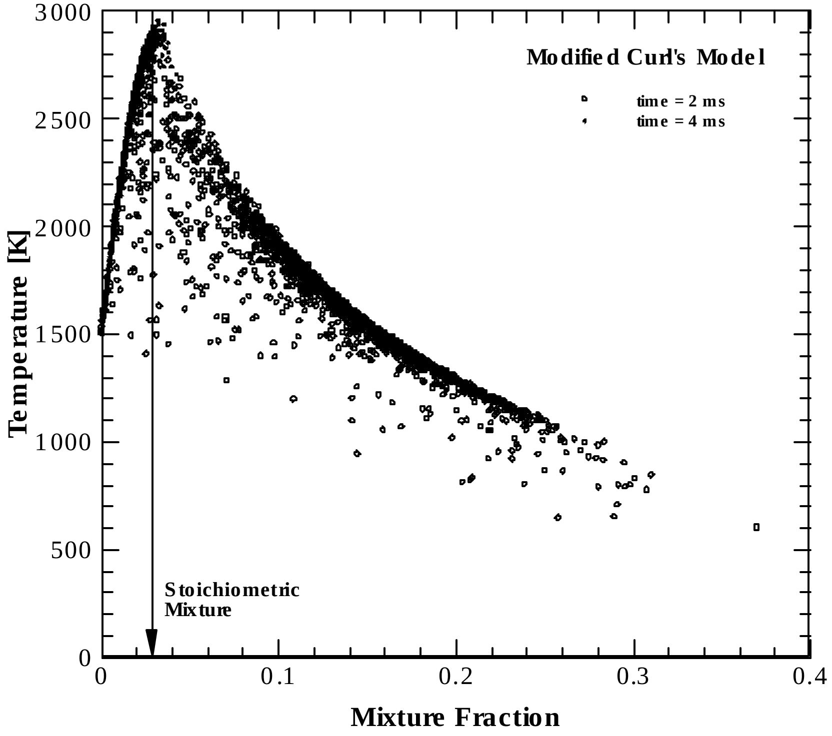
Mean Temperature

Mean H Mass Fraction

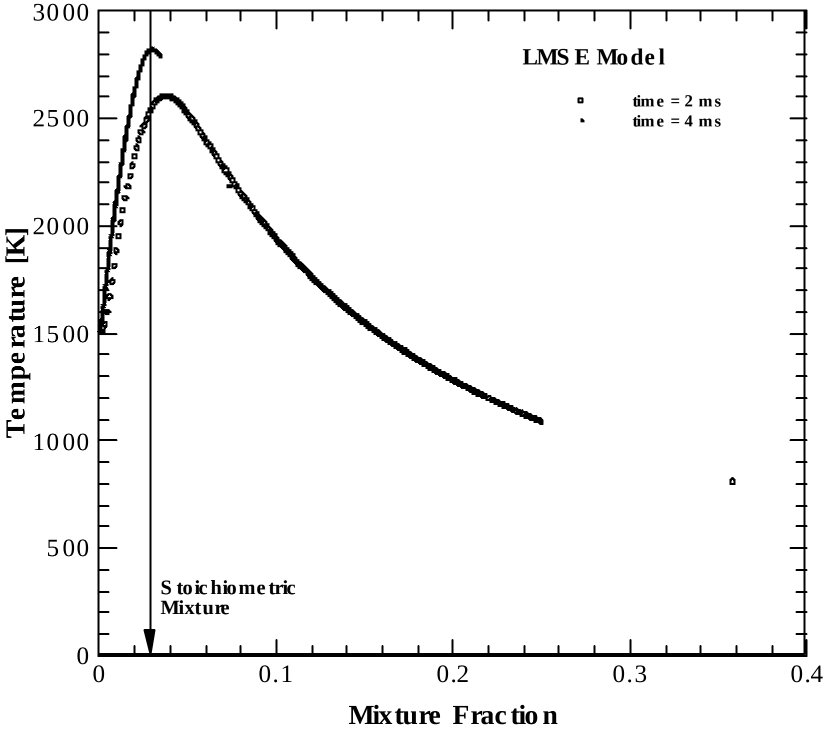


Comparison of two mixing models

Modified Curl's Model



Interaction by Exchange w/ Mean



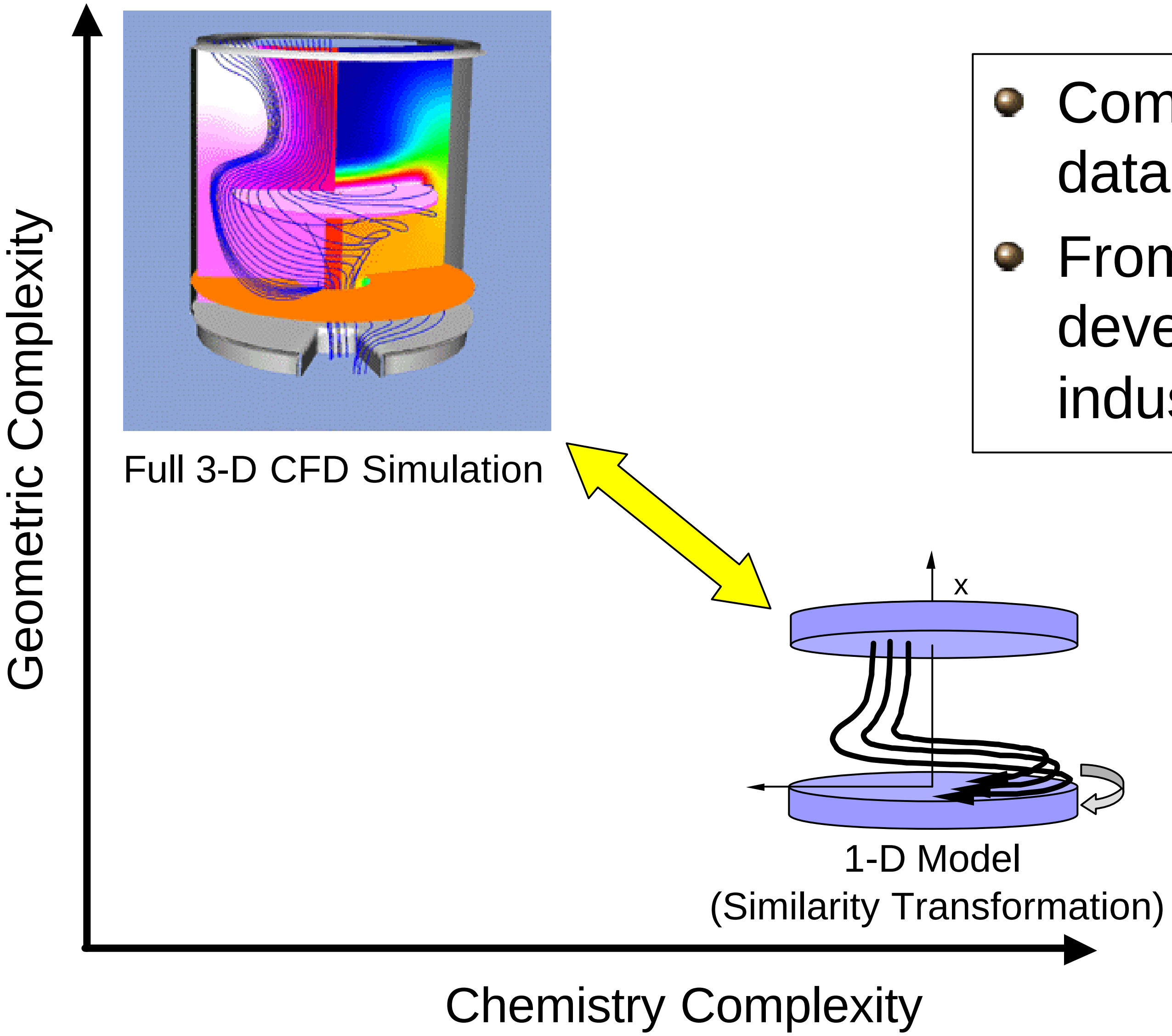
Status of CHEMKIN 3.7 Release

- Alpha testing (June 25 – July 15, 2002)
- Beta-testing (July 15 – August 15, 2002)
- Final Release: September, 2002
  - Available by download
  - Available by CD

All current customers receive CHEMKIN 3.7 automatically

CHEMKIN Plug-in
to STAR-CD

For complex geometries, modeling often requires a hierarchical approach



- Common chemistry data descriptions
- From mechanism development to industry application

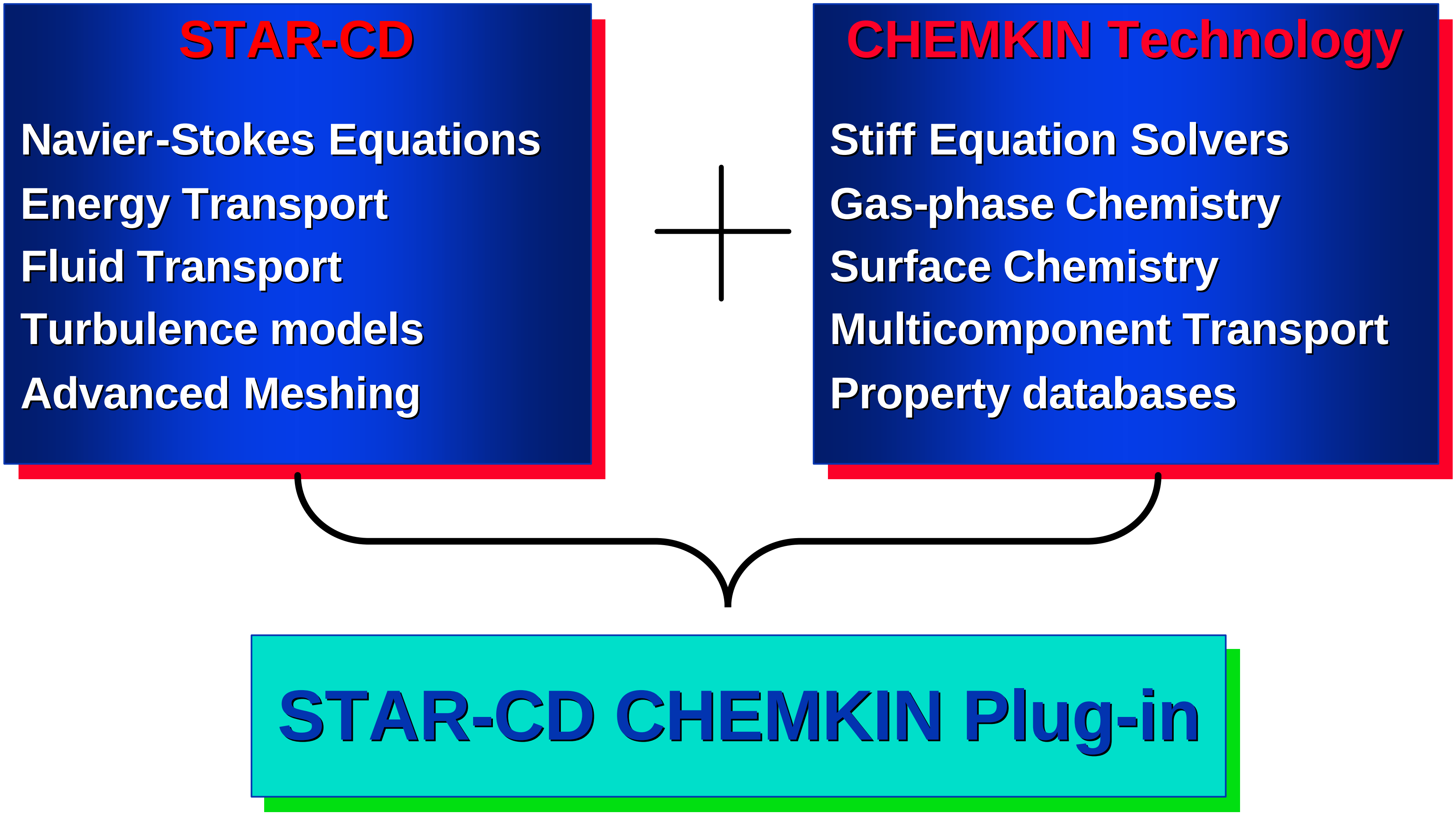
Traditional CFD approach to chemistry cannot handle “stiff” kinetics

- Time-step required to resolve kinetics is too small to be used in the transport step
  - Kinetics timescales often ~ 1.E-6 sec
  - Transport timescales often ~ 1.E-3 sec
- Species solved one at a time
  - Lose coupling between species, and with temperature
  - Instability & non-convergence
- Inaccuracy due to neglect of detailed reaction steps
  - Cannot predict trace species concentrations
  - Cannot predict effect of minor species on major species production and destruction

Reaction Design has teamed with CD-adapco to develop new chemistry capability

- **New “plug-in” to STAR-CD allows inclusion of detailed kinetics capability**
  - Based on CHEMKIN technology
    - gas-phase kinetics
    - surface kinetics
    - multicomponent transport properties
    - thermodynamic properties
  - Ability to process CHEMKIN input files directly
  - **Implementation of “stiff” equation solution methods for transient and steady-state reacting flows**
  - **Surface chemistry module for solving surface site coverage**

Linkage Between CD adapco and Reaction Design (STAR-CD CHEMKIN Plug-in)



STAR-CD

- Navier-Stokes Equations
- Energy Transport
- Fluid Transport
- Turbulence models
- Advanced Meshing

+

CHEMKIN Technology

- Stiff Equation Solvers
- Gas-phase Chemistry
- Surface Chemistry
- Multicomponent Transport
- Property databases

STAR-CD CHEMKIN Plug-in

REACTION DESIGN

Status of CHEMKIN Plug-in for STAR-CD

- CD-adapco's STAR-CD / CHEMKIN Plug-in
  - ✓ Full implementation of CHEMKIN gas-phase, surface, and transport libraries
  - ✓ Implementation of "stiff" equation solution methods for transient reacting flows
  - ✓ Unique steady-state solution algorithm for rapid convergence of gas-chemistry and transport
  - ✓ Full coupling to detailed surface kinetics
  - ✓ Applications: combustion, chemicals, catalysis, materials
  - ✓ Commercially available: January 2002

How can you obtain the CHEMKIN Plug-in to STAR-CD and the CHEMKIN Collection?

- The Plug-in is purchased from CD adapco Group
- CD adapco ships the Plug-in product
- License keys for the Plug-in are obtained through CDAG; Reaction Design provides keys that are incorporated into a STAR-CD license file.
- CD adapco provides the 1st line of tech support
- Reaction Design supports CD adapco in helping customers use the CHEMKIN Plug-in to STAR-CD

Reaction Design's Academic Program

Reaction Design strives to build a strong relationship with our academic customers

- We reduced the price of teaching licenses by 50%
- 85% discount on academic research licenses
- Opportunity to provide industrially targeted demonstration problems in lieu of research license fees
  - – Target key industrial applications
    - » After treatment, engine simulation, process catalysis, gas turbines
  - – Contact RD for approval process details
- RD Collaborative Development Agreement (RDCDP)
  - – Provide Application source code to researchers to allow development & exploration of new capabilities
- Joint proposals for government funding

Other ways in which we can work together?

- Build a web-based data clearing house
  - Thermo, transport, kinetic mechanisms
  - RD to host on not-for-profit basis
  - Allow user ratings
  - Establish data format & requirements
- Preferred partner program
  - Facilitate collaborations between industry and academic customers for mechanism development
- Develop specific capabilities to target teaching

SUMMARY

- We are working hard to increase the value and flexibility of CHEMKIN Software
- Ease-of-use and industry relevance will continue to be our ongoing focus
- We would like to find a way to strengthen our ties to academic teaching & research programs

Your guidance and direction are very important to us

Modeling Needs and Directions for Solid-Oxide Fuel Cells

Robert J. Kee*, Kevin Walters*, Huayang Zhu*, and Anthony M. Dean**
*Engineering Division
**Chemical Engineering Department
Colorado School of Mines
Golden, CO 80401

Figure 1 illustates the general layout of a planar solid-oxide fuel cell (SOFC), which is an emerging technology for highly efficient electrical-power generation. The membrane electrode assembly (MEA), which is comprised of an electrolyte sandwiched between electrodes (anode and cathode), is itself sandwiched between metal interconnect structures. As illustrated here, the fuel and air channels are formed in the interconnect structure. The electrolyte is a dense ceramic (e.g., yttria-stablized zirconia, YSZ, or gadolinia-doped ceria, GDC), which is impermeable to gas flow but is an oxygen-ion O^{2-} conductor. Since the ion conduction depends on electrolyte thickness, it is important that the electrolyte be as thin as possible (usually a few tens of microns) to reduce cell resistance. The composite electrodes are porous metal-loaded ceramics (cermets), which are mixed conductors that can carry both ionic and electrical current. The metal loading, which can be on the order of 50%, serves to promote heterogeneous catalysis and forms part of the triple-phase boundary. The MEA layer is often designed such that either the anode or the cathode provides structural support for the layer. The supporting electrode, say the anode, is usually on the order of a millimeter thick. The flow channels, which must deliver fuel and air uniformly across the active layer, usually have characteristic dimensions of around a millimeter. Since each layer develops around 1/2 volt at maximum power density, many stacked layers are electrically connected in series to increase the overall stack voltage.

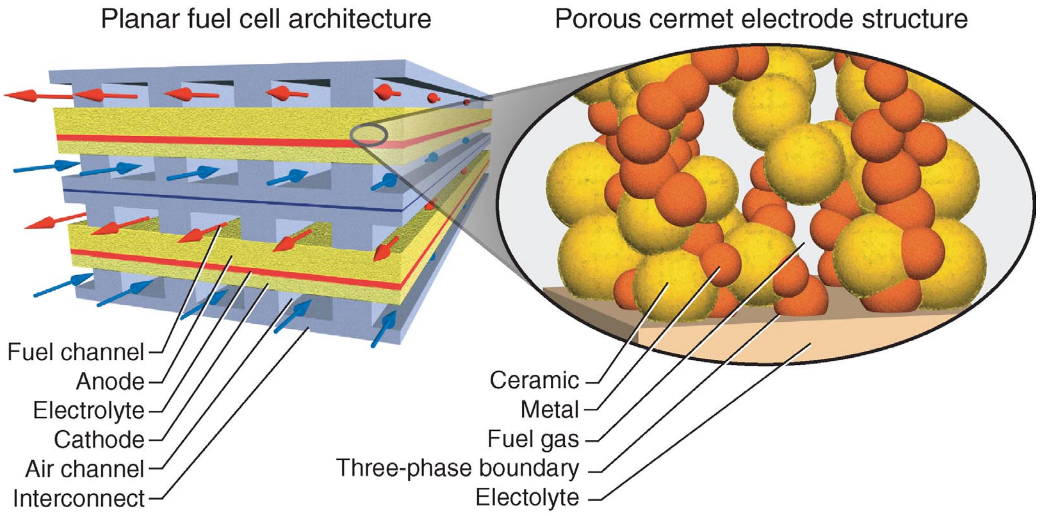


Figure 1: Typical layout of a planar, solid-oxide, fuel cell. The left-hand panel illustrates the system at the scale of the flow channels, while the right-hand panel illustrates the small-scale structure of the porous cermet electrode.

Flow channels

During operation, gaseous fuel (e.g., natural gas) flows through the anode channels and air flows through the cathode channels. Effective performance depends on uniform fuel and air delivery over the entire layer, but with pressure losses as small as possible to minimize the parasitic power required to compress and drive the feed streams. The cathode (e.g., Sr-doped $LaMnO_3$ LSM) catalyzes ion formation, providing oxygen ions for transport through the electrolyte, $O_2 + 4e^- \rightarrow 2O^{2-}$. On the anode side of the electrolyte, the fuel reacts electrochemically with the oxygen at the so-called triple-phase boundaries that are formed at the intersection of the gas-metal-ceramic phases. Globally, for methane, $\frac{1}{2}CH_4 + 2O^{2-} \rightarrow H_2O + \frac{1}{2}CO_2 + 4e^-$.

In a direct-electro-chemical-oxidation (DECO) type SOFC system, there is no need for upstream fuel preparation. The fuel is reformed either in the channels or electrodes, and/or directly oxidized at the triple-phase boundaries within the electrode structure. The major benefits to this type of system (compared to polymer electrolyte membrane (PEM) technology) include simplifying balance-of-plant issues as well as enabling a variety of hydrocarbon fuels. While natural gas is currently the most widely considered fuel, encouraging experimental results for butane and other hydrocarbons have been reported. However, at nominal operating temperatures of 700-900°C, fuel stability and carbonaceous deposit formation within the fuel channels and porous anode present significant potential limitations.

There is a great need to understand the elementary kinetics (homogeneous reaction, heterogeneous catalysis, and electrochemical kinetics) of fuel pyrolysis and oxidation within the fuel-cell environment. At typical SOFC operating temperatures (700-900°C), hydrocarbon fuels can pyrolyze and lead to molecular-weight growth and carbonaceous deposits. Even though pure fuel enters the anode channels, the electrochemical reactions (which depend on cell voltage and current density) produce water vapor and carbon dioxide. The water vapor, especially, tends to inhibit molecular-weight growth. Ourr current models consider large reaction mechanisms (e.g., approximately 3000 reaction steps), and use the formation of small aromatics (e.g., benzene, fulvene, cyclopentadiene, and methyl-cyclopentadiene) as indicators of coking propensity. There are important design and operational tradeoffs to control fuel residence time, temperature, and cell electrical performance.

Understanding and modeling the chemically-reacting-flow fundamentals contributes greatly to facilitating these engineering tradeoffs. We have developed a modified plug-flow model that incorporates an elementary-reaction-mechanism representation of fuel pyrolysis and oxidation, as well as accommodating the effects of ion flux through the electrode-electrolyte assembly. Given a cell's specific electrical resistance and operating voltage, the electrochemical flux of oxygen into the fuel channnels can be determined from the species composition in the channels. In the current models, the oxygen ions react electrochemically according to a global surface-reaction mechanism, producing an electrical current and delivering the stoichiometric equivalent of CO_2 and H_2O into the channel. The presence of steam, especially, has the potential to reduce coking kinetics by both dilution and gasification.

Electrodes

Each of the SOFC components (i.e., anode, cathode, electrolyte, and interconnect) and their interfaces contribute overall resistance. The ohmic polarization resistance is usually dominated by the electrolyte, which depends on the intrinsic resistivity of the material and the electrolyte thickness. Since the electrolyte resistivity is usually quite high, there are great benefits to making the electrolyte as thin as possible. Activation polarization is caused by charge-transfer processes and depends on the properties of the electrode-electrolyte interfaces. Concentration polarization is mainly related to the gaseous transport through the porous electrode, which is controlled by the electrode microstructure, as characterized by porosity, pore size, tortuosity. To improve the overall system performance, the parameters that affect polarizations must be optimized. It is particularly important to enhance the performance of the composite electrodes, which depend on a complex interplay of materials, microstructures and the chemical/electrochemical reaction kinetics.

There are three distinct material phases within which electrode transport occurs (right-hand panel of Fig. 1). First is the gas phase. For the anode the open pore structure must be such that it facilitates convective and diffusive transport of gaseous fuel from the fuel channels to the electrolyte surface and transport of products back toward the channels. The cathode primarily transports air from the air channels towards the elecrolyte interface. The pore size is often comparable to the mean-free-path length, which means that Knudsen diffusion is important. The second phase is the metal, which is responsible for the transport of electric current. The metal also serves as a heterogeneous catalyst for the reaction of gaseous species. The third phase is the ceramic electrolyte, which must carry ion O^{2-} current. The metal-ceramic-gas common boundary of these three phases is usually called *triple-phase boundary* (TPB), which is the chemically and electrochemically active area for fuel oxidation and charge-exchange (conversion of ion current into electric current). Since the composite porous cermet is a mixed ionic and electronic conductor, the charge-transfer processes can be extended some distance from the electrolyte-electrode interface into the electrode. In addition to transport within each phase, there may be transport of adsorbates along the solid surfaces.

The electrodes can be responsible for two types of so-called *overpotentials*, which serve to limit fuel-cell performance. The concentration overpotential occurs as a result of gas-phase transport limitations within the electrode structure. This situation usually arises under conditions where the current density is high. The resistance to flow in the porous structure limits the transport of fresh fuel to, and product transport from, the triple-phase boundaries, thus limiting performance. A more-open pore structure usually reduces tranaport overpotentials. Alternatively, under low-current-density conditions, the overpotential may be caused by rate-limiting reaction kinetics at the triple-phase boundaries. This overpotential can be reduced by increasing temperature, providing higher-activity catalysts, or creating more surface-reaction area. However, these measures may also tend to promote deleterious carbon deposits. Anode performance also requires high non-electrochemical catalytic activity to assist in-situ reforming processes, but without causing carbon deposition. In all cases, models can assist the design and optimization of systems that minimize losses and maximize performance.

We formulate the electrode models as systems of continuum partial differential equations. While this approach has significant computational advantages, there are some important considerations that may compromise the validity. In this setting, the material properties and the state variables must be *homogenized*. For example, there is a specific length of triple-phase boundary (and thus area available for heterogeneous charge-exchange reaction) per unit volume of composite electrode material. However, as can be seen from the right-hand panel of Fig. 1, there is significant structure on the microscopic scale. With certain analogies to turbulence, for example, it is not clear a-priori that average reaction rates may be based simply on the average mean-field state variables that emerge from the continuum setting. In any case, since there are critical system-level, engineering, tradeoffs that must be made concerning electrode design, the development and validation of predictive (even qualitatively predictive) models is important.

Probing Reaction Mechanisms with Chemkin III

R.S.Tranter and K. Brezinsky,
Department of Chemical Engineering, University of Illinois at Chicago
M.D. Allendorf
Combustion Research Facility, Sandia National Laboratories

At UIC a high-pressure single pulse shock tube has been developed and is used to investigate combustion reactions at high temperatures, 1050 -1450 K, and high pressures 5 – 1000 bar. For the purposes of simulation the reaction zone behind the reflected shock wave can be considered to be a constant pressure reactor in which reaction only occurs in the gas phase and the Senkin module of Chemkin is appropriate for simulating this system. Of course it is necessary to provide the initial reaction conditions (temperature, pressure and species concentrations) and a suitable reaction mechanism to complete the model.

During the investigation of a particular problem e.g. ethane oxidation and pyrolysis, it is normally necessary to simulate a couple of hundred experiments, obtain sensitivity analyses for some of these experiments, identify key reactions and then repeat the simulations with suitable modifications and so on until an adequate match to the experimental data is obtained. Chemkin is routinely used to either perform these tasks or to obtain data to aid these tasks and from the point of view of simulating complex chemical systems Chemkin performs admirably.

Based on our experience using Chemkin for the above described experiments the following strength and weaknesses have been identified

Strengths:

- Good tool for simulating chemistry
- Relatively easy to use
- Exporting data to ASCII files useful
- Large number of modules for different problems

Weaknesses:

- GUI is very poor
- No reaction path analysis in GUI
- Separate program required for normalizing sensitivities in SENKIN
- No provision for batch processing
- No on-line help
- Expensive

A number of improvements to Chemkin follow from the above described strengths and weaknesses. These will also be discussed.

CHEMKIN-BASED SIMULATIONS OF LARGE SCALE PULVERIZED FUEL FLAMES

By

Stephen Niksa and Guisu Liu
Niksa Energy Associates
1745 Terrace Drive
Belmont, CA USA
neasteve@pacbell.net

Third Biannual International Workshop on CHEMKIN in Combustion
Sapporo, Japan, July 21, 2002

ABSTRACT

The rudimentary chemistry in CFD simulations of pulverized fuel (p. f.) fired furnaces has proven to be adequate for predicting exhaust NO_X emissions across the normal operating range of utility boilers, which is limited. But it is too simple to connect to any fuel properties so a multitude of model parameters must be adjusted for every new fuel to forecast emissions in fuel switching or co-firing scenarios. One obvious remedy would be to incorporate more chemistry into the CFD reaction submodels, but the progress in this direction during the past decade has been almost imperceptible. A much more promising strategy is now evident in the literature: Ignore the turbulence/chemistry interactions and use equivalent networks of idealized reactor elements to depict only the bulk flow patterns. This single premise enables the most advanced p. f. decomposition submodels and elementary reaction mechanisms to be incorporated into p. f. flame simulations, without approximation.

NEA's Advanced Post-Processing (APP) method first analyzes a CFD furnace simulation to subdivide the flow into regions of common chemistry and operating conditions. Then the bulk flow patterns in each region are represented with an equivalent network of idealized reactor elements whose residence time distributions, temperature histories, and entrainment rates are evaluated directly from the CFD simulation. Detailed reaction mechanisms are then applied over the reactor network, including the most fully validated reaction mechanisms for coal devolatilization and char oxidation and complete elementary reaction mechanisms for chemistry in the gas phase and on soot. CHEMKIN evaluates the progress of chemistry in the gas phase and on soot, and a p. f. decomposition submodel called PC Coal Lab® evaluates O_2 consumption on the p. f.

CHEMKIN-BASED SIMULATIONS OF LARGE PULVERIZED FUEL FLAMES

Stephen Niksa and Gui-su Liu
Niksa Energy Associates
Belmont, CA

Presentation to the Third Biannual International Workshop on CHEMKIN in Combustion
July 21, 2002, Sapporo, Japan

Performance of Conventional Chemistry Submodels

- *Exhaust NO_X levels can be tuned-in; Good impact of OFA, BOOS; Poor burner design.*
- *Poor CO predictions.*
- *Poor UBC predictions, without coordinated testing.*
- *No fuel quality impacts.*

Fuel Switching Affects All Stages of Flame Chemistry

	Hv Bit.	**Subbit.**	**Biomass**	**CFD Pars.**
Volatiles Yield	Moderate	High	***Very High***	V^∞
Devol. Rate	Moderate	Fast	***Very Fast***	A_D, E_D
Swelling	***Very High***	None	Negative	Ω
Volatiles CV	High	Moderate	Low	C/H/N
Burnout Rate	Moderate	Fast	Fast	A_C, E_C

- *These differences affect flame stability, temperature profiles, heat release, and emissions, especially* NO_X *and LOI.*
- *CFD parameters can either be measured or estimated from databases, if the expertise is available.*

Volatile Fuels Are Grossly Different

Primary Devolatilization Products from PC Coal Lab®.

	hvA Bit.	W. Subbit.	Switchgrass
Properties			
Volatiles	33.2	36.6	47.6
Fixed Carbon	49.9	38.7	7.7
Moisture	1.9	19.3	15.2
Ash	15.1	5.4	29.5
%C, daf wt. %	83.4	74.9	56.1
%H	5.5	4.9	5.4
%O	7.5	18.8	35.6
%N	1.8	0.9	2.4
%S	1.8	0.4	0.4
Volatiles,daf wt.%			
Wt. Loss	61.9	64.3	85.7
Tar	48.6	35.8	42.5
CO	0.8	5.1	22.1
CO_2	1.5	6.3	3.5
H_2O	4.1	7.5	6.8
CH_4	2.4	4.6	2.1
C_2H_4	1.0	1.9	0.8
C_2H_6	0.6	0.3	0.2
C_3H_6	0.9	1.5	0.4
Alcohols	-	-	3.3
H_2	0.5	0.4	0.8
HCN	0.1	0.6	-
NH_3	-	-	1.8
H_2S	1.3	0.3	0.3
Char Properties			
% C	97.4	98.9	97.3
% H	0.4	0.4	2.5
% N	2.2	0.6	0.0
d/d_0	1.16	1.04	0.68
ρ, g/cm^3	0.37	0.19	0.71

Secondary Pyrolysis Products from PC Coal Lab®.

Yield, daf wt. %	hvA Bit.	W. Subbit.	Switchgrass
Wt. Loss	61.9	64.3	**85.7**
Soot	**43.4**	**32.6**	**13.1**
CH_4	0.3	0.6	**7.4**
C_2H_2	0.3	0.0	1.2
C_2H_4	-	-	1.5
H_2	**4.2**	**4.9**	1.7
CO	4.8	12.4	**41.4**
CO_2	1.5	6.3	8.1
H_2O	4.1	7.5	7.7
HCN	1.3	1.1	-
NH_3	-	-	2.9
H_2S	1.3	0.3	0.3

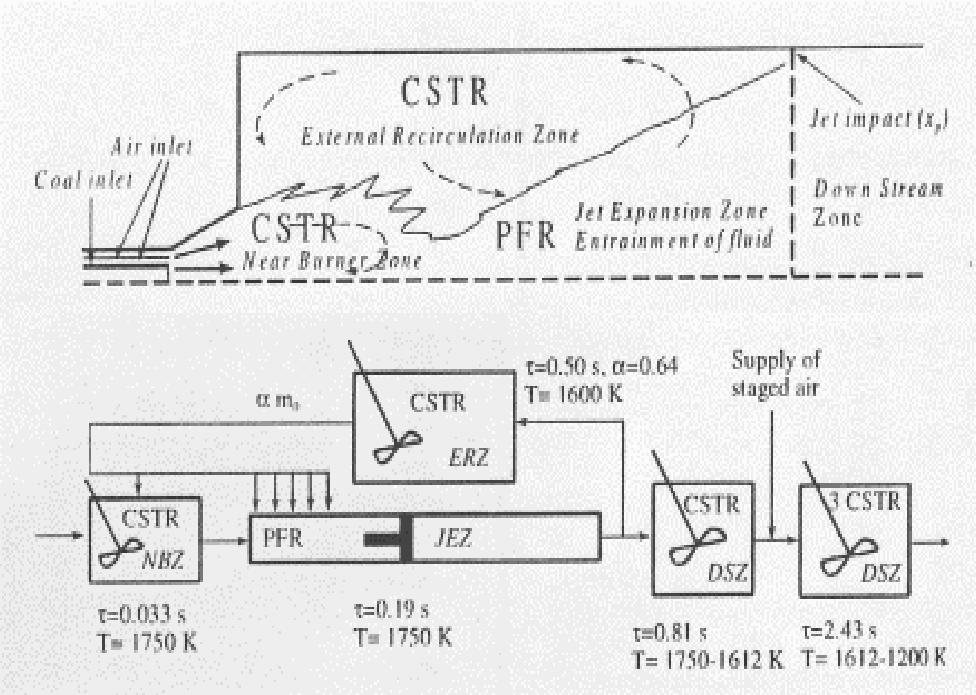
Validated Reaction Mechanisms Are Available for Fuel Quality Impacts

- *FLASHCHAIN® predicts the complete distribution of volatiles from any coal, pet coke, and biomass at any operating conditions, given only the proximate and ultimate analyses.*
- *Gas phase reaction mechanisms are predictive, but soot chemistry needs to be clarified.*
- *Carbon Burnout Kinetics (CBK) Model describes the impact of variations in d_P, T_{FURN}, and X_{O2}, given a 1-point calibration for the initial intrinsic reactivity.*

ALL *Turbulence Models are Incompatible with Detailed Chemistry*

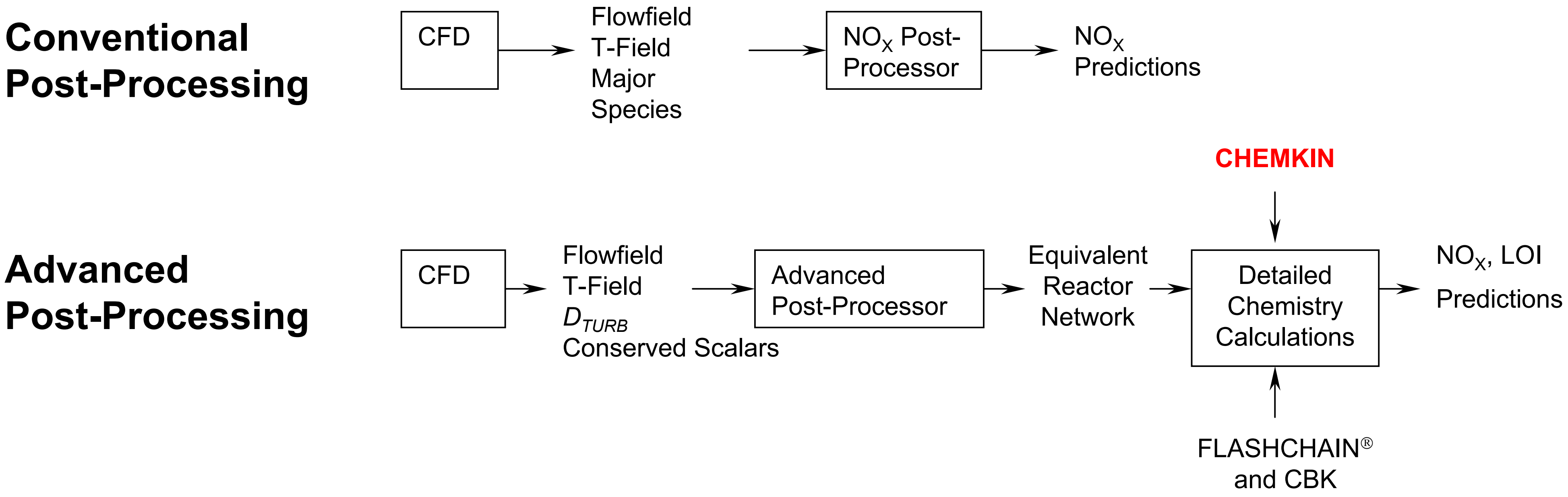
- *Ignore the turbulence/chemistry interactions, and use equivalent networks of idealized reactor elements to depict only the bulk flow patterns.*

Detailed Chemistry Is Feasible in Equivalent Reactor Networks



- *ENEL began in mid-90’s.*
- *Glarborg et al. at Technical University of Denmark, with later work at VTT, Finland.*
- *NEA began in late-90’s.*

NEA's Advanced Post-Processing (APP) Method Starts With Conventional CFD



Conventional Post-Processing

CFD → Flowfield, T-Field, Major Species → NO_X Post-Processor → NO_X Predictions

Advanced Post-Processing

CFD → Flowfield, T-Field, D_{TURB}, Conserved Scalars → Advanced Post-Processor → Equivalent Reactor Network → Detailed Chemistry Calculations → NO_X, LOI Predictions

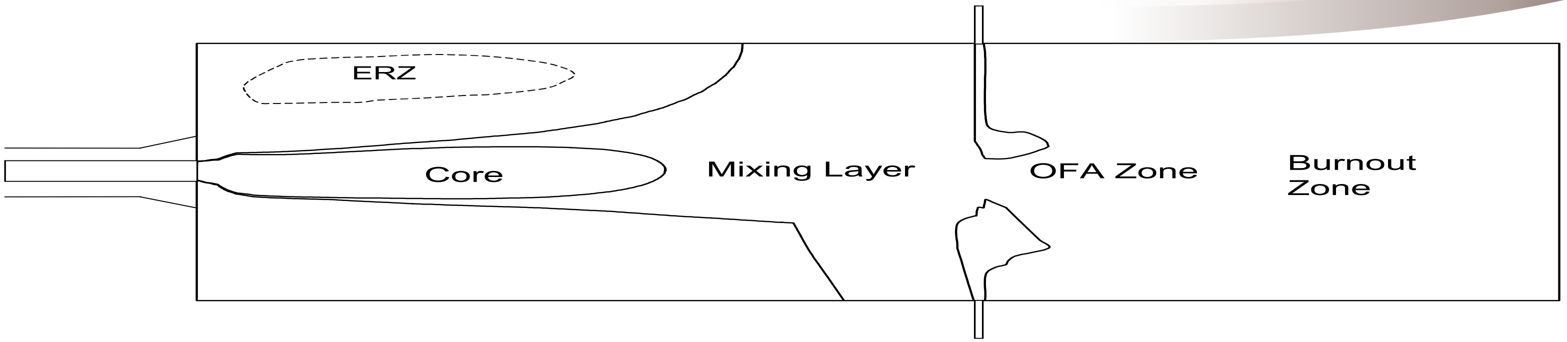
CHEMKIN → Detailed Chemistry Calculations

FLASHCHAIN® and CBK → Detailed Chemistry Calculations

APP Matches Flow Patterns In Terms of Time, Temperatures, and Entrainment Rates

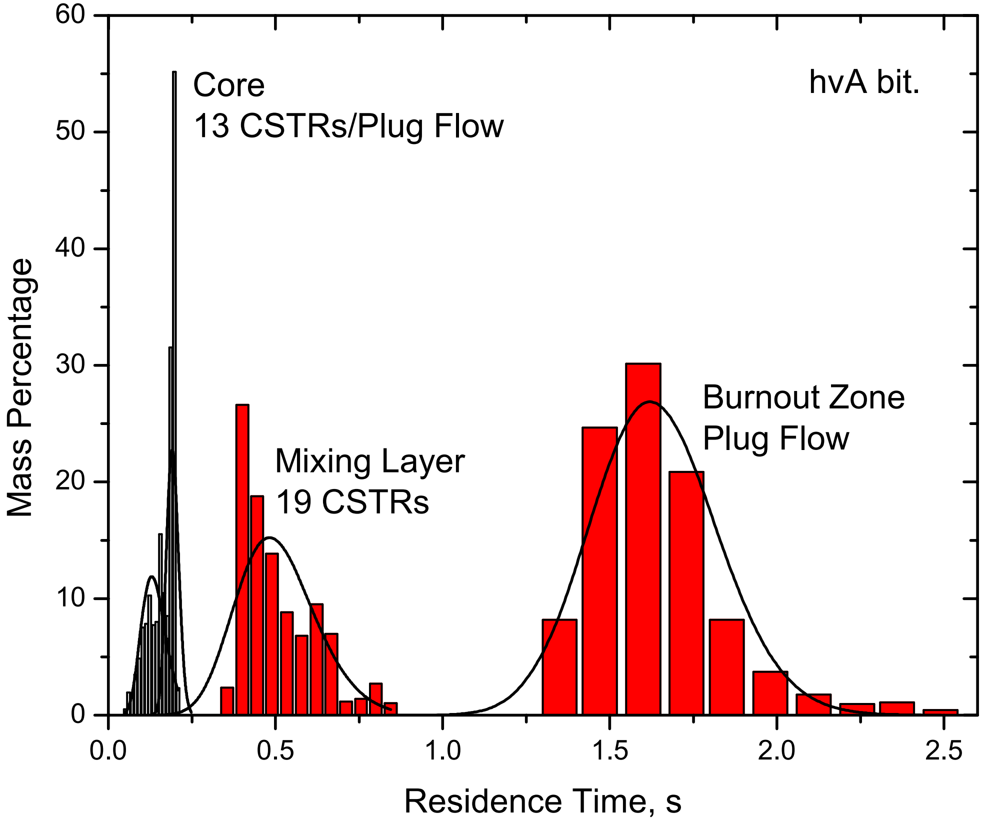
- *Subdivide flow into regions of common chemistry.*
- *Use particle tracking to evaluate RTDs, T-histories over each region.*
- *Evaluate fluxes across boundaries to specify entrainment rates.*
- *Assign N-CSTRs to match RTD in each region.*
- *Assign τ_j, T_j from the average T-histories across each region.*
- *Evaluate near-burner particle T-history for a devolatilization simulation.*
- *Simulate the chemical reaction mechanisms across each region.*

SRI's 1.7 MW_t Tunnel Furnace With Weak Swirl Contains 5 Regions



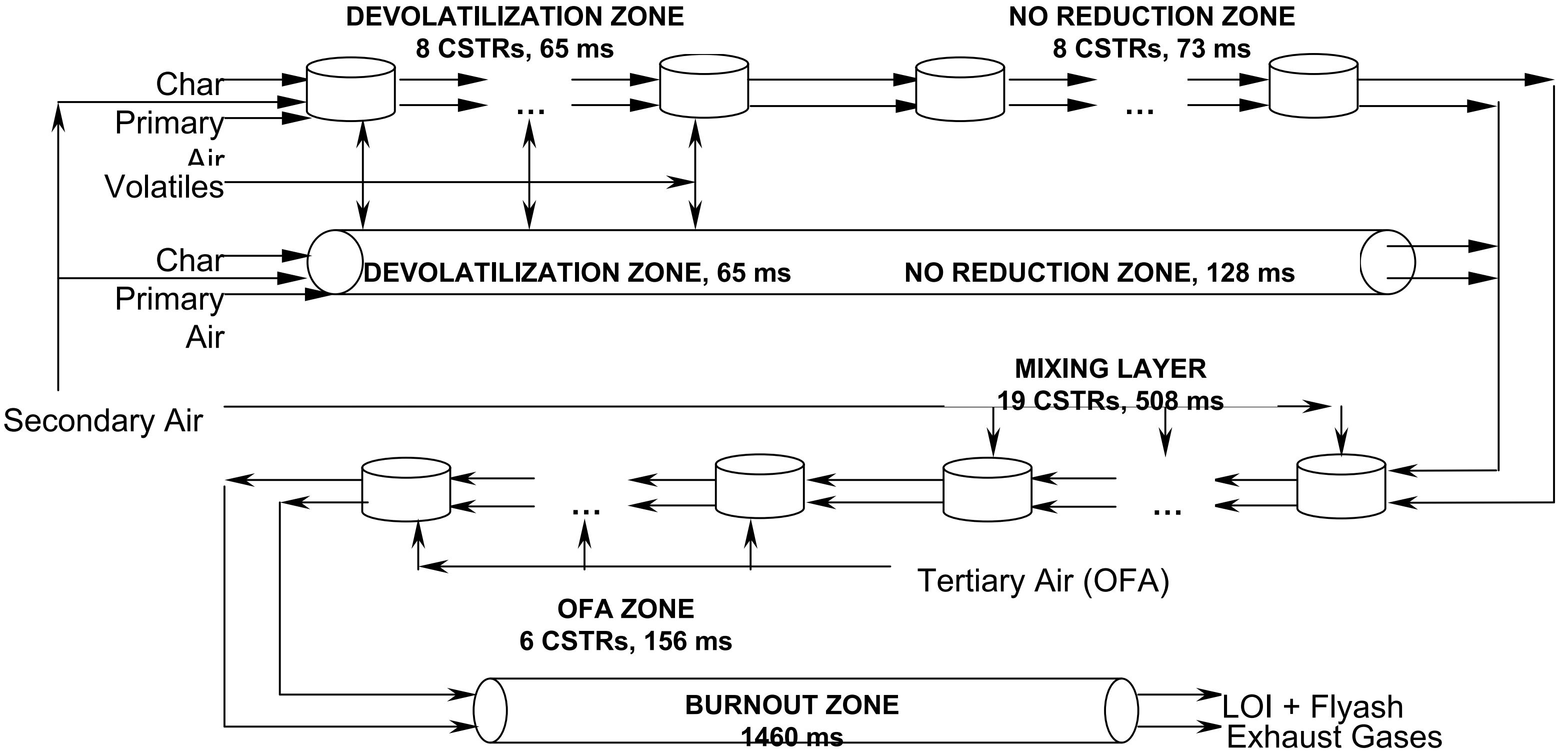
- *Emissions represent full-scale T-fired boilers.*
- *Near the burner, all particles remain in the core.*
- *T-profile across mixing layer passes through a maximum.*
- *OFA regions specified from O_2 m. f.*
- *ERZ was negligible.*

Analytical RTD Assignments



- *Impose near-burner exchange at core inlet.*
- *Core is superposed PFR + CSTR-series.*
- *Other regions are CSTR-series.*

Equivalent Reactor Network



DEVOLATILIZATION ZONE
8 CSTRs, 65 ms

NO REDUCTION ZONE
8 CSTRs, 73 ms

Char

Primary Air

Volatiles

Char

Primary Air

DEVOLATILIZATION ZONE, 65 ms

NO REDUCTION ZONE, 128 ms

Secondary Air

MIXING LAYER
19 CSTRs, 508 ms

Tertiary Air (OFA)

OFA ZONE
6 CSTRs, 156 ms

BURNOUT ZONE
1460 ms

LOI + Flyash

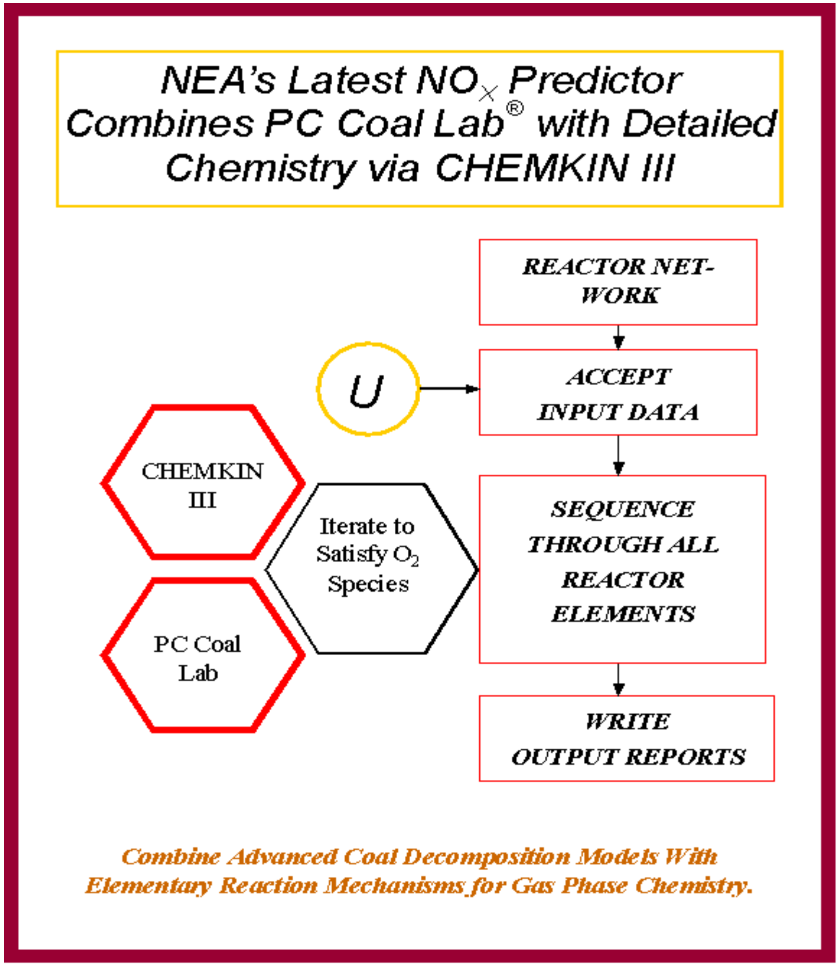
Exhaust Gases

Complete Reaction Mechanisms for All Stages of Combustion

Devolatilization	
Fuel Type	Any coal or petroleum coke and most forms of biomass (woods, grasses, paper, and agricultural residues).
Yields	Sample-specific predictions from FLASHCHAIN® based on only the proximate and ultimate analyses.
Composition	Gases resolved as molecular species. C/H/O/N/S compositions of char and tar.
Secondary Volatiles Pyrolysis	Represents instantaneous soot production from tar with simultaneous release of CO, H_2, and HCN and destruction of all hydrocarbons except CH_4 and C_2H_2.
Char Properties	
Composition	C/H/O/N/S composition from FLASHCHAIN®.
Size Changes	Swelling-factor correlation assigns the char PSD from the fuel PSD.
Bulk Density	Determined from volatiles yield and the swelling factor correlation.
Carbon Density	Correlated with the C-content of the parent coal.
Homogeneous Chemistry	444 elementary reactions among 66 species, including all products of secondary volatiles pyrolysis and N-species.
Soot Chemistry	
Oxidation	NEA's four-step elementary reaction mechanism for oxidation by O_2 matches NSC kinetics. Simultaneous oxidation by O and OH.
Recombinations	Recombinations of H into H_2 and OH into H_2O.
NO Reduction	Single quasi-global process.
Char Burnout	
Oxidation	Burnout based on CBK8, which represents transitions through all combustion regimes, thermal annealing, and ash encapsulation. Initial oxidation rate for a coal char should be calibrated with data.
Char-N Conversion	The fixed portion of char-N converted into NO at the nominal burning rate should be calibrated with baseline NO_X emissions.

- *FLASHCHAIN® predicts all char properties for the CBK simulations.*
- *FLASHCHAIN® predicts fluxes of all fuels for gas phase reaction mechanism.*
- *Soot oxidation by O_2, O, OH plus H, OH recombinations.*
- *Prof. Glarborg's 444-step reburning mechanism for N-species conversion and volatiles combustion.*

Incorporate Elementary Reaction Mechanisms Via CHEMKIN III



NEA's Latest NO_X Predictor Combines PC Coal Lab® with Detailed Chemistry via CHEMKIN III

REACTOR NETWORK

U

ACCEPT INPUT DATA

CHEMKIN III

Iterate to Satisfy O_2 Species

PC Coal Lab

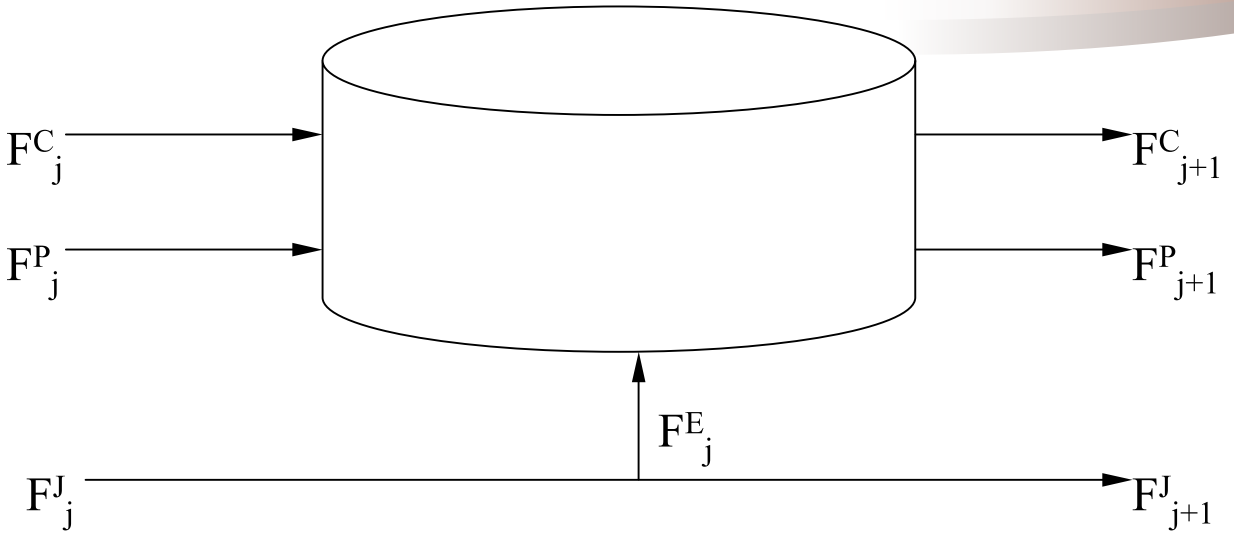
SEQUENCE THROUGH ALL REACTOR ELEMENTS

WRITE OUTPUT REPORTS

Combine Advanced Coal Decomposition Models With Elementary Reaction Mechanisms for Gas Phase Chemistry.

- *CHEMKIN for the mechanisms involving gases and soot.*
- *PC Coal Lab® for FLASHCHAIN® and CBK.*
- *Easy implementation for CSTR-series.*
- *PC-Based calculations with 20 – 30 min run times.*

The CSTR is the Key Element



- *F^C_j – Inlet condensed flow into jth CSTR.*

  F^P_j – Inlet gas flow into jth CSTR.

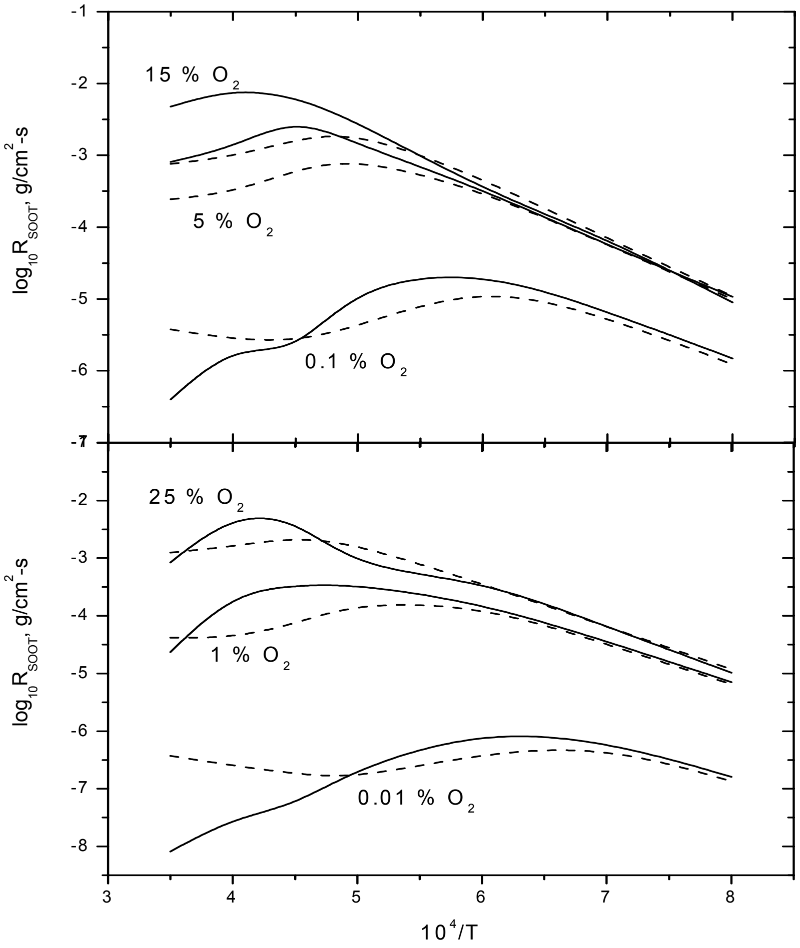
  F^E_j – Entrained air flow into jth CSTR.

The O-Species Balance Determines the Relative Impact of Homogeneous and Heterogeneous Chemistry

$$F_j^E y_{O_2,j}^E + F_j^P y_{O_2,j}^P - F_{j+1}^P y_{O_2,j+1}^P = \frac{\Delta X_j^C F_0^C (1-\chi_0^A)\nu_C}{M_C'} - M_{O_2} V_j \omega_{O_2}$$

- *Extent of coal conversion across the CSTR,* ΔX_j*, determined with FLASHCHAIN® and CBK.*
- *Homogeneous reaction rates,* ω_{O2}*, assigned from elementary reacton mechanisms using CHEMKIN III.*

Soot Oxidation By O_2 Adheres to Nagle/Strickland/Constable Kinetics



$$\omega = \left(\frac{k_A P_{O_2}}{1 + k_Z P_{O_2}} \right) \chi + k_B P_{O_2} (1 - \chi)$$

$$\text{where} \quad \chi = \left[1 + \frac{k_T}{k_B P_{O_2}} \right]^{-1}$$

For Nagle-Strickland-Constable Kinetics:

$C_A + O_2 \rightarrow O + Co$

$C_B + C_D + O_2 \rightarrow CO + O + C_A$

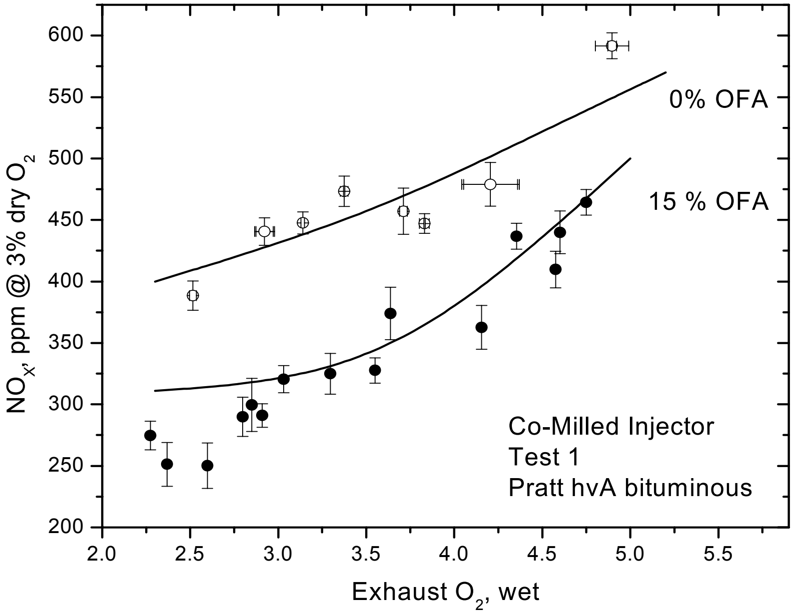
$C_B + C_O \rightarrow CO + C_A$

$C_A \rightarrow C_D$

Co-Fired Flames

- *Baseline CFD: Pratt hvA bituminous only w/15 % OFA, 3.5 %O_2 in exhaust.*
- *Co-Fired CFD: 20 % sawdust on Pratt hvA w/15 % OFA, 3.5 %O_2 in exhaust.*
- *Emissions evaluation database for flames of Pratt hvA, 10 % sawdust, 20 % sawdust, 15 % switchgrass, and 20 % switchgrass with 0, 15, 30 % OFA, $2.5 \leq \%O_2 \leq 4.5$ in exhaust.*

Exhaust NO Depicted Within Experimental Uncertainty for Baseline hvA flame

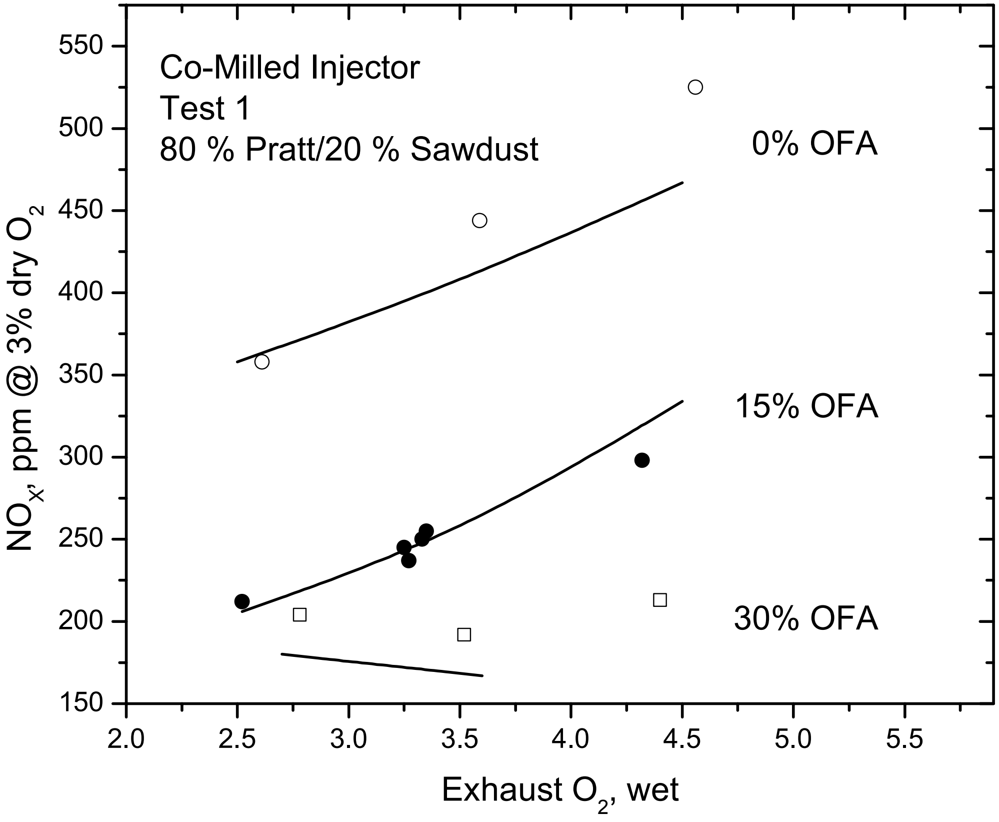


Temperature and Mixing Rate Extrapolations

X_{O2}^{WET}, %	Extent of Staging, %		
	0	15	30
2.5	1.00b/b	0.95b/.25b	0.95b/.25b
3.5	1.05b/b	1.00b/b	0.95b/b
4.5	1.05b/b	1.05b/b	1.00b/b

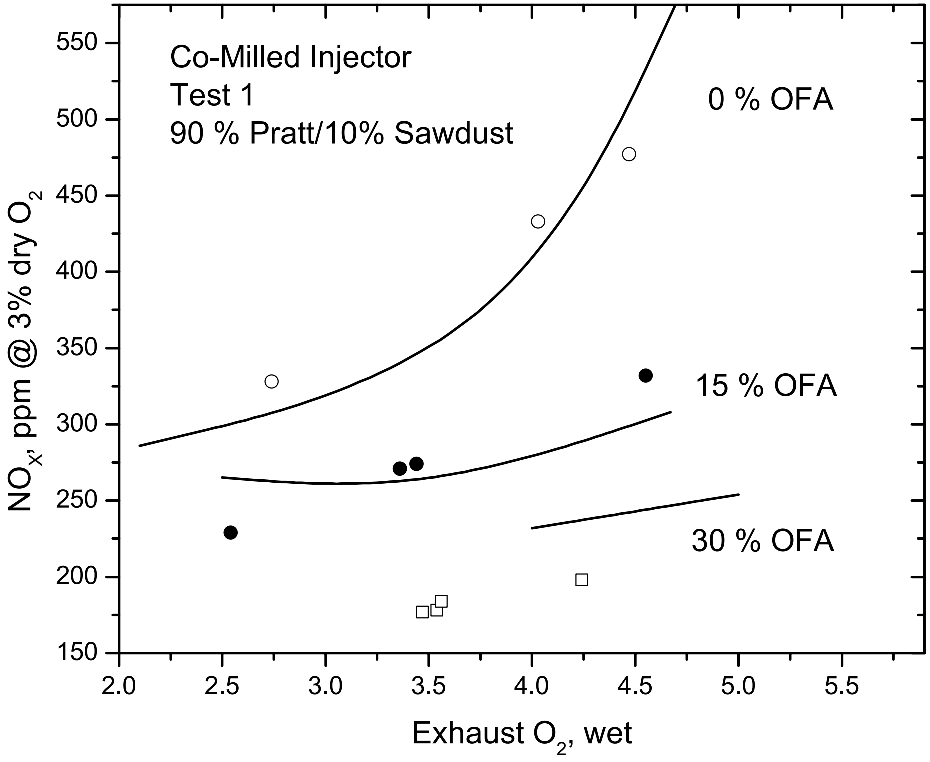
- *Flaw at low O_2 with 15 % OFA associated with numerical stability.*
- *38 % char-N conversion to NO for all cases.*
- *Assigned initial intrinsic char reactivity parameter.*
- *Calibration matrix for all OFA and x_{O2} levels.*

Exhaust NO Predicted Within Experimental Uncertainty for 20 % Co-Milled Sawdust on Pratt



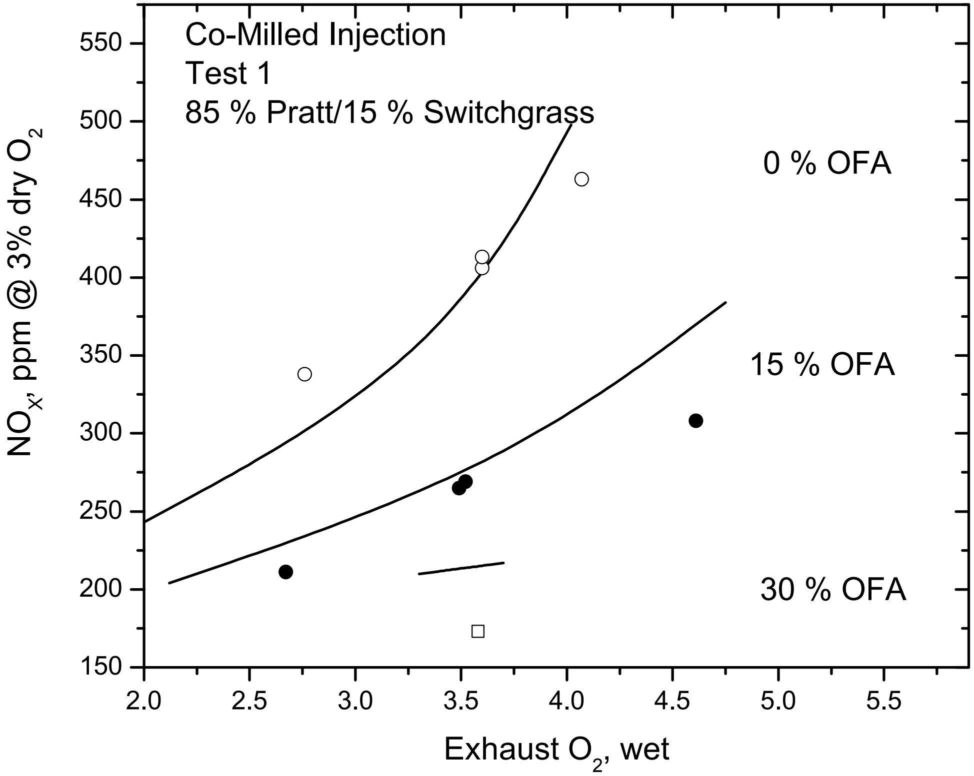
- *Based on baseline extrapolation procedure, with new CFD simulation for 3.4 % O_2, 15 % OFA, and the biomass proximate and ultimate analyses.*
- *No model parameter adjustments.*

Exhaust NO Predicted Within Experimental Uncertainty for 10 % Co-Milled Sawdust on Pratt



- *Based on baseline extrapolation procedure, with interpolated operating conditions.*
- *No model parameter adjustments.*

Exhaust NO Predicted Within Experimental Uncertainty for 15 % Co-Milled Switchgrass on Pratt



- *Based on baseline extrapolation procedure, plus interpolated operating conditions from sawdust on Pratt.*
- *No model parameter adjustments.*

Fuel-N Levels Do Not Forecast Impact of Co-Firing on Exhaust NO_X Levels

Flame	**Measured NO_X**	**Predicted NO_X**	**Fuel**	**Fuel-N, daf wt.%**
hvA Baseline	320	323	hvA bituminous	**1.8**
20 % sawdust on hvA	255	255	Sawdust	**0.1**
15 % switch grass on hvA	270	275	Switchgrass	**2.4**

- *Despite its very high N-content, switchgrass reduced NO_X.*
- *Predicted NO_X exhibits this tendency, whereas a conventional NO_X submodel would not.*

Summary of Evaluations

- *Based on 2 CFD simulations, 1 for hvA bit. with 15 % OFA, 3.5 % O_2 and 1 for 20 % sawdust on hvA with 15 % OFA, 3.5 % O_2.*
- *All extrapolation procedures based on the hvA baseline tests, including adjustments to inlet air exchange, T-profiles and mixing time constants, plus the char-N conversion fraction, 0.38.*
- *Without any parameter adjustments, NEA's APP analysis predicts the fuel quality impacts on NO_X emissions within experimental uncertainty.*
- *UBC levels are reasonable, but need more analysis.*

Summary of the APP Method

- *Requires specialized CFD output, but no new CFD computations.*
- *Assigned RTDs well-represented by CSTR-series, PFR.*
- *Tractable networks.*
- *Detailed chemistry accurately represents fuel quality impacts.*
- *Ideal for gasification, trace species analysis.*
- *Scalable, can be automated.*

APP Has Already Been Successfully Applied at Various Scales

- *Lab-scale coal flames for detailed products, including N-Species.*
- *1.7 MW_t pilot-scale coal/biomass flames.*
- *Full-scale p. f. boilers: 550 MW wall-fired and 330 MW T-fired systems.*

Investigation of Engine Knock by Zonal and In-Cylinder Flow Modeling

Shahrokh Hajireza

Key Words: zonal modeling, CFD, SI engine, engine knock, auto-ignition, exothermic centers, detailed chemical kinetic mechanism, Shell model

Auto-ignition in SI engines is an abnormal combustion mode and may lead to engine knock, which is an undesired phenomenon in SI engines. It may cause damage and it is a source of noise in engines. Knock limits the compression ratio of the engine, which in its turn causes the fuel conversion efficiency lower.

The presentation is concentrated on to clarify, explain and compare different models such as zero-, one- and three dimensional models, which have been developed for the analysis of auto-ignition and engine knock.

The first model category, i.e. zero-dimensional zonal model, was developed for spatially homogeneous mixtures of primary reference fuels (PRF) of *n*-heptane and *iso*-octane, *ref.* [1-4]. These models enable studies of transient behavior of the gas with detailed chemistry for such complex fuels. In zonal models, the gas volume in the combustion chamber is divided into a number of control volumes or zones in order to compensate for the spatial variation of quantities. Each zone is modeled either as a plug-flow reactor or a perfectly stirred reactor (depending on which zone it is). In addition it is assumed to be a homogeneous mixture with a uniform temperature, mole, and mass fraction of species. The spatial variation of the pressure is neglected, i.e., it is assumed to be the same in the whole combustion chamber at every instant of time. The ordinary differential equations of energy and species were derived and solved. The occurrence of homogeneous auto-ignition was studied in each zone as function of different engine and fuel parameters. The calculated temperature profiles were in a good agreement with corresponding experimental results.

Another kind of zonal models was also developed in which the gas in the combustion chamber was divided into three zones. In that model, the burned gas and the unburned gas in the core region were assumed as homogeneous mixtures and the unburned gas in the region close to the wall was modeled in the way that in homogeneity was considered in one dimension, *ref.* [5,6]. The laminar, compressible, unsteady flow and thermal fields were solved by an implicit method. A detailed chemical kinetic mechanism for the mixture of *n*-heptane and *iso*-octane was included in the model. The autoignition history, development of hot spots and the propagation of reaction fronts were simulated. The results showed that the inhomogeneous initial fields of temperature, oxidizer and fuel caused the hot-spot autoignition or development of exothermic centers. In addition, ignition of the exothermic centers leads the propagation of reaction fronts to the surroundings. The propagation velocities of the reaction fronts were estimated.

As the third model category, a three-dimensional CFD model was developed for the in-cylinder flow analysis, *ref.* [7]. The normal combustion resulted from ignition by sparks were modeled by a turbulent combustion model. The governing equations, for mass continuity, momentum, energy and species concentrations for transient, turbulent and compressible flow and thermal fields, were solved. The commercial CFD code STAR-CD was adapted for the calculations. The auto-ignition modeling has been treated by the Shell model, which estimates the local reaction rates of five generic species. These generic species represent hydrocarbon fuel, the radical formed from the fuel, branching agent, intermediate species and products, respectively. The first stage of auto-ignition in the end gas was predicted by the Shell model. In addition the mean temperature profile was calculated and compared with the calculations by two-zone model and a skeletal mechanism, consisted of 74 species and 510 reactions, when the initial data for the CFD model was obtained from the two-zone model. Strong and weak points of each model category will be presented and discussed.

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[2] Hajireza, S., Mauss, F. and Sundén, B., *Two-Zone Model of Gas Thermodynamic State in SI Engines with Relevance for Knock*, COMODIA 98, pp. 203-208, 1998.

[3] Hajireza, S., Sundén, B. and Mauss, F., *A Three-Zone Model for Investigation of Gas Behavior in the Combustion Chamber of SI Engines in Relation to Knock*, SAE 1999-01-0219, 1999.

[4] Hajireza, S. and Sundén, B., *Prediction of Heat Transfer to the Walls for Autoignition Related Situations in SI Engines*, SAE Trans, SAE 2000-01-1084, 2000.

[5] Hajireza, S., Mauss, F. and Sundén, B., *Effect of Inhomogeneities in the Temperature Field of the End Gas on the Autoignition in SI Engines*, SAE Trans., SAE 2000-01-0954, 2000.

[6] Hajireza, S., Mauss, F. and Sundén, B., *Hot-Spot Autoignition in SI Engines*, Proc. of the Combustion Institute, vol. 28, pp. 1169-1175, 2000.

[7] Hajireza, S., *Investigation of Auto-Ignition Occurrence in SI Engines by In-Cylinder Flow Modeling*, to be presented as work-in-progress poster at 29th Symposium (Int.) on Combustion, The Combustion Institute, 2002.

Investigation of Engine Knock by Zonal and In-Cylinder Flow Modeling

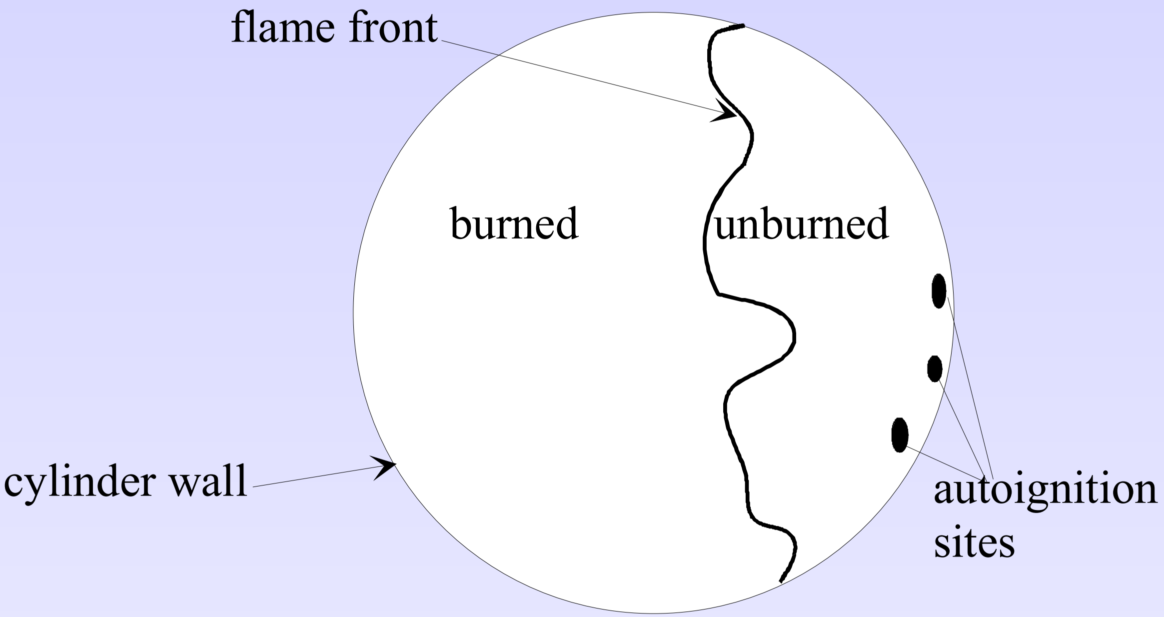
Shahrokh Hajireza

SAAB AUTOMOBILE
POWERTRAIN AB

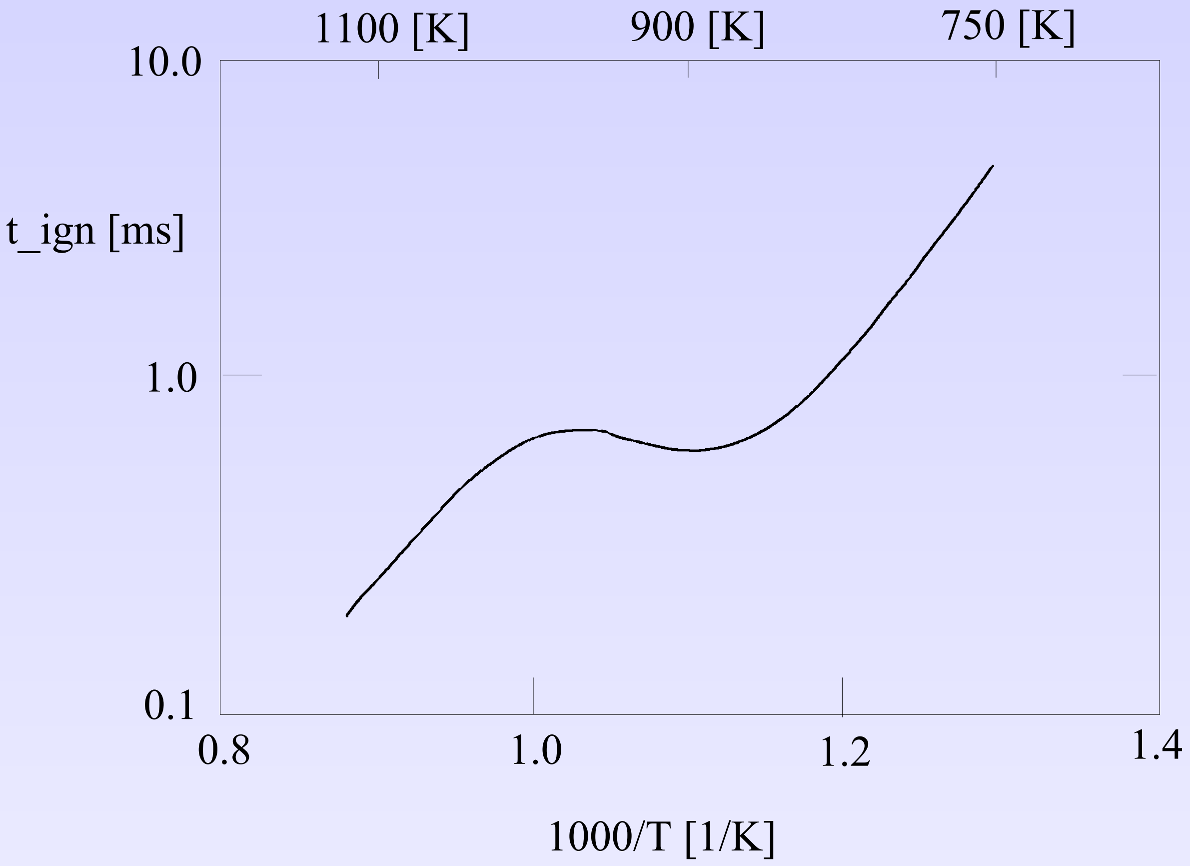
Contents

- Introduction
- 0-D Models (Zonal)
- 1-D Models (Zonal + 1-D Geometry)
- 3-D Models (CFD)

Inhomogeneities in the End Gas



Ignition of Higher Hydrocarbons in Different Temperature Regimes



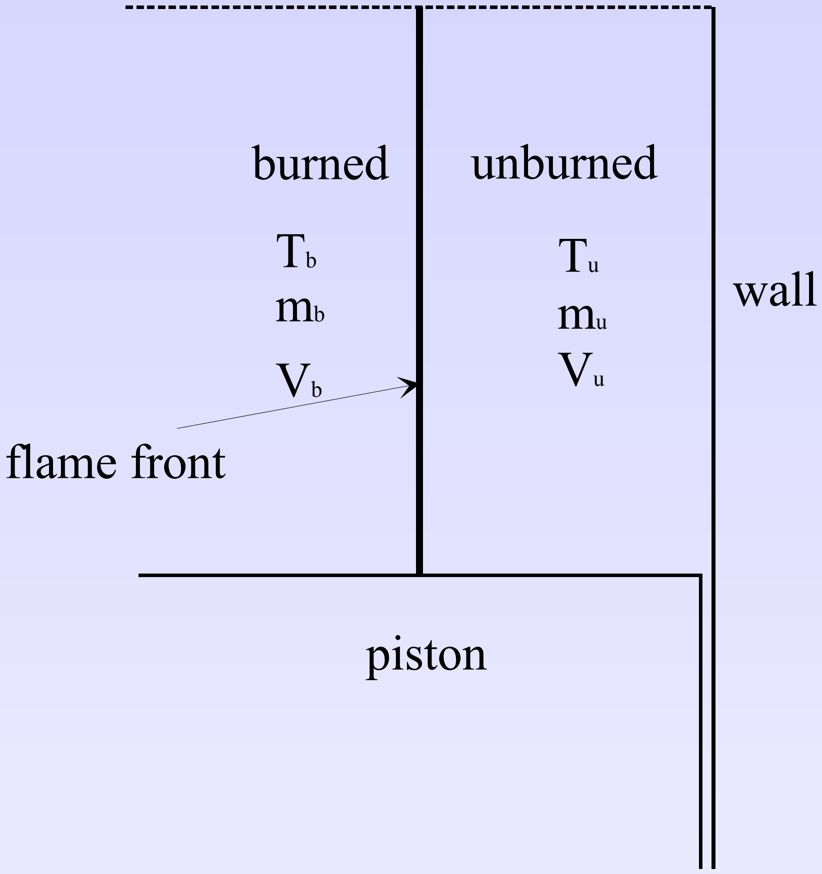
Zeldovich’s Gradient Mechanism

Small Temperature Gradient => Thermal Explosion

Large Temperature Gradient => Deflagration

Intermediate Temperature Gradient => Detonation

Thermal Analysis of the End-Gas by Zonal Models



Assumptions

- Zero-dimensional analysis.
- Simplified geometry.
- Homogeneous end gas.
- Flame velocity is estimated by Wiebe function.
- The adiabatic flame temperature is calculated by minimizing Gibb’s free energy at each time step.
- The gas is assumed to follow the ideal gas law.

Chemical Kinetic Model

- The chemical kinetic mechanism for *iso*-octane and *n*-heptane is based on a mechanism for C_1-C_4 and C_5-C_8 hydrocarbons.
- This mechanism involves 510 chemical reactions and 75 species.
- The mechanism is such that RON of the fuel can be adjusted as an initial condition in the program.

Numerical Method

- Higher order backward differential scheme.

- A set of non-linear algebraic equations: $F(\Phi) = 0$,

where Φ is a vector of unknowns.

- Newton's method produces a sequence of vectors $\Phi^{(n)}$.

$$\Phi^{(n+1)} = \Phi^{(n)} - J^{-1} F\left(\Phi^{(n)}\right)$$

where

$$J = \left(\frac{\partial F}{\partial \Phi}\right)_{\Phi(n)}$$

Burned gas temperature

$$m_b C_{p_b} \frac{dT_b}{dt} = V_b \frac{dp}{dt} - m_b \left(\sum_{j=1}^{N_s} h_{j,b} \frac{M_{j,b}}{\rho_b} \sum_{k=1}^{N_r} \nu_{j,k} \omega_k \right)$$

$$+ \dot{m}_b \sum_{j=1}^{N_s} Y_{j,f} \left(h_{j,f} - h_{j,b} \right) - A \sigma \varepsilon T_b^4$$

Burned gas species

$$\frac{\partial Y_{j,b}}{\partial t} = \frac{M_{j,b}}{\rho_b} \sum_{k=1}^{N_r} \nu_{j,k} \omega_k + \frac{\dot{m}_b}{m_b} \left(Y_{j,f} - Y_{j,b} \right)$$

Differential equation for unburned gas temperature

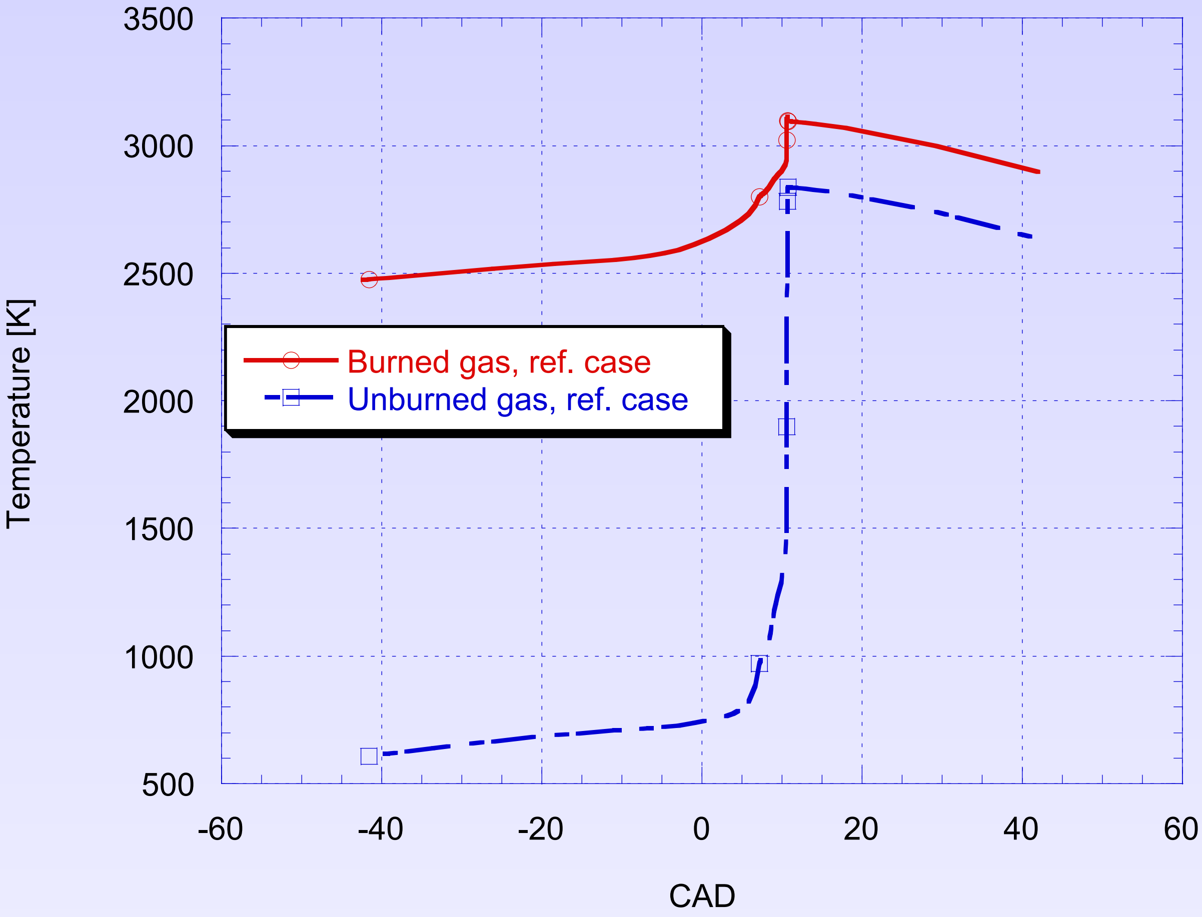
$$\alpha A\left(T_f + T_w - 2T_u\right) + A\sigma\varepsilon\left(T_u{}^4 - T_w{}^4\right) =$$

$$m_u\left(\sum_{j=1}^{N_s} h_j \frac{M_j}{\rho} \sum_{k=1}^{N_r} \nu_{j,k}\omega_k\right) + m_u C_{p_u}\frac{dT_u}{dt} - V_u\frac{dp}{dt}$$

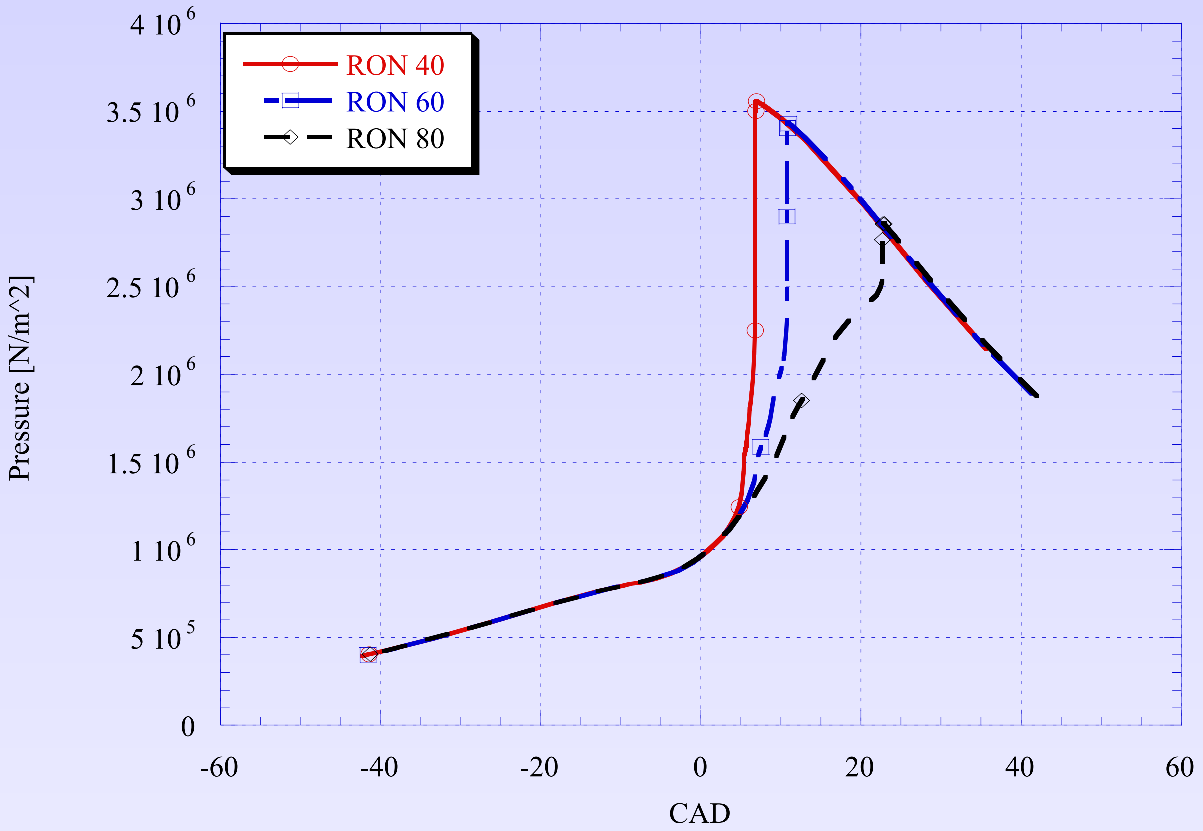
Species Conservation

$$\frac{dY_j}{dt} = \frac{M_j}{\rho}\sum_{k=1}^{N_r} \nu_{j,k}\omega_k$$

Calculated Temperature Profiles in the Burned and Unburned Gases



RON Dependency of the Cylinder Pressure



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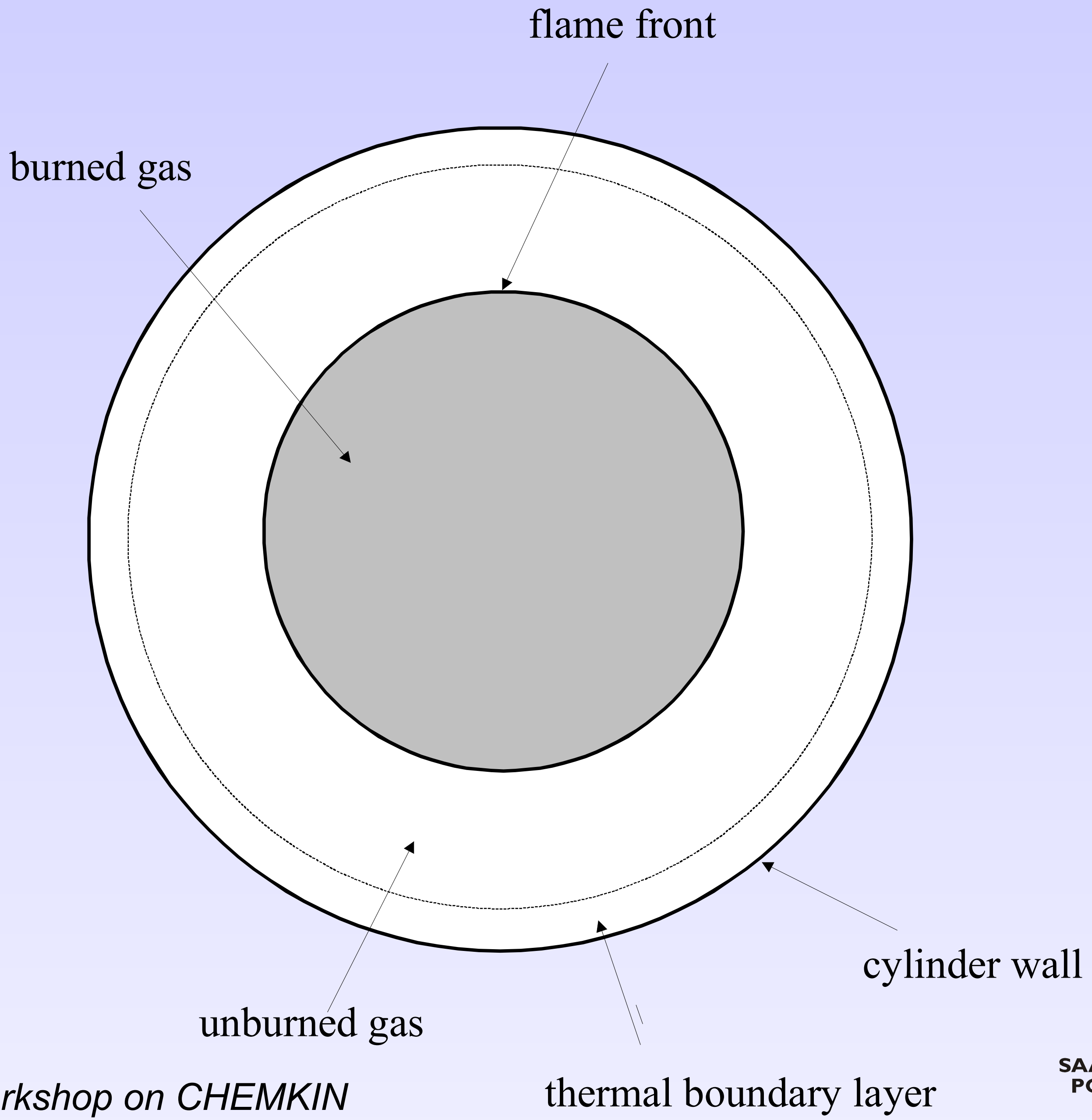
Three-Zone Model



Differential Equation for the Unburned Gas Temperature (Zone II)

$$m_u C_{p_u} \frac{dT_u}{dt} = V_u \frac{dp}{dt} - m_u \left(\sum_{j=1}^{N_s} h_{j,u} \frac{M_{j,u}}{\rho_u} \sum_{k=1}^{N_r} \nu_{j,k} \omega_k \right)$$

$$- \dot{m}_\delta \, \eta(-\dot{m}_\delta) \sum_{j=1}^{N_s} Y_{j,\delta} \left(h_{j,\delta} - h_{j,u} \right) - \lambda A \frac{T_u - T_\delta}{\delta}$$

and for the Unburned Gas Species

$$\frac{dY_{j,u}}{dt} = \frac{M_{j,u}}{\rho_u} \sum_{k=1}^{N_r} \nu_{j,k} \omega_k$$

$$- \frac{\dot{m}_\delta}{m_u} \left(\eta(\dot{m}_\delta) Y_{j,u} - Y_{j,u} + \eta(-\dot{m}_\delta) Y_{j,\delta} \right)$$

Differential Equation for the Unburned Gas Temperature in the Thermal Boundary Layer (Zone III)

$$m_\delta C_{p_\delta} \frac{dT_\delta}{dt} = V_\delta \frac{dp}{dt} - m_\delta \left(\sum_{j=1}^{N_s} h_{j,\delta} \frac{M_{j,\delta}}{\rho_\delta} \sum_{k=1}^{N_r} \nu_{j,k} \omega_k \right)$$

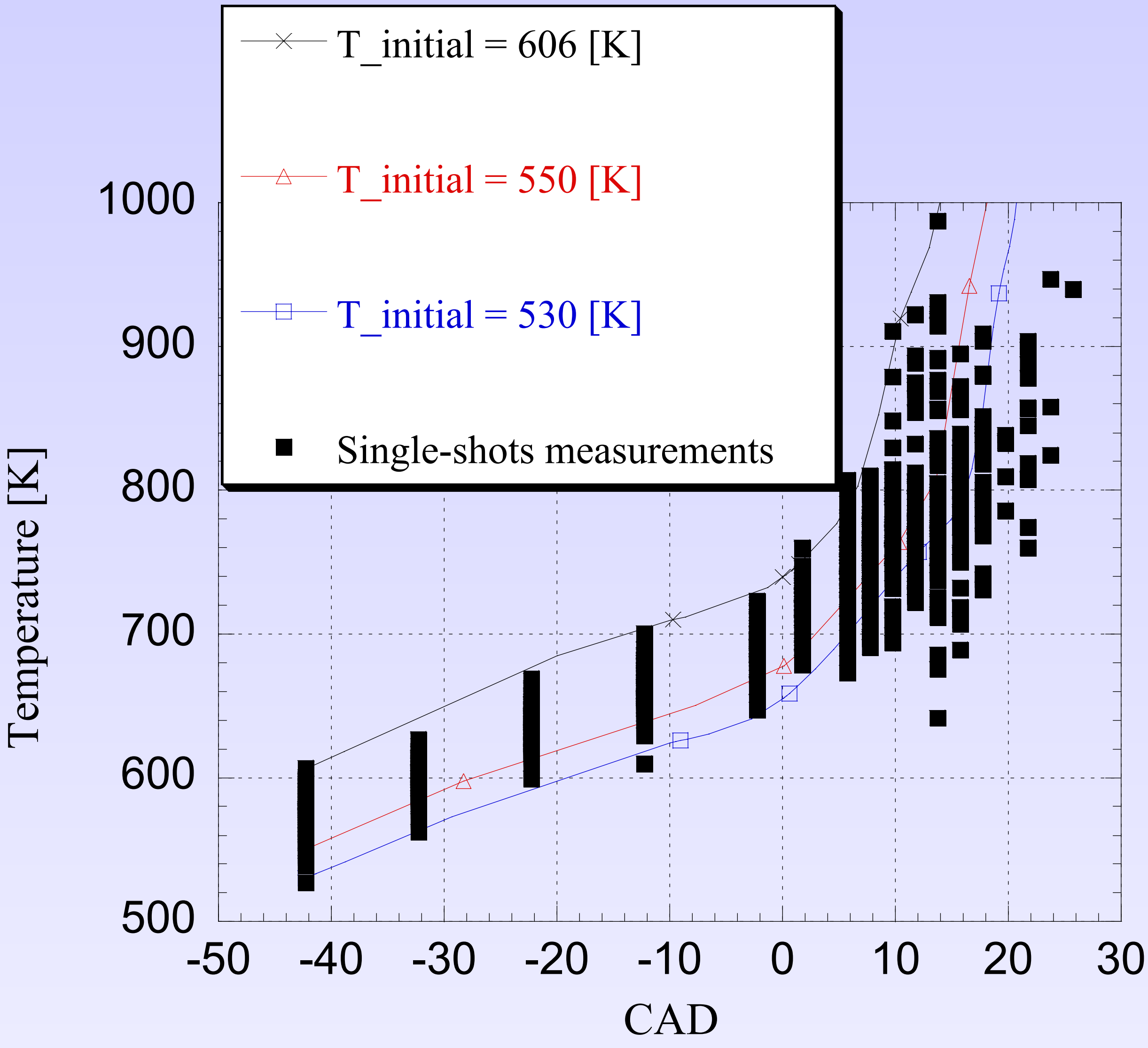
$$- \dot{m}_\delta\, \eta(\dot{m}_\delta) \sum_{j=1}^{N_s} Y_{j,u} \left(h_{j,\delta} - h_{j,u} \right) - \alpha A_w \left(T_\delta - T_w \right) - \lambda A \frac{T_\delta - T_u}{\delta}$$

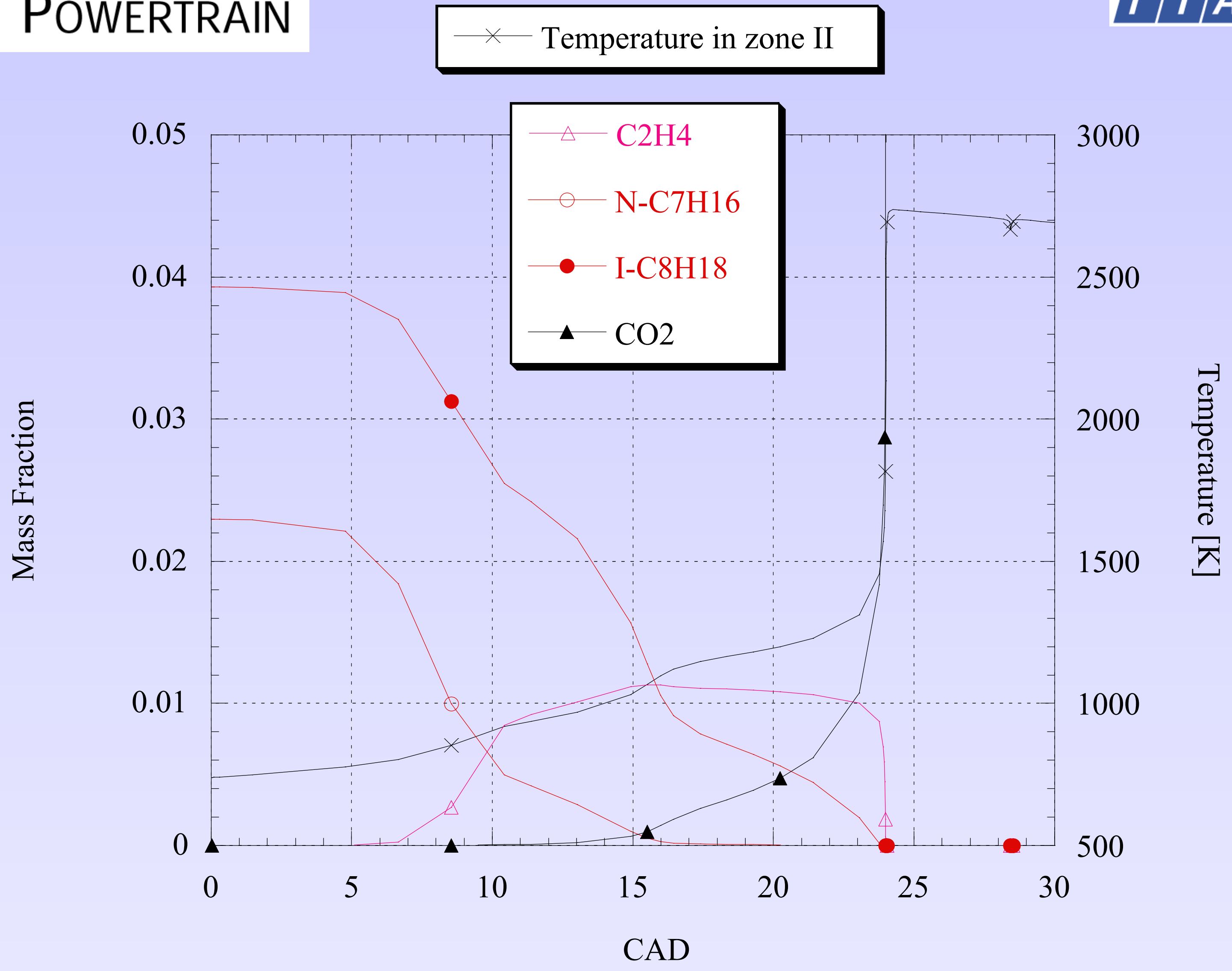
and for the Species

$$\frac{dY_{j,\delta}}{dt} = \frac{M_{j,\delta}}{\rho_\delta} \sum_{k=1}^{N_r} \nu_{j,k} \omega_k$$

$$+ \frac{\dot{m}_\delta}{m_\delta} \left(\eta(\dot{m}_\delta) Y_{j,u} - Y_{j,\delta} + \eta(-\dot{m}_\delta)\, Y_{j,\delta} \right)$$

Comparison with Experimental Results




Temperature in zone II
C2H4
N-C7H16
I-C8H18
CO2
Mass Fraction
0.05
0.04
0.03
0.02
0.01
0
Temperature [K]
3000
2500
2000
1500
1000
500
CAD
0
5
10
15
20
25
30

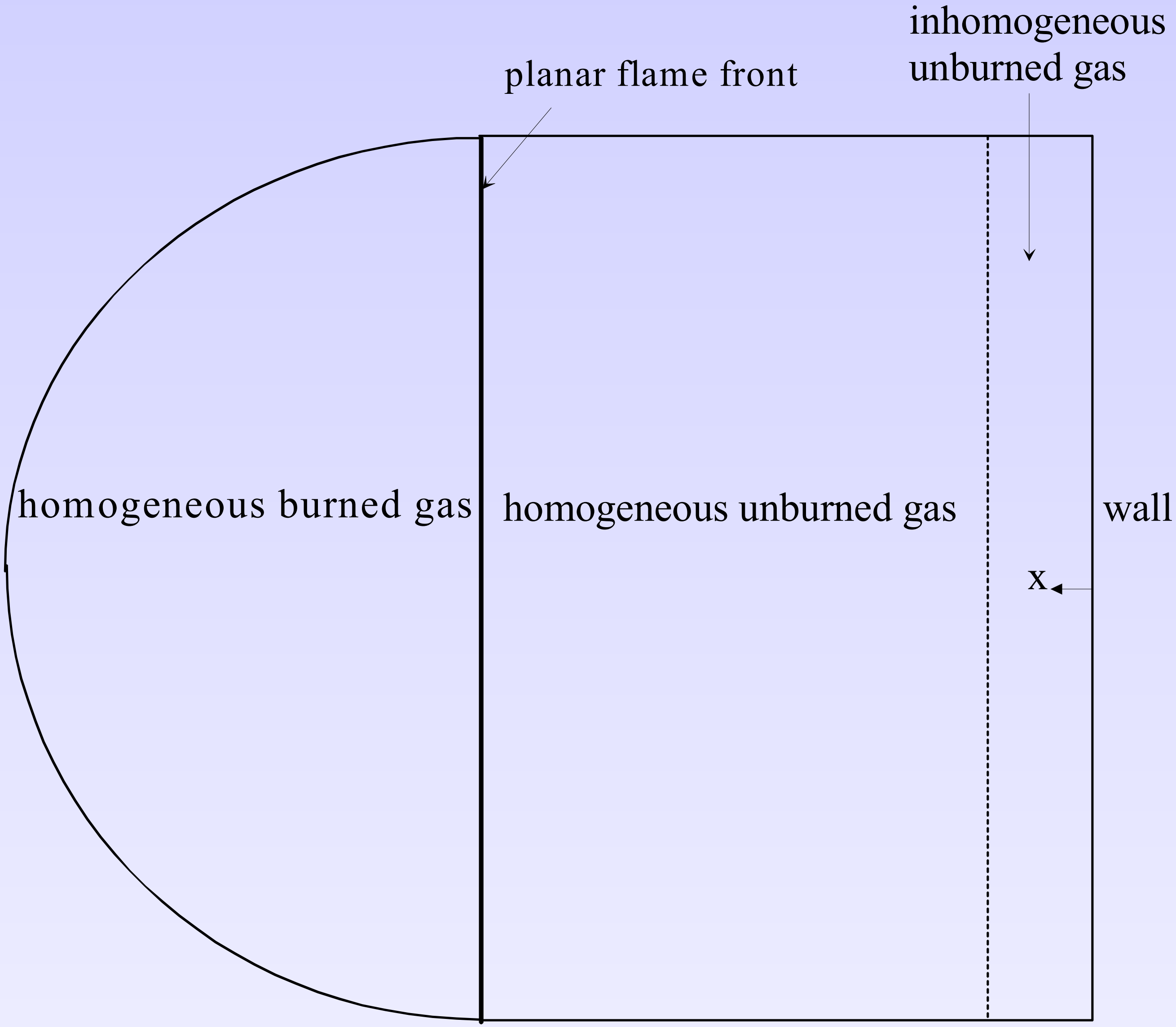
Conclusions

+ The models allow to investigate the auto-ignition onset in SI engines by considering the chemical and thermal effects.

+ The models were found to be efficient tools for developing chemical reaction mechanisms and reduction techniques.

- Spatial effects such as: mixing, turbulence, inhomogeneities can not be taken into account.

Two-Zone Model + 1-D Geometry



inhomogeneous unburned gas

planar flame front

homogeneous burned gas

homogeneous unburned gas

wall

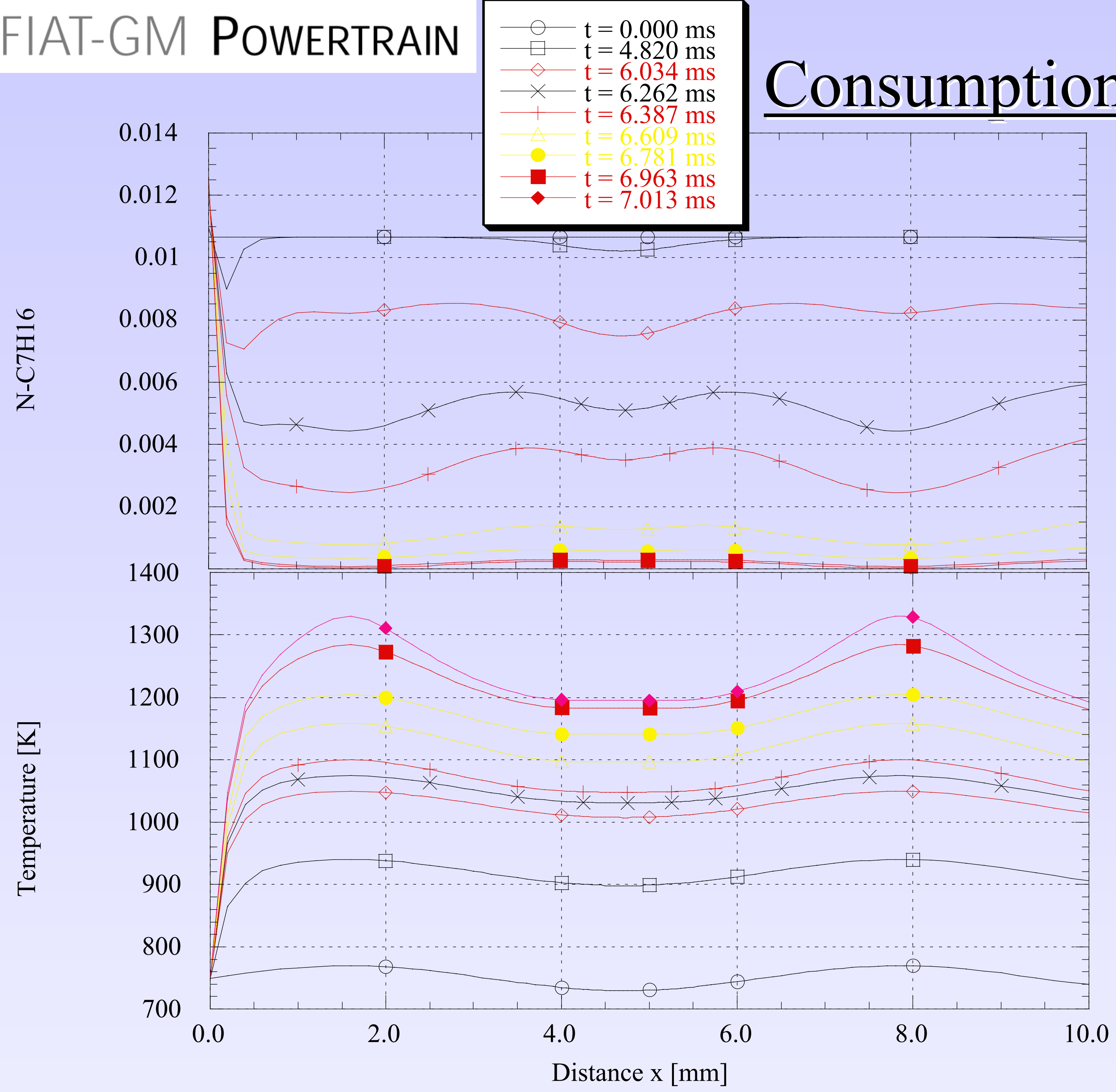
Boundary Conditions

1. At the wall- Dirichlet for T, u and no active chemical reaction, i.e.

$$\rho \frac{\partial Y_j}{\partial t} = \frac{\partial}{\partial x}\left(\rho Y_j v_j\right)$$

2. At the open boundary- Neumann for all variables

Consumption of *n*-Heptane



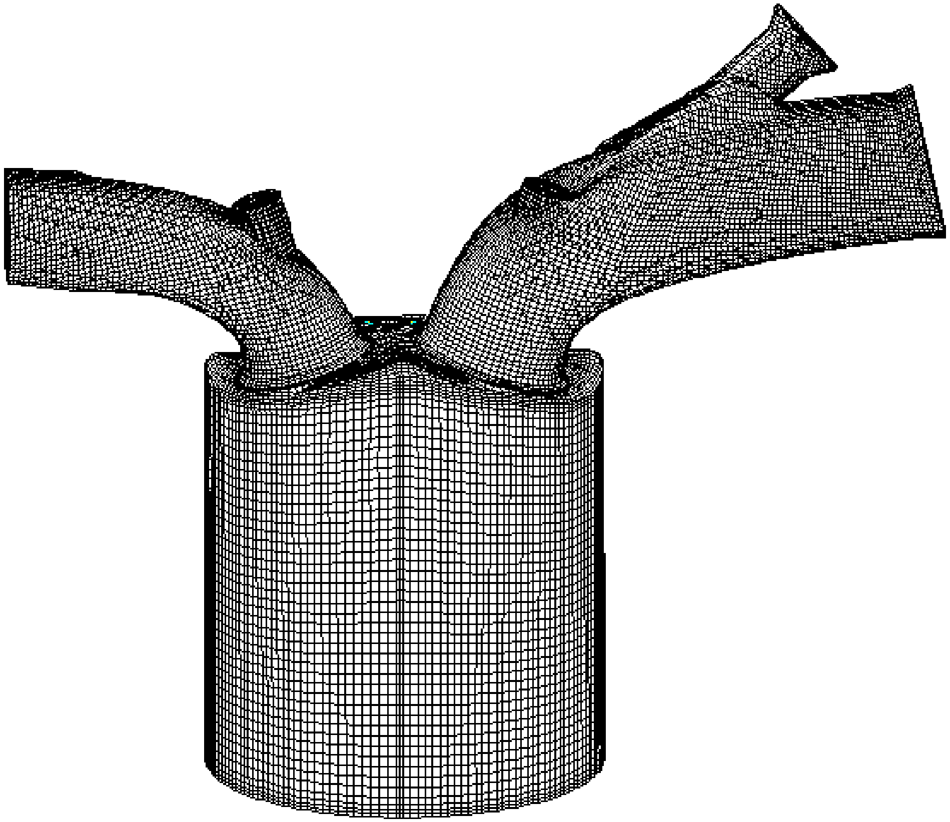
Conclusions

+ Detailed chemical kinetic and thermodynamic analyses.

+ This model allows investigation of inhomogeneities effect in a limited way (only one-dimensional).

- The effect of turbulence and mixing is still missing.

3-D In-Cylinder Flow Model



- 230,000 Computational Cells
- Transient, Turbulent, Compressible Flow
- High Re-number k-ε
- Weller 1-Equation
- Shell Auto-ignition

Boundary Conditions and Initial Values

* Species: Neumann BC

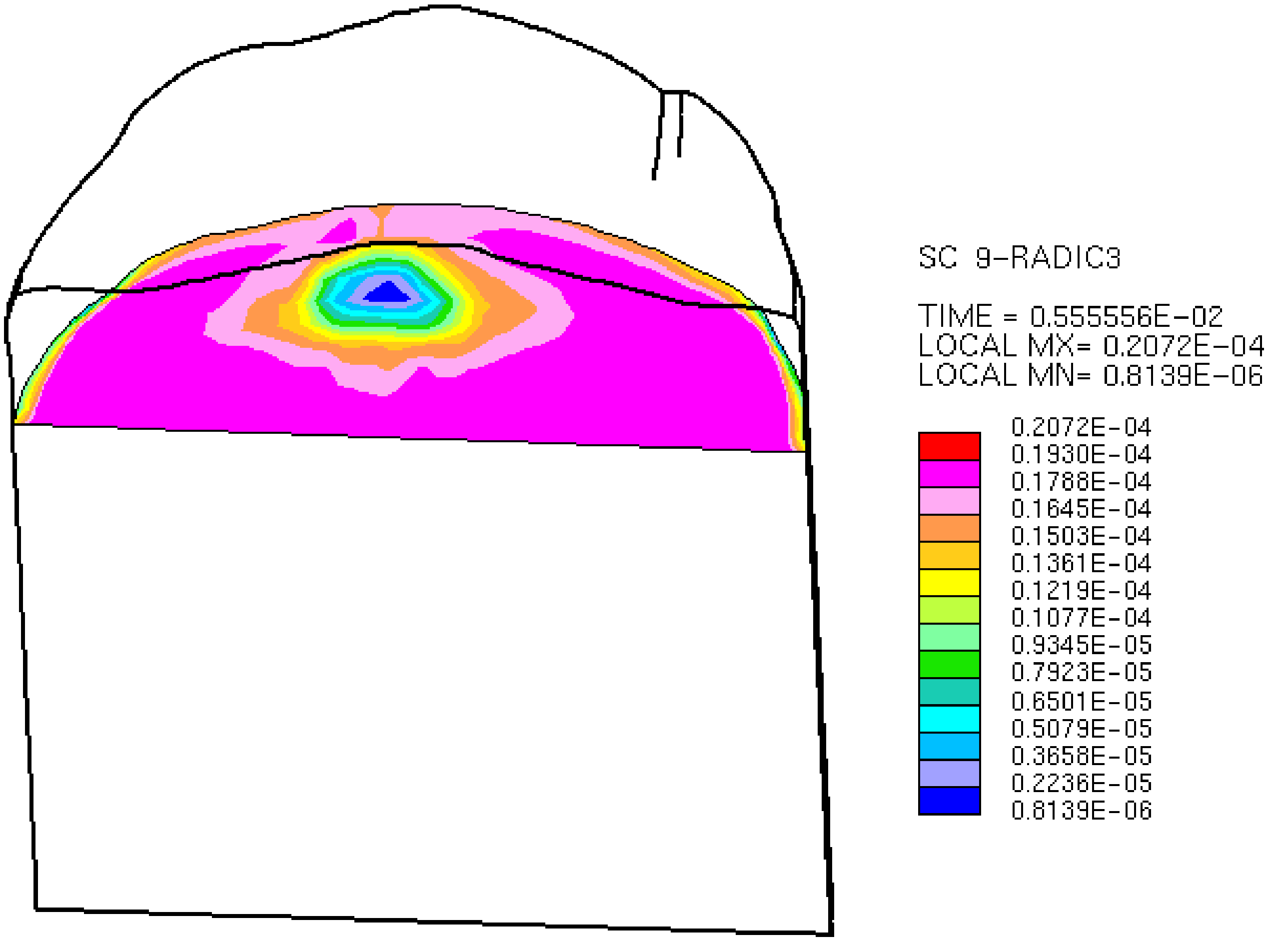
* Temperature and Velocities: Dirichlet BC

* Engine Speed : 1500 RPM

* RON = 70

* Timing of Ignition = -10 CAD

* Duration Time of Combustion = 50 CAD


SC 9-RADIC3
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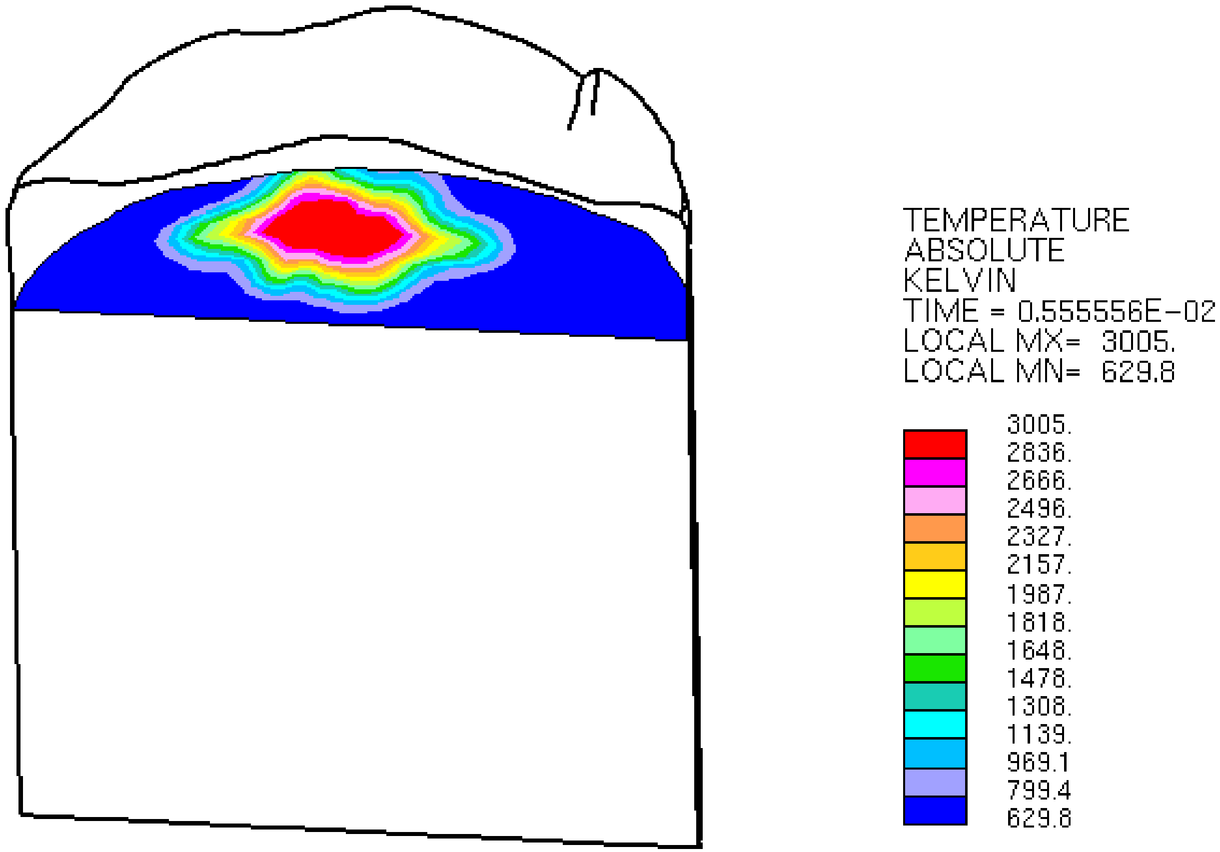
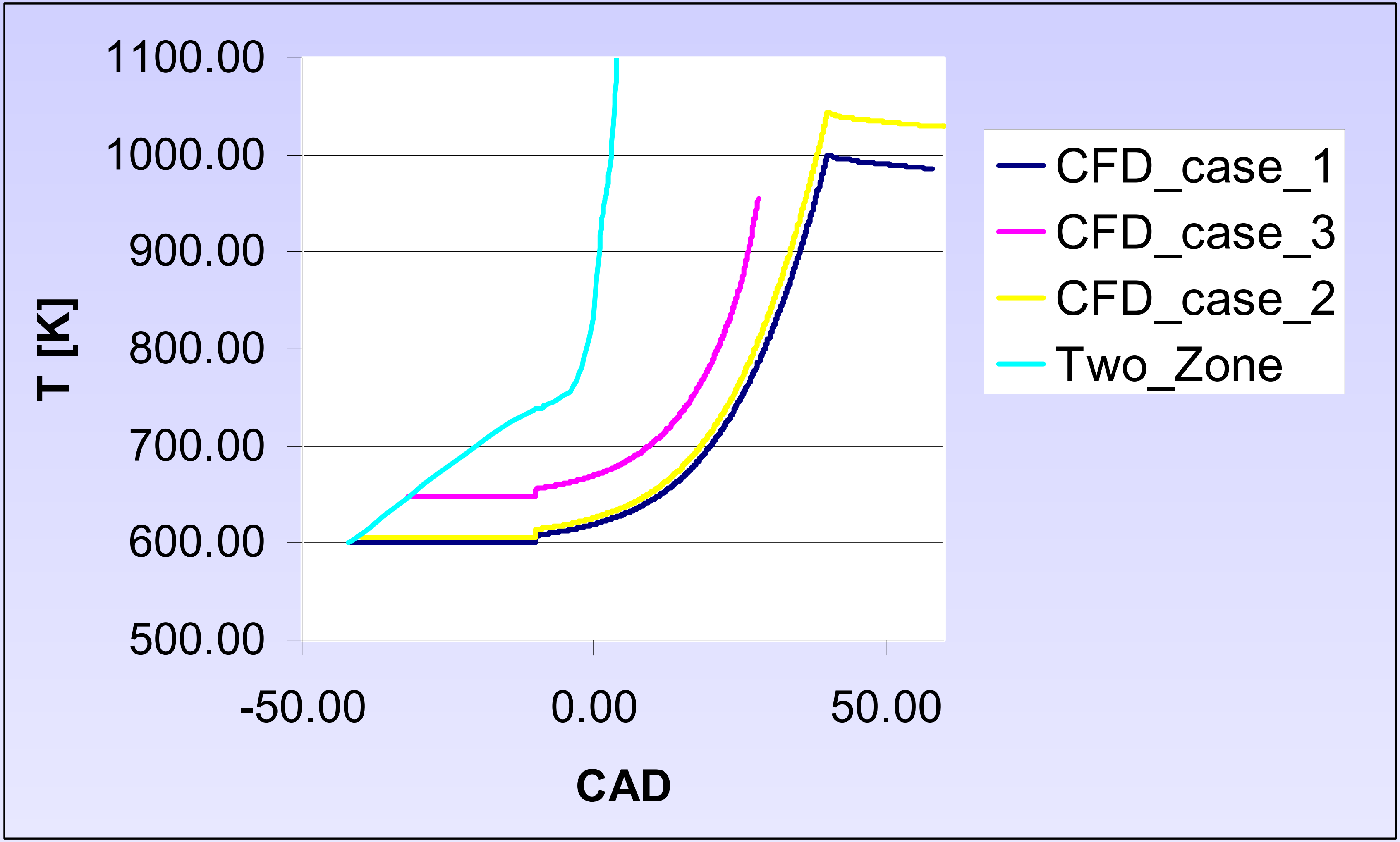
LOCAL MX= 0.2072E-04
LOCAL MN= 0.8139E-06
0.2072E-04
0.1930E-04
0.1788E-04
0.1645E-04
0.1503E-04
0.1361E-04
0.1219E-04
0.1077E-04
0.9345E-05
0.7923E-05
0.6501E-05
0.5079E-05
0.3658E-05
0.2236E-05
0.8139E-06


TEMPERATURE
ABSOLUTE
KELVIN
TIME = 0.555556E-02
LOCAL MX= 3005.
LOCAL MN= 629.8
3005.
2836.
2666.
2496.
2327.
2157.
1987.
1818.
1648.
1478.
1308.
1139.
969.1
799.4
629.8

CFD Model vs Two-Zone Model



Conclusions

\+ To Understand the Flow and Thermal Fields Behavior

\+ To Capture the 3-D and Spatial Effects => Real Geometry

\+ To Allow Analysis of Turbulence and Mixing

\- Too Simple Combustion Model

Conclusions

To Perform Both Kinds of Analyses:

- Separately
- Separately but Deliver Data from One to Another
- by Implementing Reactions Directly in the CFD Code and using
    1. One Solver for Both
    2. Two Different Solvers

Toward Reaction Knowledge Base for Combustion Modeling

Akira Miyoshi

Department of Chemical System Engineering

University of Tokyo, Japan

The *reaction knowledge base*, a possible future style of the mechanism, for combustion modeling will be presented and discussed. As on of its important components, generalized formulae for RRKM / Master calculation are briefly introduced. Along with the transition-state theory (TST), the RRKM / Master calculation provides almost universal approach for *a priori* evaluation of rate parameters as well as the analysis of the experimental rate parameters.

Object-Oriented Mechanism and Reaction Knowledge Base: A desirable style of the reaction mechanism will be *object-oriented*, that is, a well encapsulated mechanism for which users do not have to read the implementation in detail. For the combustion of aliphatic fuels, the approach like 'automatic generation of the mechanism' may be extended as the reaction knowledge base, which do not apparently contain mechanism, but contains logic and theories for the mechanism / rate estimation.

Generalized formulae for RRKM / Master calculations: As a straightforward extension of the most typical steady-state dissociation (SSD) problem with a single well,

$$\mathbf{Mg} = -k_{\mathrm{tot}}\mathbf{g}\,, \tag{1}$$

problems with multiple well and chemical activation (CA) problems can be represented in simple matrix forms as follows.

[2-well SSD] $$\begin{pmatrix} \mathbf{M}_1 & \mathbf{M}_{12} \\ \mathbf{M}_{21} & \mathbf{M}_1 \end{pmatrix}\begin{pmatrix} \mathbf{g}_1 \\ \mathbf{g}_2 \end{pmatrix} = -k_1\begin{pmatrix} \mathbf{g}_1 \\ \mathbf{0} \end{pmatrix} \tag{2}$$

[1-well CA] $$\mathbf{Mg} + R\boldsymbol{\eta} = \mathbf{0} \tag{3}$$

[2-well CA] $$\begin{pmatrix} \mathbf{M}_1 & \mathbf{M}_{12} \\ \mathbf{M}_{21} & \mathbf{M}_1 \end{pmatrix}\begin{pmatrix} \mathbf{g}_1 \\ \mathbf{g}_2 \end{pmatrix} + R\begin{pmatrix} \boldsymbol{\eta}_1 \\ \mathbf{0} \end{pmatrix} = \mathbf{0} \tag{4}$$

Several examples will be also presented.

LOW TEMPERATURE OXIDATION MECHANISM OF DIMETHYLETER (DME) IN HCCI ENGINES

N. Choi, H. Yamada and A. Tezaki
Department of Mechanical Engineering, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Homogeneously charged compression ignition of DME-air mixture has been investigated experimentally in an externally motored single cylinder piston engine, and analyzed by using SENKIN-based simulation.

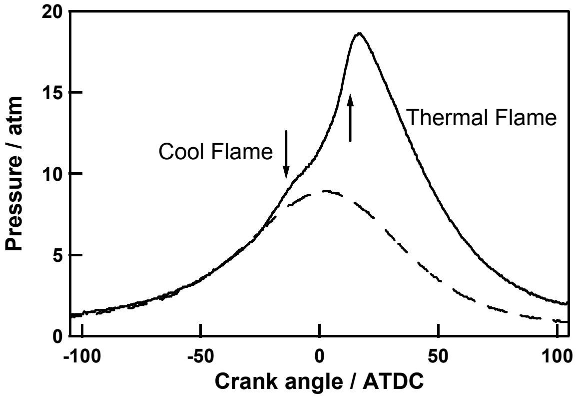


Fig. 1 Pressure profile of DME-air mixture in an HCCI operation, $\Phi = 0.55$, $T_{\mathrm{intake}} = 443$ K, compression ratio = 6.8. Broken line is a trace for air without fuel.

DME is the simplest hydrocarbon molecule that exhibits typical two-stage autoignition. Figure 1 shows a pressure profile of the mixture in a compression cycle, where a small heat release (cool flame) is followed by the final complete combustion (thermal flame).

Laser-induced fluorescence measurement was conducted to detect formaldehyde *in situ* in a research engine having optical ports in the head plate. The observed LIF intensity profiles were converted to crank-angle resolved concentrations with corrections for collisional quenching and pressure broadening. It is clearly shown that formaldehyde is rapidly formed at the cool flame, and disappears at the thermal flame. It is also demonstrated that the exhaust gas composition simply reflects that of a cool flame when the thermal flame is suppressed.

Mass spectrometric analysis was applied to quantify emission of HCHO and residual DME at the engine exhaust mainly at the single cool flame conditions. It was found that extent of DME consumption and formaldehyde formation against initial amount of DME is nearly constant against equivalent ratio and intake temperature as shown in Figs. 2-3. This means that the cool flames are quenched at the same percentage of fuel partial consumption in spite that the final temperature is varied.

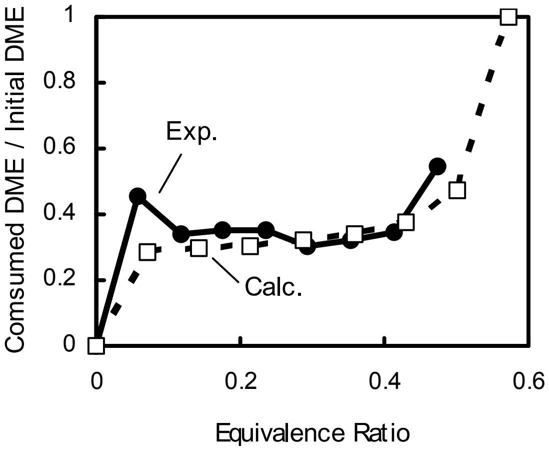


Fig. 2 Measured and calculated DME consumption relative to initial DME amount as a function of equivalence ratio, $T_{\mathrm{intake}} = 414$ K.

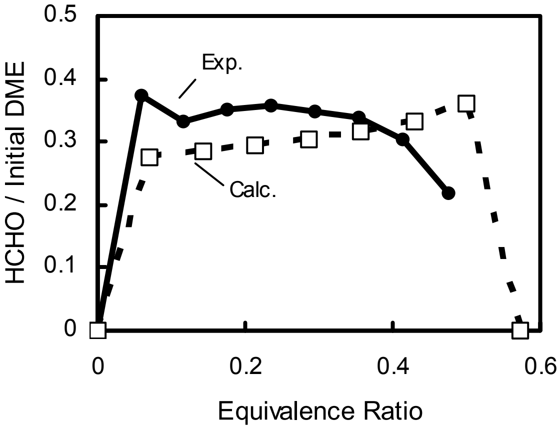


Fig. 3 Measured and calculated HCHO emission relative to initial DME amount as a function of equivalence ratio, $T_{\mathrm{intake}} = 414$ K.

This behavior is satisfactorily reproduced by SENKIN simulations operated in VTIM mode with given volume profiles of compression cycles as shown in Figs. 2-3. The detailed chemical kinetics mechanism of DME oxidation established by Curran et al. has been used for the reaction scheme. Calculated ignition limit in terms of equivalence ratio and intake temperature is also in good agreement with observation. Ignition timing against initial conditions is in qualitative agreement.

The degenerate chain branching mechanism in cool flames is summarized in Table 1. Pass 1 is energetically the lowest pathway dominant at lower temperature, while Pass 3 is the highest one. By the change in the contribution of the pathways having different chain branching nature, the self sustaining mechanism through OH regeneration is only effective in the range 720 - 850K. Formaldehyde is a major intermediate product that plays an important role to end the cool flame by the character of chain termination.

The overall process can be simplified to the following two competing steps controlling OH regeneration:

$CH_3OCH_3 + OH \rightarrow \alpha OH + \beta HCHO$ (1')
$HCHO + OH \rightarrow$ termination (9')

where the factors α and β are determined by the rate constants of 1-8. The regeneration rate of OH is described as

$$\frac{d[OH]}{dt} = \{(\alpha - 1)[DME] - \frac{k_9}{k_1}[HCHO]\}k_1[OH]$$

The chain reaction is sustainable while the term $\{(\alpha - 1)[DME] - (k_9/k_1)[HCHO]\}$ remains positive. In most of the current experimental condition, this term turns negative by the increase of HCHO before the decrease of α via temperature rise. Because α, β and k_9/k_1 are nearly constant in a narrow range of temperature, the endpoint of the cool flame is dominantly dependent on the ratio [HCHO]/[DME]. The ratio [HCHO]/Δ[DME] is supposed to be slightly less than β, which is around 1.3 in the current temperature range, and obtained as a function of DME consumption by numerically integrating the equations. It was found that this ratio is always close to 1. At 750 K, α and k_9/k_1 are given to be 1.5 and 1.87, respectively, consequently the endpoint is estimated to be [HCHO]/[DME] = 0.27, which corresponds to $[HCHO]/[DME]_0 = 0.22$. This result is in reasonable agreement with observation.

Table 1 Chain reaction mechanism in DME cool flame regime

$CH_3OCH_3 + OH \rightarrow CH_3OCH_2 + H_2O$	(1)	Initiation:
$CH_3OCH_2 + O_2 = CH_3OCH_2O_2$	(2)	Pass 1: Release of two OH radicals via O_2 addition, isomerization and second O_2 addition
$CH_3OCH_2O_2 \rightarrow CH_2OCH_2O_2$	(3)	
$CH_2OCH_2O_2H + O_2 = O_2CH_2OCH_2O_2H$	(4)	
$O_2CH_2OCH_2O_2H \rightarrow HO_2CH_2OCHO + OH$	(5)	
$HO_2CH_2OCHO \rightarrow OCH_2OCHO + OH$	(6)	
$CH_2OCH_2O_2H \rightarrow 2CH_2O + OH$	(7)	Pass 2: Single OH release without second O_2 addition
$CH_3OCH_2 \rightarrow CH_3 + CH_2O$	(8)	Pass 3: Decomposition of methoxy-methyl without O_2 addition
$HCHO + OH \rightarrow H_2O + HCO$	(9)	Termination by intermediate HCHO

MEASUREMENTS AND MODELING OF SOOT AND NO_X FORMATION IN NON-PREMIXED FLAMES

ARVIND ATREYA[*]
Department of Mechanical Engineering and Applied Mechanics
The University of Michigan, Ann Arbor, MI 48109-2125

ABSTRACT

An understanding of soot and NO_x formation in turbulent non-premixed flames is important for controlling combustion generated pollutants and predicting thermal radiation from flames. The prediction of soot is particularly important because flame radiation also affects the NO_x production rate via flame temperature.

To understand and model soot and NO_x formation, a detailed experimental and numerical study on a basic unit of a turbulent non-premixed flame - a radiating laminar flamelet - is conducted. Experimentally, methane counterflow diffusion flames and partially premixed flames are used to represent these flamelets and their thermal, chemical and sooting structure is measured. The effects of operational variables, namely, the preheat temperature, the chemical composition of the reactants, the strain rate and dilution by products of combustion on soot and NO_X formation are investigated. The results of this experimental and numerical study and recent attempts at developing an overall soot model are presented.

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[*] Tel: (734) 647 4790; Fax: (734) 647 3170; E-mail: aatreya@engin.umich.edu

Integrating CHEMKIN with Education

Hong G. Im
Department of Mechanical Engineering
The University of Michigan
Ann Arbor, MI 48109, USA

As a sequel to the report by Professor Stephen Turns at the previous Chemkin Workshop, this presentation is intended to share some of my recent experience with Reaction Design's version of the Chemkin package in the graduate-level course offered in Winter 2001. Examples of homework and final projects will be summarized, demonstrating the depth and breadth of various fundamental and applied research problems that can be tackled by Chemkin. Results of user survey directly taken from the students as well as from other instructors will be discussed. Overall, there is a clear indication that the RD Chemkin has been improved since its introduction, and has become an essential part of the educational tools in providing basic understanding of chemically-reacting systems. It was also found that many users who are not computational experts preferred the graphical user interface of the RD Chemkin over the non-commercial predecessor. The presentation will conclude with some suggestions for further improvement.

Third Biennial International Workshop on CHEMKIN
Sapporo, Japan
July 21, 2002

Integrating Chemkin with Education

Hong G. Im
Department of Mechanical Engineering
University of Michigan
Ann Arbor, Michigan, USA

Outline

- **Teaching Experience at UM, Winter 2001**
  - Homework and Projects
- **Feedback from Students (15)**
- **Feedback from Instructors (4)**
- **Summary and Suggestions**

Note: Survey was primarily for RD CHEMKIN

ME 532 Advance Combustion

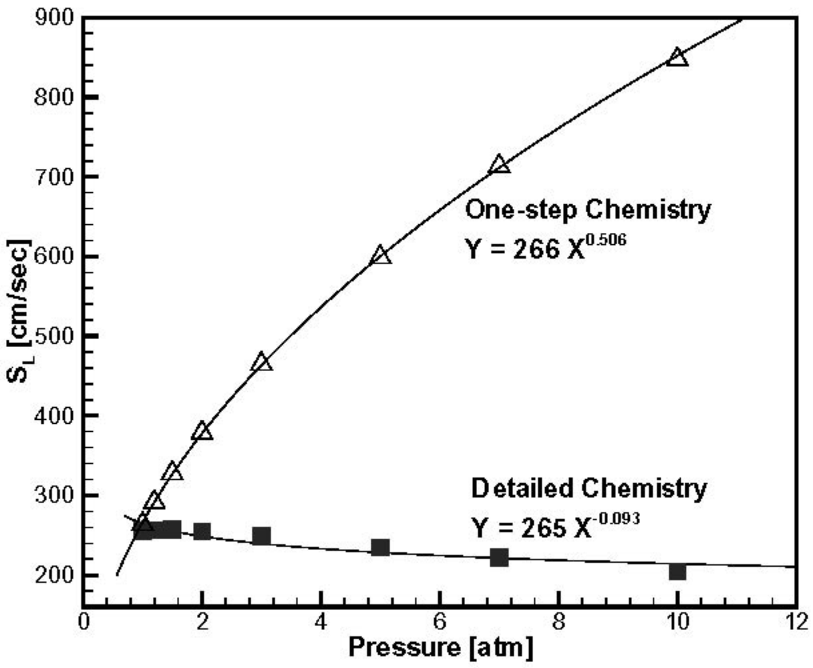
- **Introductory to intermediate graduate level**
  - Chemical thermodynamics/kinetics
  - Basic oxidation mechanisms of hydrogen/hydrocarbon
  - Laminar premixed/diffusion flames
  - Pollutant formation and environmental issues
  - Flame instabilities
  - Criticality phenomena (ignition/extinction)
  - Introduction to turbulent combustion
- **Three homework problems used CHEMKIN**
- **Final project of mini-research problems**

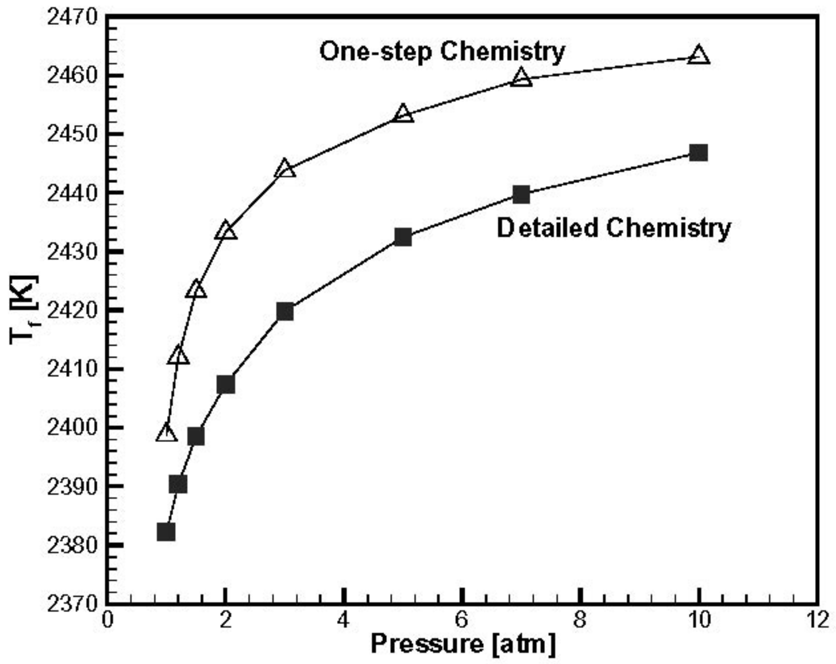
Homework Problems (1)

- **EQUIL**
  - Adiabatic flame temperature and equilibrium composition
  - Effects of pressure and equivalence ratio (Le Chatelier’s principle).
- **PREMIX**
  - Laminar flame speed of hydrogen-air flame
  - Effects of pressure (overall reaction order)
  - Effects of equivalence ratio and inert dilution

Homework Problems (2)

- **PREMIX Application**
  - Detailed chemistry vs. one-step “fake” chemistry





Final Project (1)

1. Analysis of various NOx paths for premixed flames at different pressures and temperatures
2. Effects of physical/chemical parameters on flame speed variation
3. Numerical study of the effects of curvature on premixed laminar flames
4. Structure of methane oxygen enriched counterflow diffusion flames
5. Influence of pressure and temperature on NOx formation in counterflow diffusion flames
6. Simulation of chemical vapor deposition using rotating disk reactor model
7. The effects of methane reforming using a counterflow diffusion flame model
8. Partial oxidation and steam reforming of hydrocarbons
9. Ignition delay times for high temperature silane combustion
10. Parametric study of pressure and temperature effects on time-averaged ignition

Final Project (2)

11. Analysis of various NOx paths for diffusion flames at different pressures and temperatures
12. Analysis of various NOx paths in air for premixed and diffusion flames at different pressures and temperatures for methane and methanol simulating high swirl, small-bore diesel conditions
13. Formation of pollutants with DME combustion
14. Sensitivity analysis of emulsified diesel fuels in Chemkin
15. Effects of water and fuel additives on NOx formation
16. Homogeneous charge compression ignition control with water injection
17. Effect of inlet air temperature on HCCI ignition charcteristics
18. The effects of octane number on IMEP, NOx emissions, and CO emissions in an HCCI engine
19. A study of the effect of various parameters on the performance of HCCI engines
20. Effect of EGR on HCCI engine performance
21. Effects of EGR on homogeneous ignition as an application to HCCI

Final Project (3)

- **Physical Issues**
  - Physical parameters on flame speed variation
  - Oxygen enrichment in diffusion flame
  - NOx formation in premixed/diffusion flames
  - Chemical vapor deposition
  - Fuel reforming (SRF/POX)
  - Combustion/pollutant formation in engines
  - HCCI combustion: ignition control, parametric effects (EGR, Intake air temp)

Final Project (2)

- **Codes Used**
  - SENKIN (10)
  - OPPDIF (4)
  - PREMIX (3)
  - AURORA (2)
  - SPIN (1)
  - Other (1)
- **Applications**
  - HCCI (6)
  - SI/Diesel engines (6)
  - Laminar premixed flames (3)
  - Laminar diffusion flames (3)
  - Fuel reforming (2)
  - Chemical vapor deposition (1)
  - Silane combustion (1)

The projects span a wide spectrum of physical disciplines and geometrical configurations

User Survey (1)

Q1: What are the features you liked about RD CHEMKIN?

- User-friendly GUI
- Versatile, modular structure
- I/O structure
- Instruction manual is easy to follow
- Post-processing capability
- Fast run time
- PC compatibility

User Survey (2)

Q2: Did you like the general GUI structure of CHEMKIN?

:*Not bad, could be improved*

- Help menu (for keywords, etc) (2)
- List commands in menus
- No minimize button, making it hard for multi-tasking
- Edit running in background.
- Excel file output option

User Survey (3)

Q3: Suggest additional features/functions

- Post-processing
- More examples and templates
- Better error messages
- GUI for generation of input files
- Customized output data (instead of the whole)
- Reaction rates in the output
- More physical models (radiation, etc.)
- Multi-zone capability for SENKIN (engine application)
- User-defined function for additional terms (e.g., heat loss in SENKIN)

User Survey (4)

Q4: A new application code that you would like

- Unsteady flames (counterflow, spherical)
- Droplet, spray combustion
- Turbulent combustion

Q5: What did you like/dislike about the instruction manual?

- Well documented, detailed description of equations
- Useful examples
- Too long, commands are hard to find.
- Group input keywords by relevance/usage
- Explanation of certain default values of inputs

User Survey (5)

- **Other comments**
  - More detailed error messages instead of “IDID=-7”
  - Increase the number of species and equations for post-processor
  - More examples, templates
  - More systematic compilation of various reaction/thermo/transport mechanisms

    (Web-based data archive)

Instructor Survey (1)

- **Under what platform have you/students used RD CHEMKIN?**
  - Windows (3)
  - Unix (3)
- **Applications**
  - Flame speed (PREMIX)
  - Ignition time (SENKIN)
  - Industrial problem related to emission control (SENKIN)
  - Thermal NO (SENKIN)
  - Kinetic evaluation (PLUG)
  - Equilibrium calculations (EQUIL)
  - HCCI combustion modeling (AURORA)
  - CH_4 reforming in fuel cell systems (AURORA/SENKIN)
  - Low-BTU gasifier/combustion (AURORA/SENKIN)

Instructor Survey (2)

- **Examples where CHEMKIN was essential for education**
  - Detailed chemistry capability
  - Understanding steady-state/partial-equilibrium approximation

- **Major Improvements Over Pre-RD Versions**
  - GUI
  - Technical Support
  - Data management
  - Some improved features in AURORA

Instructor Survey (3)

- **Did you like the GUI?**
  - Quite old-fashioned, but straightforward
  - Need production rate analysis, sensitivity analysis

- **Suggestions for New Features/Functions**
  - Help menus
  - Preference file should be customizable
  - Selective post-processing (Sensitivity analysis)
  - Improved handling of surface chemistry and electrochemistry. Surface chemistry lacks proper interaction potentials for some kinetic calculation.
  - Convergence warning in AURORA

Instructor Survey (4)

- **New Application Code?**
  - 1-D transient flame code

- **Instruction Manuals**
  - Pros: clear description of the code and equations
  - Cons: lack of sample problems

- **Was RD technical support prompt and helpful?**
  - All agreed.

Summary

- **CHEMKIN is becoming an essential tool in education**
  - User-friendly GUI
  - PC/Windows compatibility
  - Variety of application problems
  - Easy for parametric case studies
  - Site license to universities are becoming competitive
- **Further improvements**
  - Help menus, list of commands/keywords
  - More detailed error messages for unsuccessful runs
  - More refined GUI, post-processing
  - Compilation of reaction mechanisms on RD website
  - Compilation of problems (instructional package)

“Discussion on Requirements of Software to Accompany a Combustion Textbook”

Professor Robert Dibble
Department of Mechanical Engineering
University of California
Berkeley CA 94720

Abstract

Over the past 10 years, we at Berkeley have been building a “Numerical Combustion Workbook” that would accompany any textbook on combustion. The first section of the Combustion Workbook starts with equilibrium problems including adiabatic flame temperature calculations. The second section of the Workbook introduces chemical rate processes using the plug flow reactor model. There are many variations to the plug flow reactor, including, perfectly stirred reactor (PSR), and a well mixed balloon (WMB), which is a PSR with input but no output, the WMB simulates the time history of fluid in a turbulent jet. The last section of the Workbook brings in problems that include diffusion such as Opposed Jet flames and premixed propagating flames. We start each problem using the mechanism for hydrogen combustion and then we grow to larger chemical mechanisms. We have found that much can be learned using the chemical kinetic mechanism for oxidation of methanol including NOx reactions.

```
ELEMENTS  H   O    C   N END
SPECIES
H2 O2 H CO CO2  H2O  OH O HCO HO2 H2O2 N NO NO2 CH3OH CH2OH CH2O N2
END
```

In spite of the host of homework problems, we still have not converged on a single software to solve all the problems. The talk will discuss some of the challenges, including: what computer language should be used? (For example, Berkeley engineers are taught MATLAB; Fortran and C are optional languages.) Also, while Windows based computers are widespread, we still have some software that runs under DOS and UNIX; should this be changed? I look forward to discussing these issues.