

MODELING POLLUTION FORMATION IN DIESEL ENGINES

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Modeling combustion under conditions that prevail in a Diesel engine presents a great challenge. Lawrence Berkeley National Laboratory has invested Laboratory Directed Research and Development Funds to accelerate progress in this area. Our research has been concerned with building a chemical mechanism to interface with a high fidelity fluid code to describe aspects of Diesel combustion. The complexity of these models requires implementation on massively parallel machines. Collaborators in this effort are Michael Frenklach, Phillip Colella, and John Bell.

The level of complexity of the chemical mechanism is dictated by combustion conditions and by the question being asked. For example, flame propagation can be described with five or less reactions and ignition with approximately twenty. However, describing pollutant formation and, especially, soot and NO_x , requires substantially more complex chemistry. We will describe our efforts concerned with building such a complex mechanism. We begin with C and CO_2 chemistry and add sequentially higher hydrocarbon chemistry, aromatic production

chemistry, soot chemistry, and chemistry describing NO_x production. The metrics against which this chemistry is evaluated are flame velocities, induction times, ignition delay times, flammability limits, flame structure measurements, and light scattering. We assemble a set of elementary reactions, kinetic rate coefficients, and thermochemistry. Data are provided from experimental studies and theory. Tools used to build mechanisms of varying complexity are reaction path analysis, sensitivity, and principal component analysis. Reduction is achieved by using these tools, lumping portions of the chemistry, employing the method of moments, and invoking quasi-steady-state and partial equilibrium approximations. We modify existing Sandia codes to be able to investigate the behavior of the mechanism in well-stirred reactors, plug flow reactors, and one-dimensional flames. The modified combustion code with a chemical mechanism at the appropriate level of complexity is then interfaced with the high fidelity fluids code. The fluids code is distinguished by its ability to solve the requisite partial differential equations with adaptively refined grids necessary to describe the strong variation in spatial scales in combustion.



Diesel Collaboratory New Paradigm

- To make available electronically to members of the Collaboratory: Models, results, and tools
- To use Collaboratory computational infrastructure to make our models, results and tools, as well as those of others, available to the broader combustion community
- Team: Caterpillar, Cummins, Detroit Diesel, LBNL, LANL, LLNL, SNL, University of Wisconsin

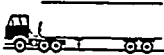


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Collaborators

Michael Frenklach
Michael Koszykowski
Ken Revzan
Nigel Moriarty
Carmen Ortiz
John Bell
Phil Colella



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Modeling Diesel Combustion

- Complexity of Problem
- Modeling the Combustion
- Tools of the Trade
- Chemical Mechanisms
- The Diesel Collaboratory
- Conclusion



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Complexity of Diesel Modeling

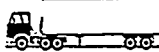
- High pressure and high temperatures
- Spray atomization of liquid fuels
- Radiation heat transfer
- Complex fluid flow
- Complex combustion chemistry



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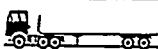
Drivers for Diesel Improvements

- * **Technical Drivers**
 - higher pressures--greater efficiency
 - better atomization
 - new fuels
- * **Regulatory Drivers**
 - more stringent regulations of criteria pollutants
 - new PM regulations
 - new fuels



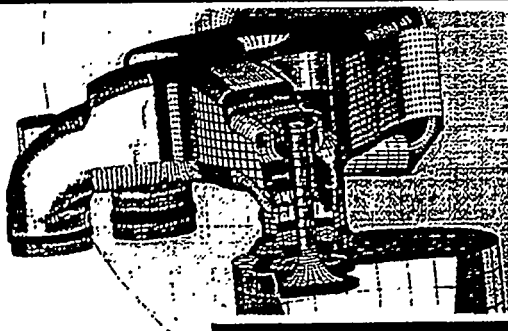
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***Optimizing Diesel combustion
performance criteria
with respect to the technical
and regulatory drivers
presents a daunting task
to a modeling team that
requires teraflop computing
resources***



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Computational Modeling of Diesel Combustion

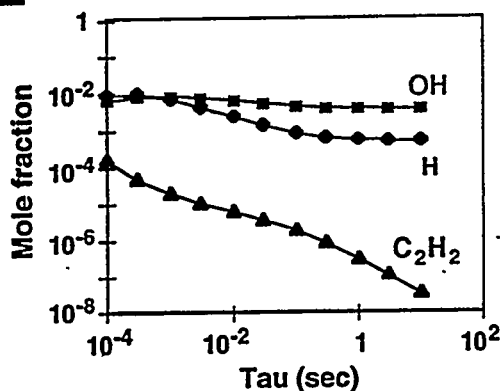


Engine model
(Industry-Lab
collaboration)

Adaptive
gridding
of flow
geometry

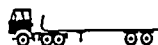
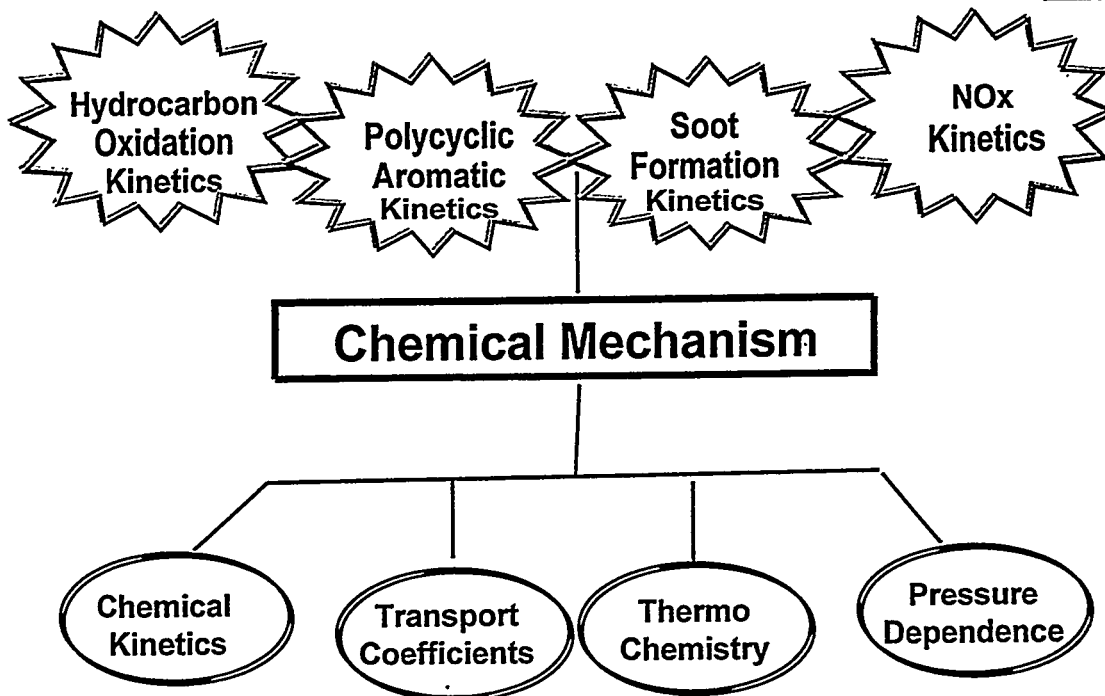


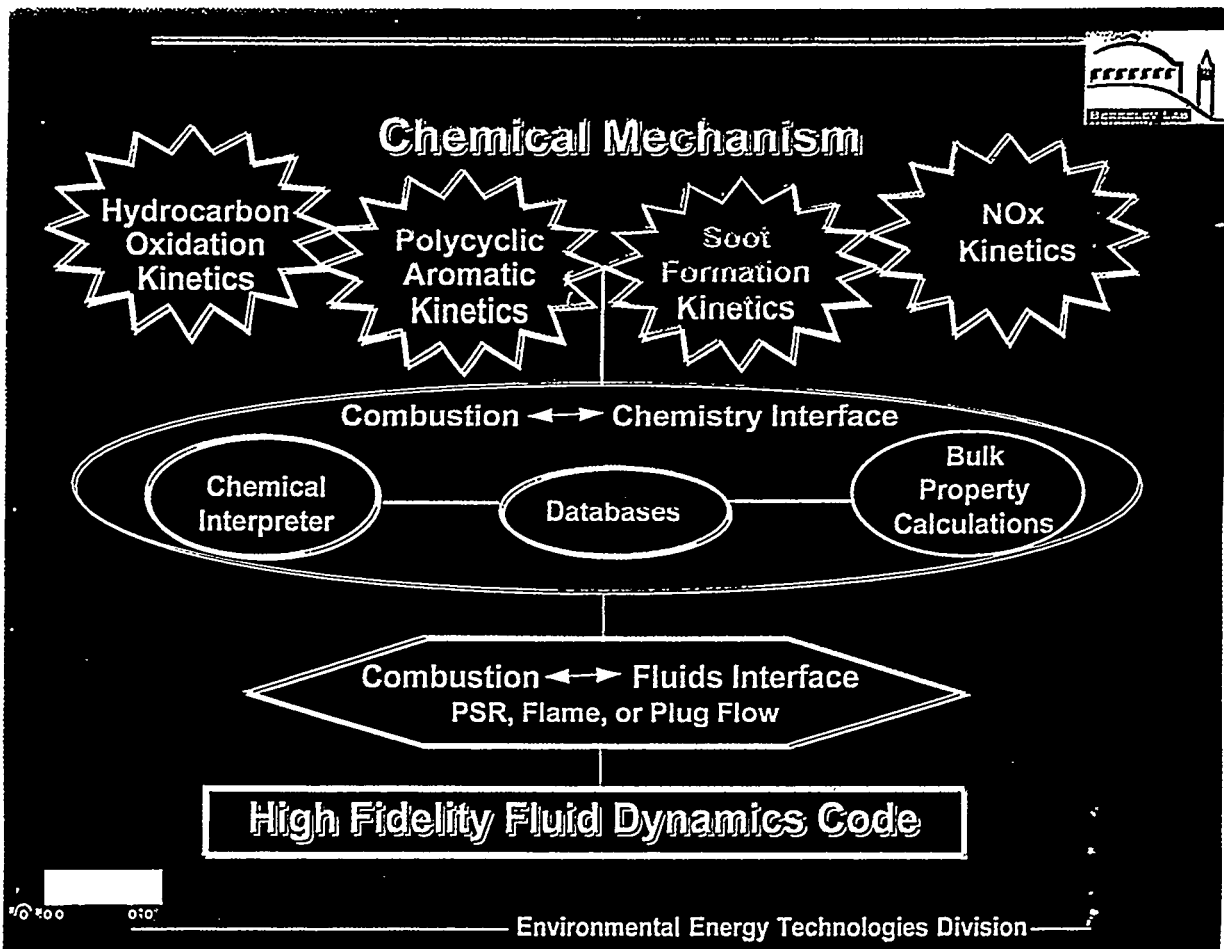
Nonequilibrium chemistry
of soot precursors



• J. Bell, P. Collela, N. Brown

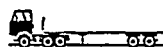
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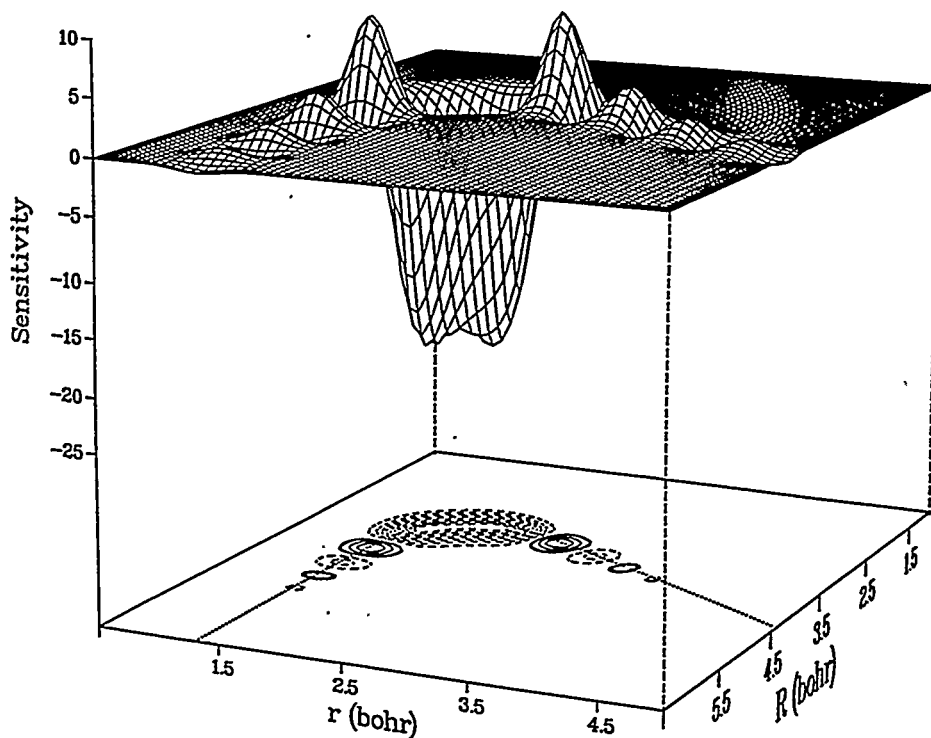


Tools of the Trade

- reaction path analysis
- sensitivity analysis
- mechanism reduction
- rate ratio asymptotics
- potential energy surface calculations
- rate coefficient calculations



Rate Coefficient Sensitivities



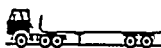
Hydrocarbon (HC) oxidation kinetics

- start with H_2 , CH_4 , C_2 chemistry
- either add aromatics or continue to increase the C skeleton
 - both are useful and comparisons with experiments test different parts of the mechanism
- higher alkanes can be reduced to C_1 and C_2 chemistry
 - abstraction with H, OH, or OH
 - alkyl radical thermal dissociates via β scission



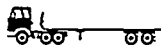
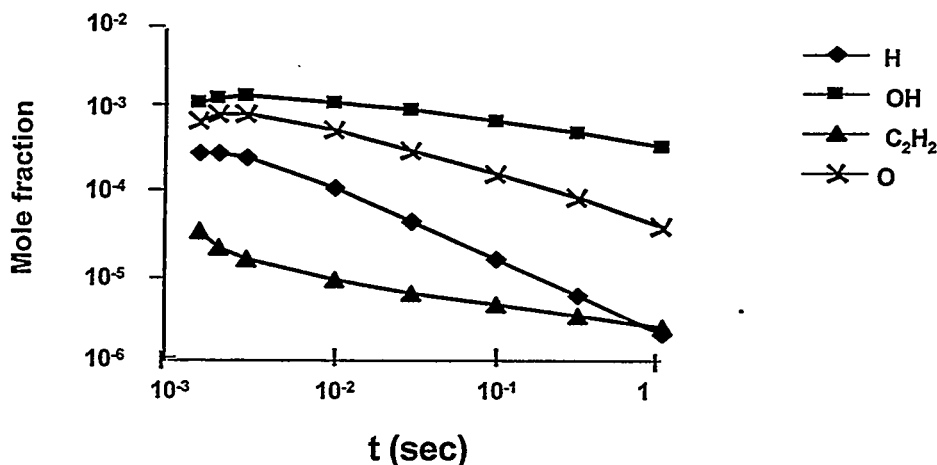
Higher alkanes

- * Dissociation and isomerization of R
- * $R + Y \rightarrow R' + HY$ (Y= H, O, OH)
- * $R' \rightarrow R'' + R'''$
- * β scission -- governs decomposition of a complex HC radical:
 - bond most likely to break is one carbon removed from the site of radical attack-- C-C rather than C-H is usually broken
- * **Research need:** dearth of experiments must be rectified, need flame structure measurements, and theoretical development for kinetics, thermochemistry, and transport



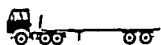
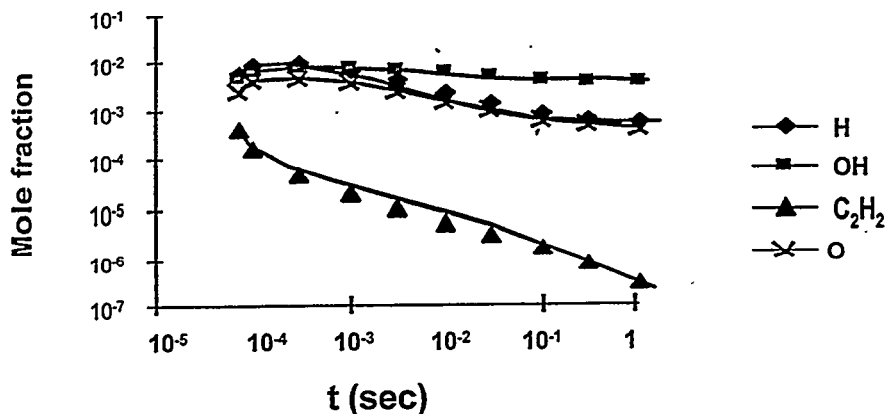
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Heptane Combustion in a Perfectly Stirred Reactor as a Function of Residence Time for $\Phi = 0.5$



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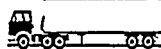
Heptane Combustion in a Perfectly Stirred Reactor as a Function of Residence Time for $\Phi = 1.0$



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Aromatic chemistry

- Formation of first ring controversy
- Acetylene--standard model
 - $C_4H_3 + C_2H_2 \rightarrow C_6H_5$
 - $C_4H_5 + C_2H_2 \rightarrow C_6H_6$
- Propargyl
 - $C_3H_3 + C_3H_3 \rightarrow C_6H_5 + H$ or C_6H_6
- Large aromatics are formed from small by steps: H abstraction, acetylene addition, and cyclization
- Theory--very useful in estimating kinetics and thermochemistry

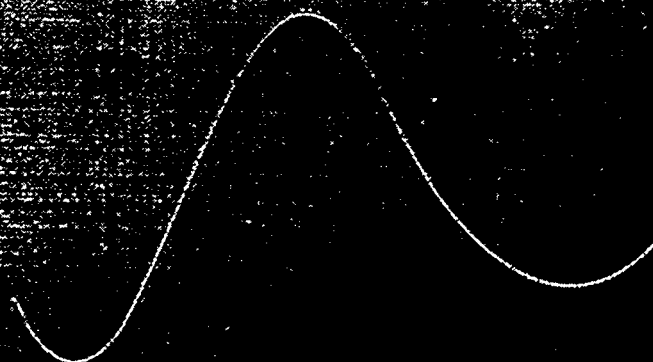


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Reaction Path

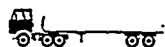
Geometries and energies using G2 theory

Reaction rates using RRKM theory

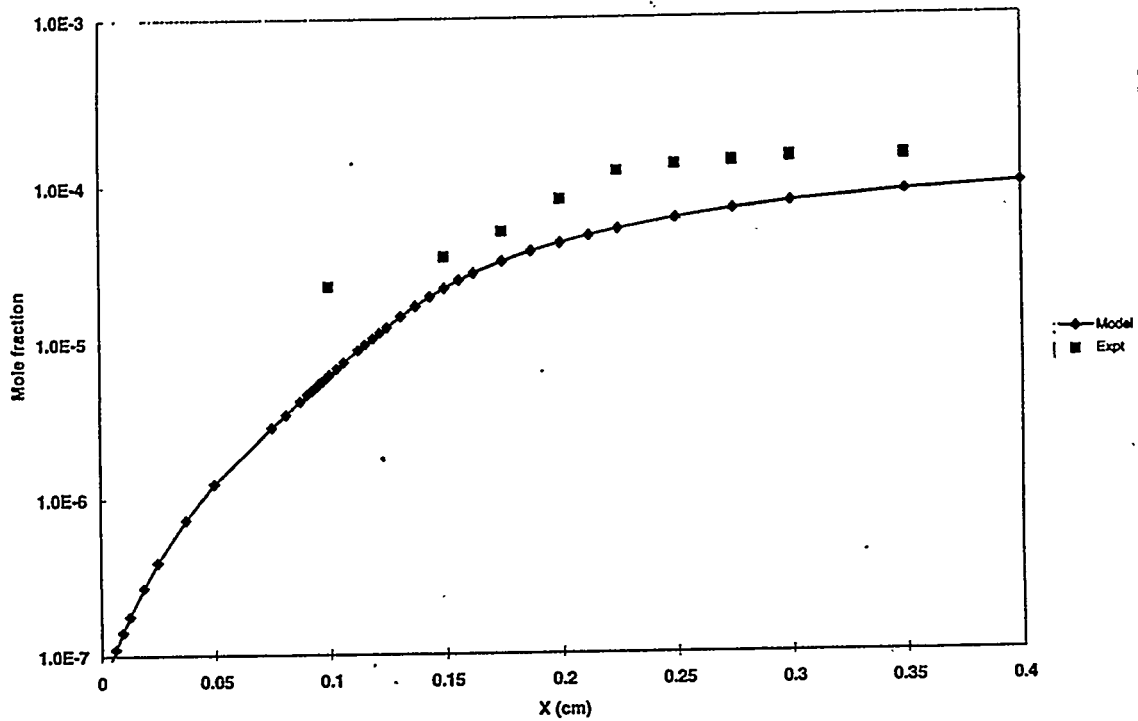


Wang-Frenklach Mechanism: Flame Conditions

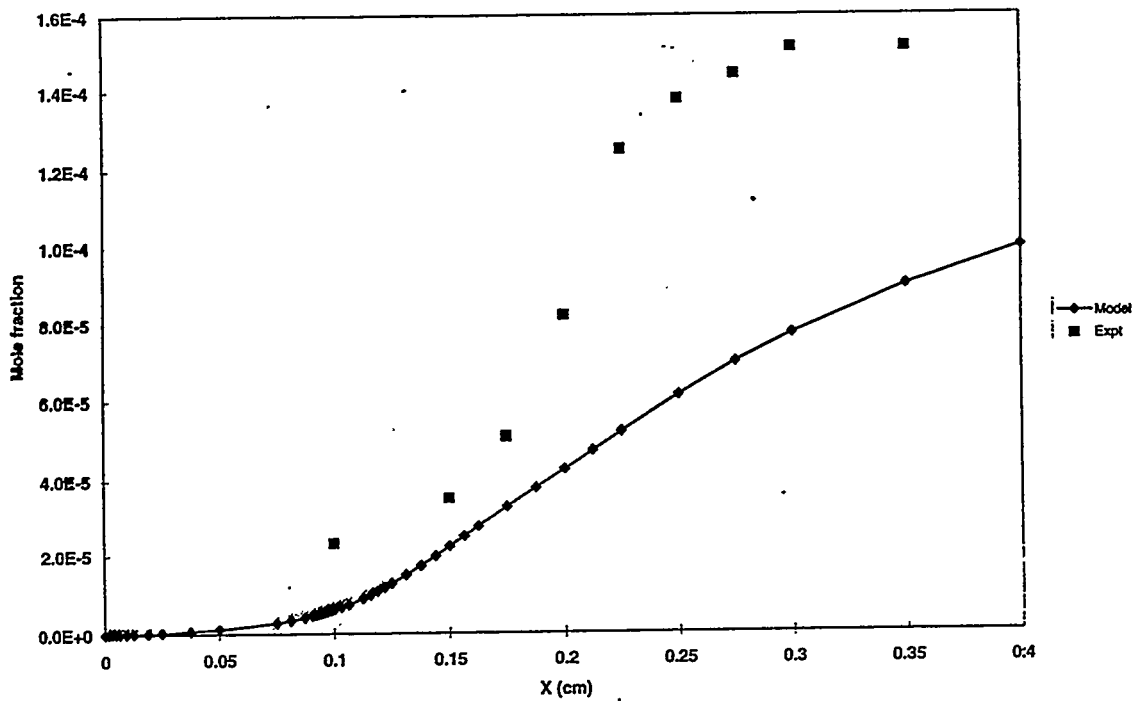
Flame #	C ₂ H ₂ (concentration in mole fraction)	C ₂ H ₄	O ₂	Ar	Pressure (Torr)	Tmax (K)	Velocity (cm/s)
1	0.465		0.485	0.05	20	1901	50
2	0.236		0.214	0.55	90	1988	20.4
3		0.165	0.179	0.656	760	1606	7.8



Flame3 (760 Torr): Benzene (A1)

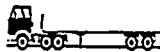


Flame3 (760 Torr): Benzene (A1)



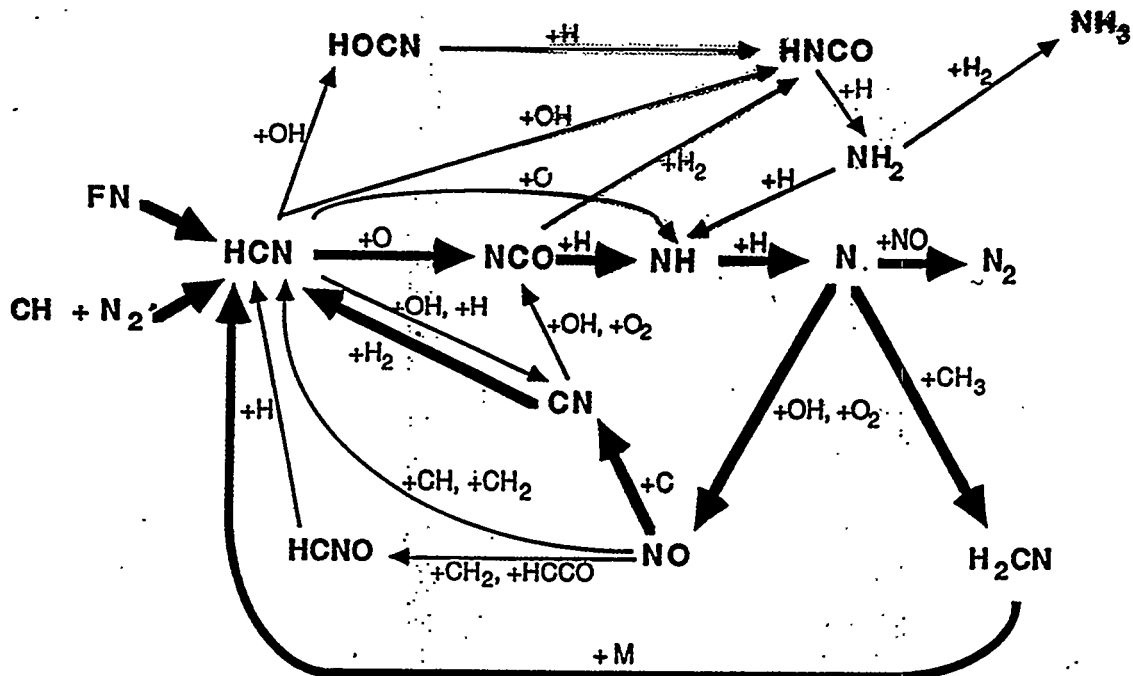
NO_x Chemistry

- Zeldovich kinetics-- $O + N_2 \rightarrow NO + N$, large E_a
- Prompt mechanism-- $CH + N_2 \rightarrow HCN + N$
- N₂O mechanism--important at high pressures, N₂O reactions with H and O
- reburn mechanisms--NO is converted to N₂--reactions with NH and N are most important
- many reactions--not equilibrated, relative importance strongly influenced by ambient conditions



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NITROGEN CHEMISTRY IN RICH FLAMES

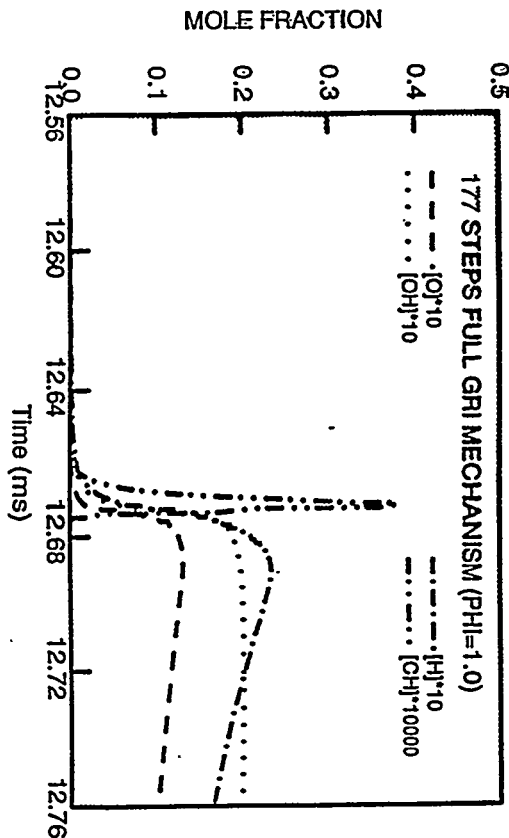
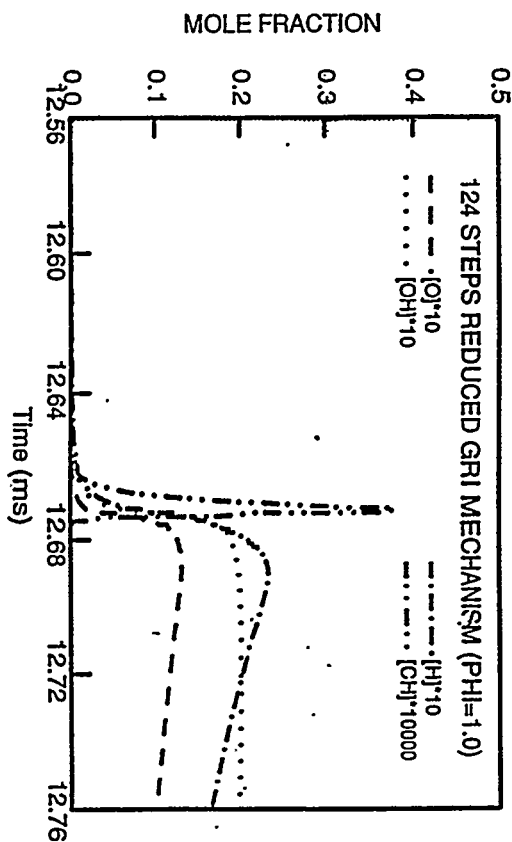


Mechanism reduction

- * System reduction -- reduces number of parameters
- * System lumping -- reduces number of species
- * Mechanism reduction uses tools of the trade and a number of approximations

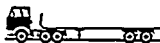


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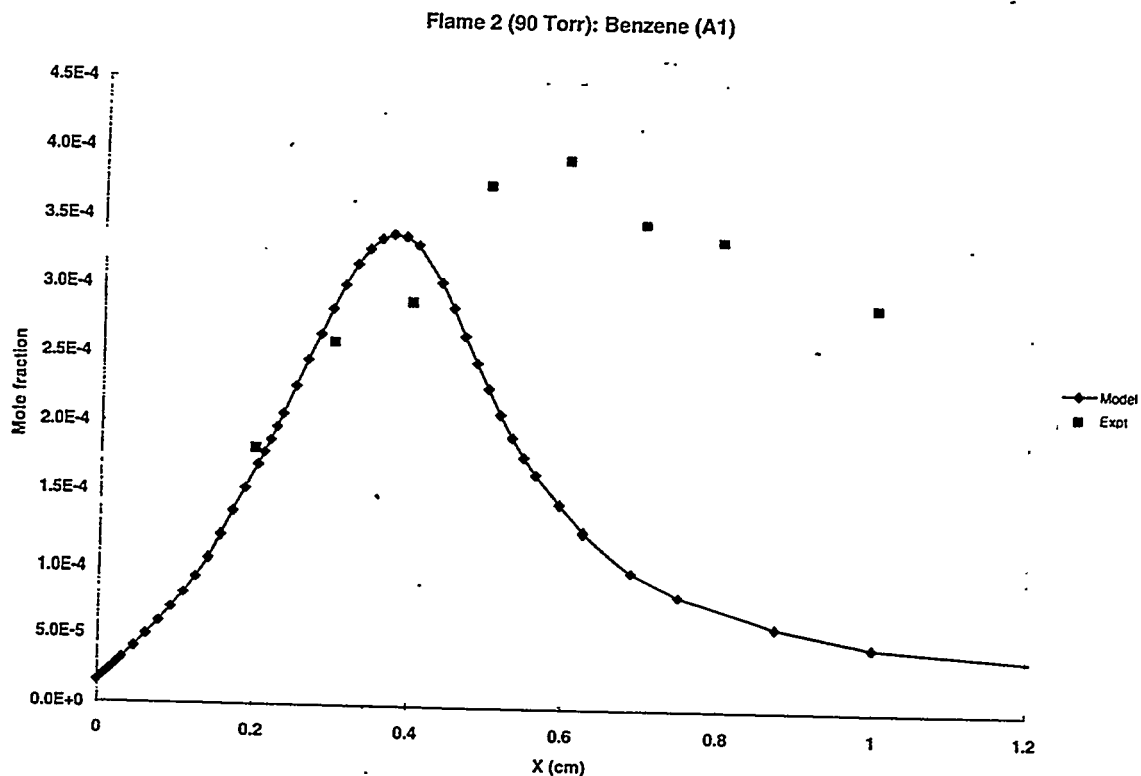


Modeling soot

- * Evolution of soot particle size distribution is described by method of moments
- * Describes 4 processes responsible for the formation, growth, and oxidation of soot particles
 - inception
 - PAH condensation
 - coagulation and surface growth

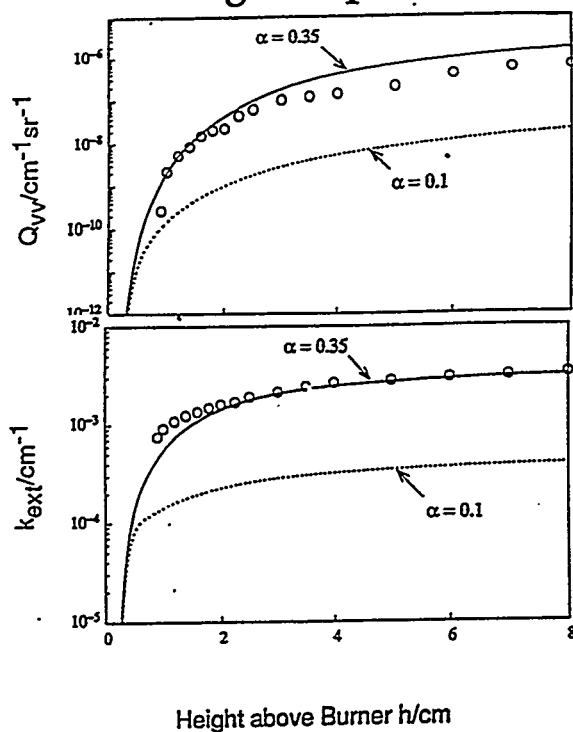


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Experimental-Modeling Comparison of Light Scattering



Conclusions

- Complexity of Problem
- Modeling the Combustion
- Tools of the Trade
- Chemical Mechanisms

