

Development of Detailed Kinetic Mechanisms to Control Emissions

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Construction of Detailed Mechanisms

Difficult but Worth the Effort

- Mechanism Generation codes require rules for kinetics and thermo
- Rule generation:
 - Categorize reaction types
 - + Hydrogen abstraction
 - + Addition/ β -scission
 - + Dissociation/recombination
 - Use thermochemical and theoretical guidance as basis for estimates
 - + **Ab-initio calculations becoming increasingly important**
- Important to account for pressure-dependence in chemically-activated systems
- Validate rules by analysis of specific systems
 - Close coupling of experiments and modeling essential
- **PAYOFF: *Models permit much more efficient identification of critical parameters***



Modeling Tightly Coupled to Experiments



Development of Detailed Kinetic Mechanisms to Control Emissions



Toyota Data Illustrates Complexities Regarding Emissions

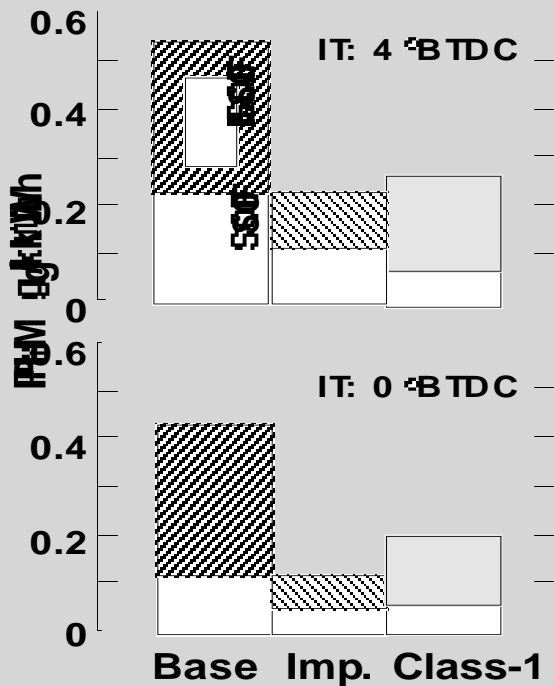


Table 2 Fuel properties

| | | Base | Improved | Class-1 |
|----------------------------|-------|--------|----------|---------|
| Density g/cc @ 15 °C | | 0.838 | 0.821 | 0.815 |
| Cetane Number | | 53.0 | 53.1 | 51.6 |
| Cetane Index (JIS) | | 58 | 59 | 54 |
| Viscosity cst @ 30 °C | | 3.546 | 2.989 | 2.390 |
| Aromatics (HPLC) vol. % | Total | 21.9 | 13.9 | 3.9 |
| | Mono- | 18.8 | 9.8 | 3.6 |
| | Di- | 1.9 | 3.4 | 0.3 |
| | Tri- | 1.2 | 0.7 | ND |
| Sulphur mass % | | 0.05 | 0.06 | 0.00045 |
| H / C | | 1.87 | 1.93 | 1.97 |
| QL kJ/kg | | 42,890 | 43,079 | 43,167 |

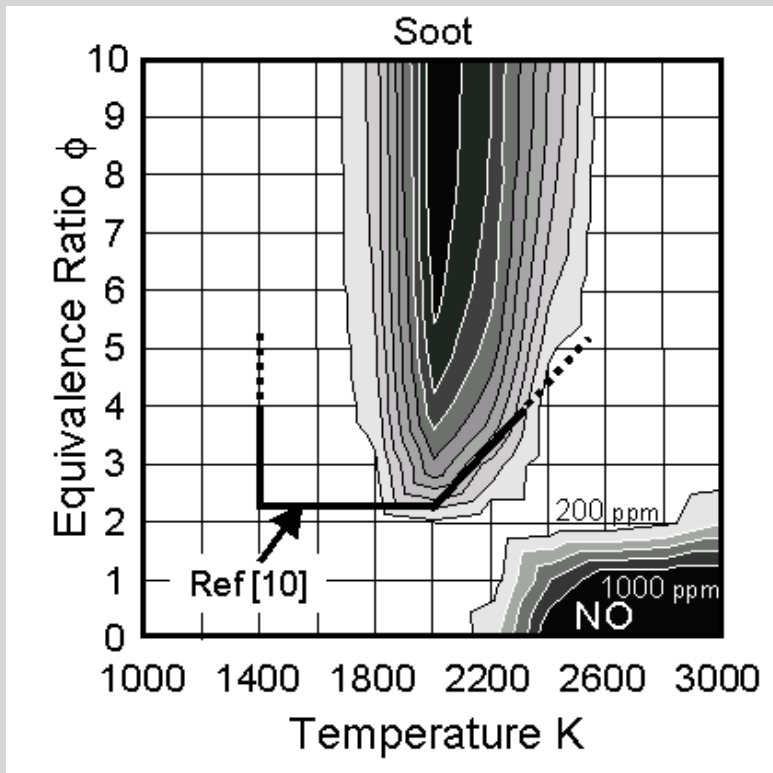
- Even though Swedish Class-1 very low in aromatics and sulfur, the high level of naphthenes (no ring-opening) leads to higher than expected emissions

SAE 892494

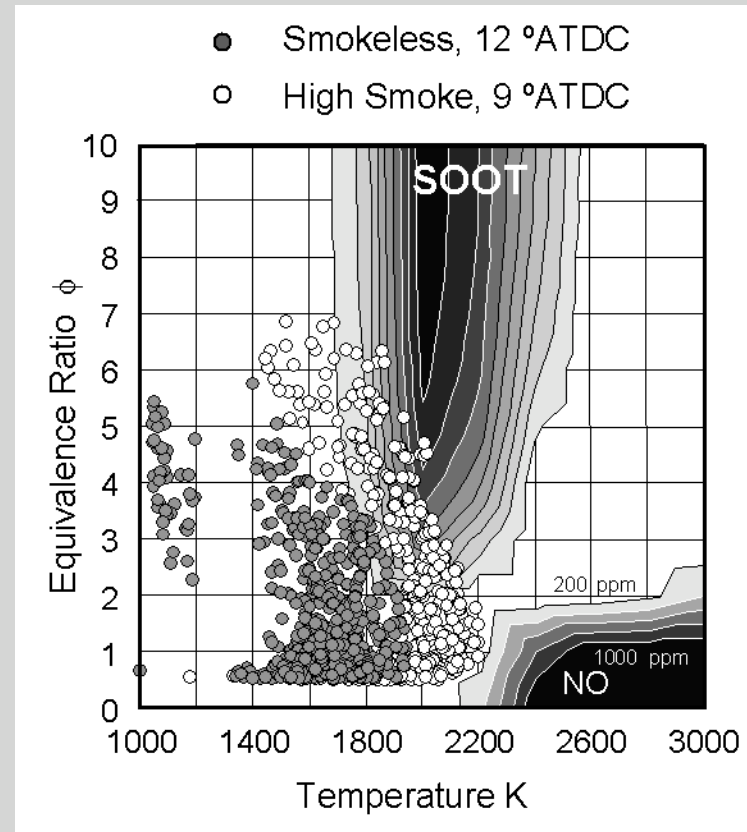


Possible to Integrate Detailed Kinetics with Engine Models

- Joint Exxon-Toyota project combined detailed kinetics with CFD to explore role of large amounts of EGR in diesel engines
 - Able to identify regime that minimized both soot and NO_x formation



SAE 2001-01-0655

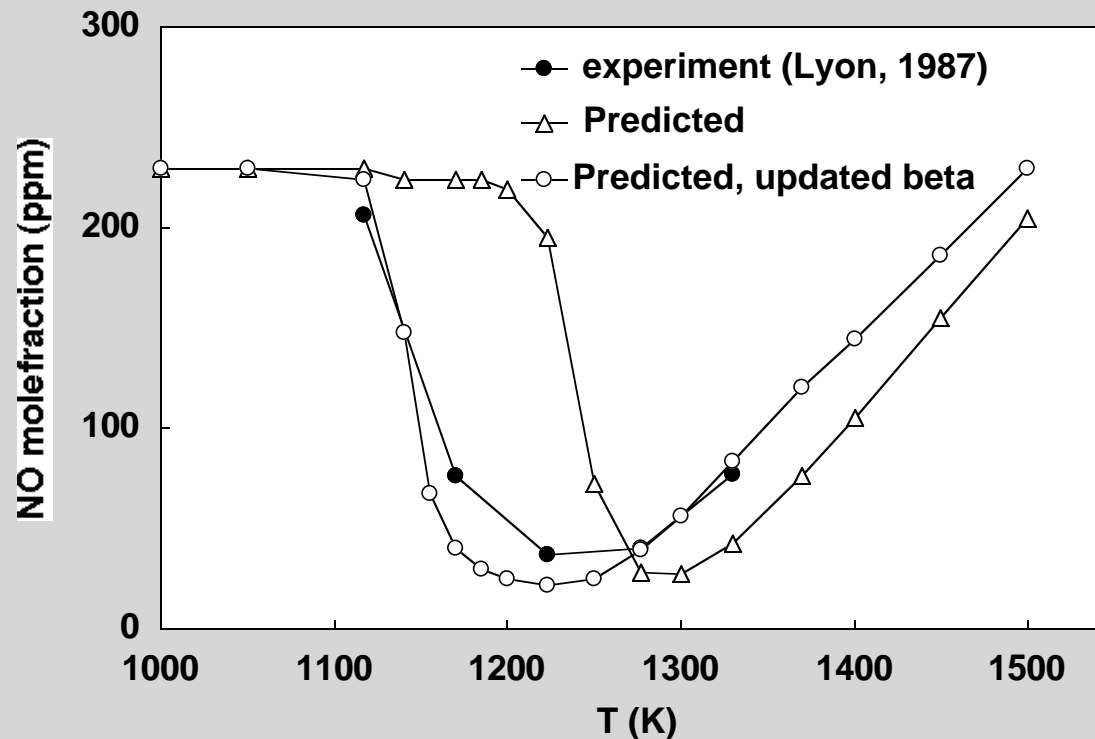


THERMAL DENOX

- **Exxon Research & Engineering Patented Process for **Selective** NOx Reduction**
 - Invented by Dick Lyon in 1975
 - Added NH_3 reacts with NO in flue gas to produce N_2
 - Optimal temperatures between 1150-1350K
 - Used in over 100 commercial units
- **Detailed Kinetic Model Developed in Early '80s**
 - Based on ammonia oxidation kinetics
 - Extended to Thermal DeNOx conditions
 - Limited (bounded) optimization to large data base
 - Fit to 371 experiments better than 7%
- **Kinetics Coupled to 3D Flow Model**
 - Useful design tool for both retrofit applications and new units
- **Revisited to Validate New Mechanism**
 - Now include new species and different reaction paths



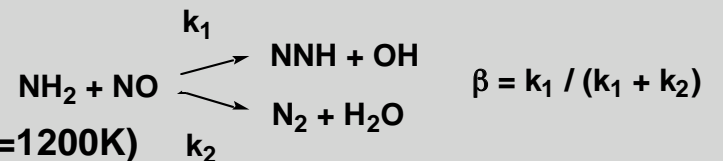
Model Captures Details Of THERMAL DENOX



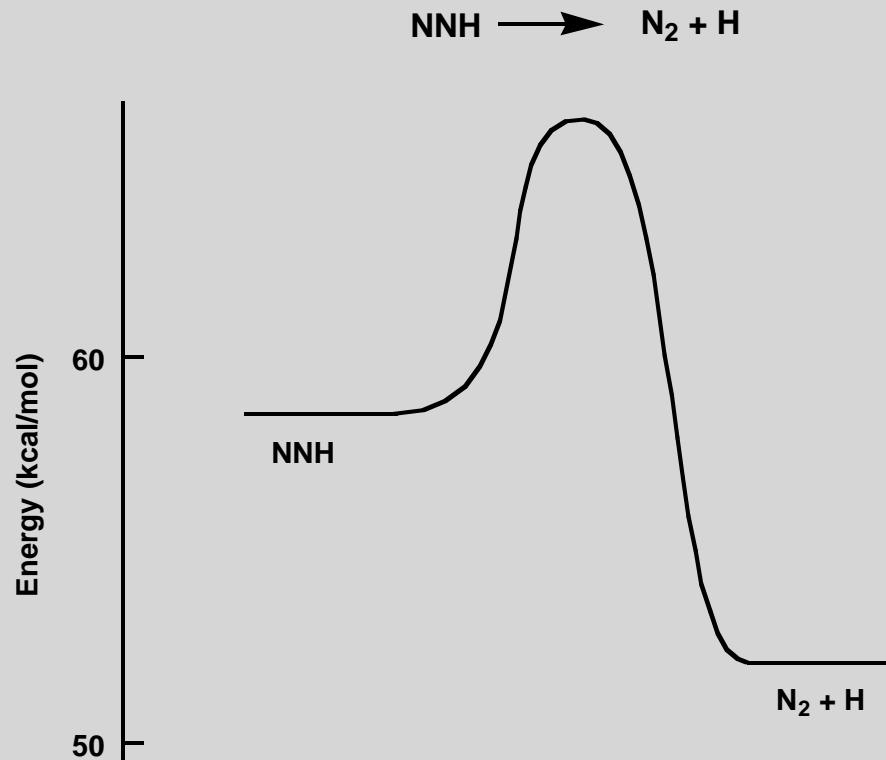
- Predictions Very Sensitive to Branching Ratio β

- Original estimate was $\beta = 0.28$

- updated is the recent Stanford measurement of 0.35 (T=1200K)

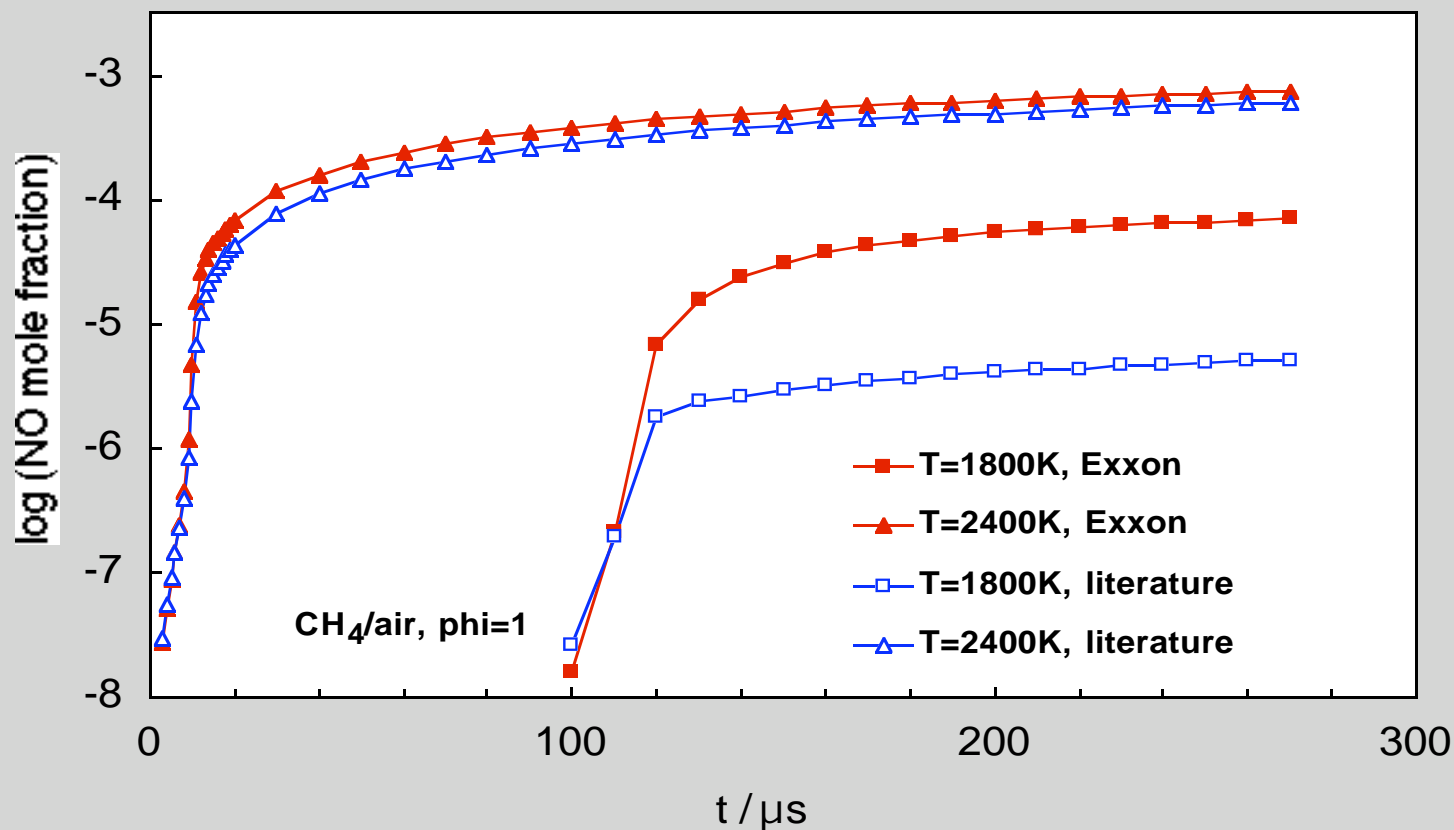


NNH Especially Important Intermediate



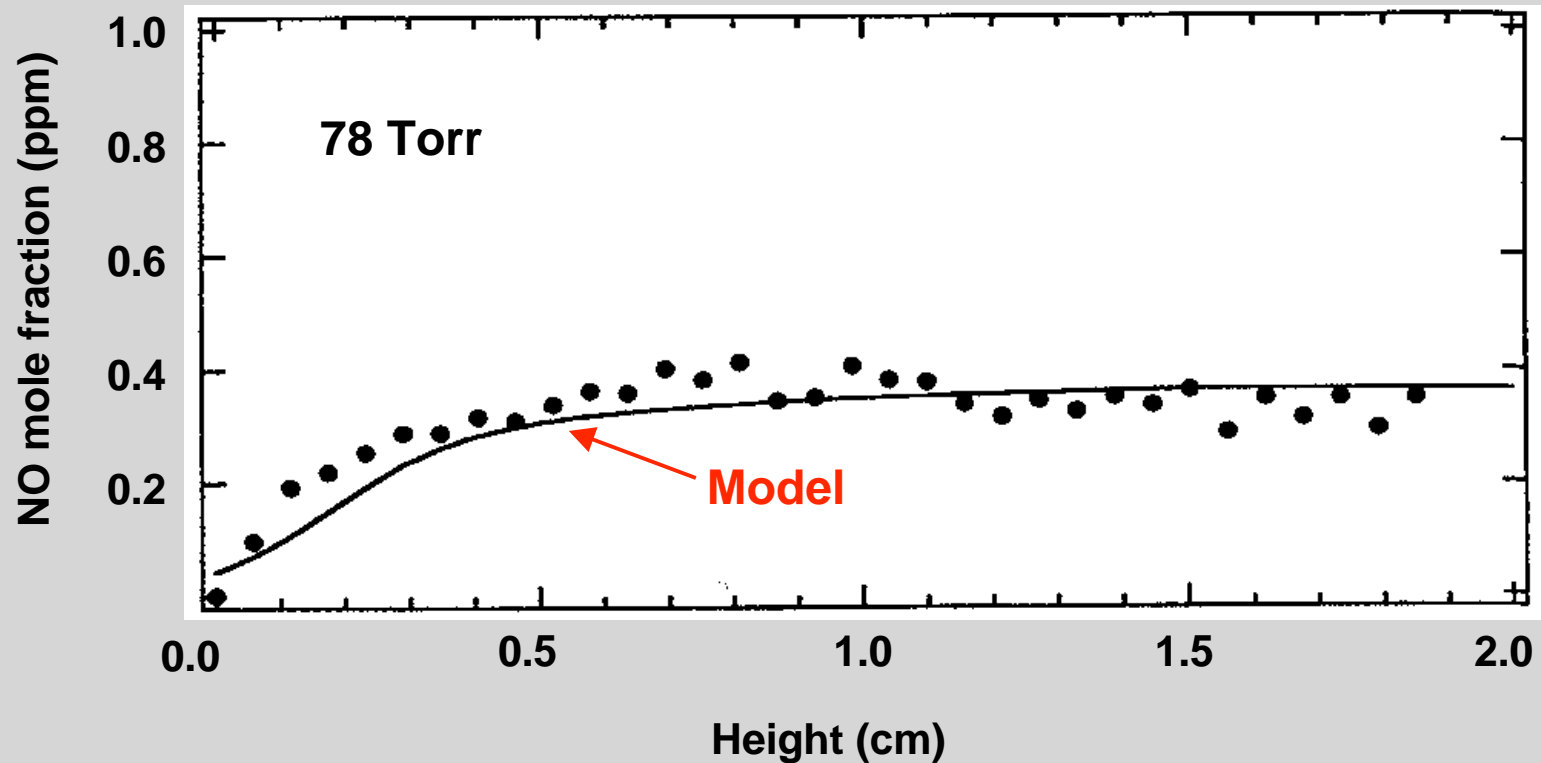
- Dissociation enhanced by tunneling through barrier

New Pathway Predicts Increased NO Production In Flames

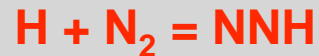


- Especially Important at Lower T, Where Thermal Mechanism Not Significant
 - Suggests that lowering T might not be so effective in reducing NO_x

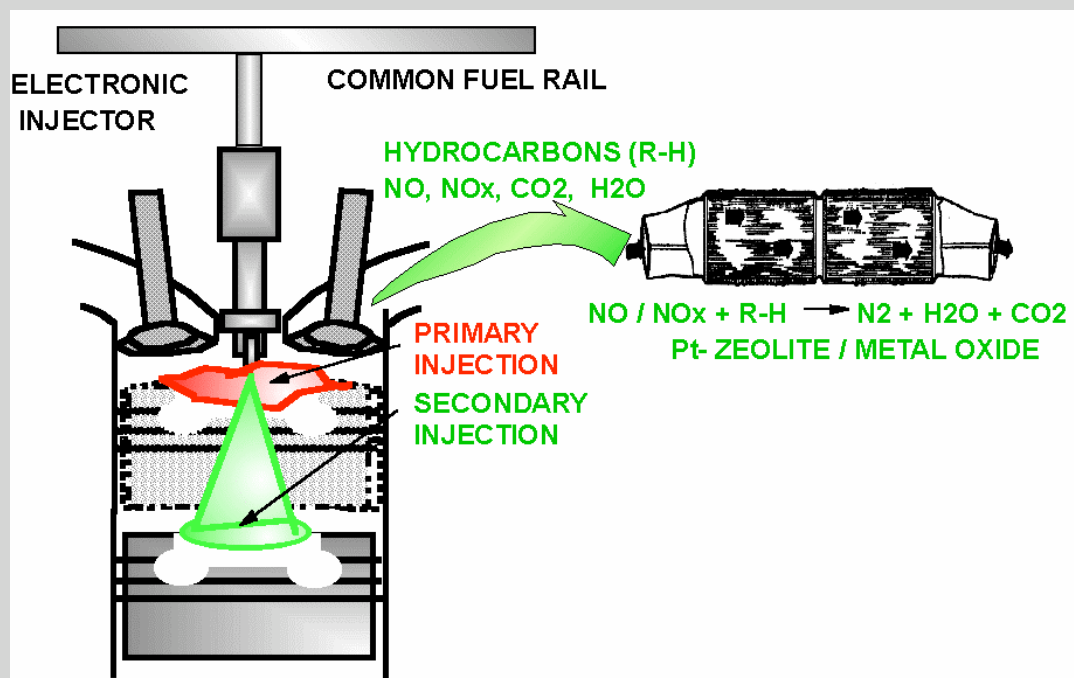
SRI Experiments Confirmed New NO_x Pathway



- Flame Conditions Set to Minimize NO Production from Other Routes
- Inclusion of NNH pathway accounts for observations



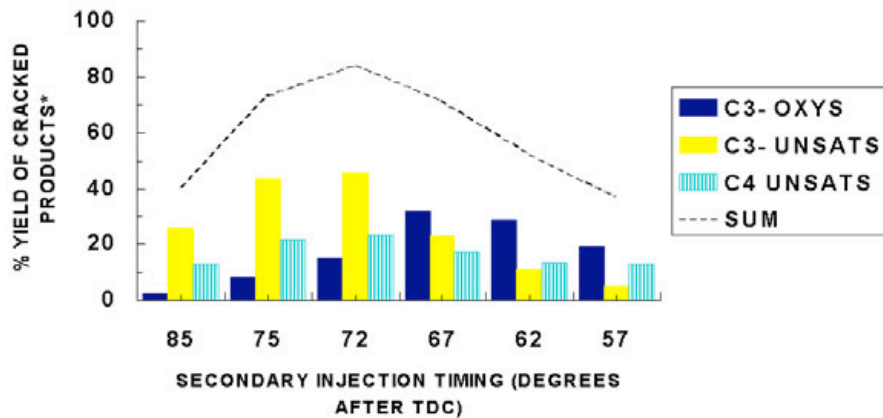
Feasibility Of Secondary Injection for NO_x Control Explored By Modeling



- Treat the Engine as a Reactor with Varying T and P
 - Combine detailed kinetics with T, P from engine simulator
- Use Model to Identify Optimum T - P for Conversion of Fuel to Active Reductant
- Look at Concurrent Nitrogen Chemistry as Well

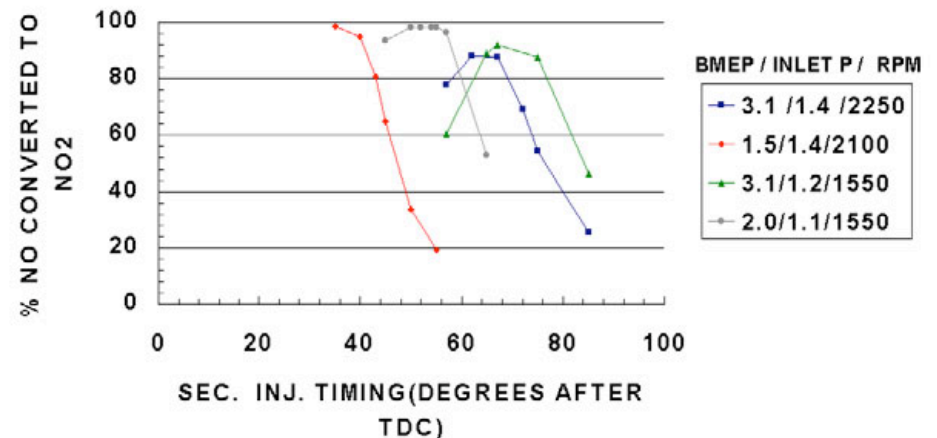
Modeling Identified Unexpected Advantages

Product Yield as a Function of Injection Timing



2% SEC. INJECTION/ SIMULATED PARAFFINS MIX

Nitrogen Oxide Conversion Depends on Injection Timing



2% SEC. INJECTION/ SIMULATED PARAFFINS MIX

- Injection Timing Effects Yield and Composition (Expected Result)
 - Catalysts more active with olefins and oxygenates as reductants
- Timing Also Effects NO / NO₂ Ratios (Surprise!)
 - NO₂ easier to reduce than NO
- Successfully Demonstrated in Engines at PSA Labs
 - U.S. patents granted

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Likely Alternative Liquid Fuel Sources

- **Tar sands**
 - Yields more aromatics and cycloparaffins, fewer alkanes than crude oil
 - > Higher sooting tendency?
 - 1 million barrels/day Canadian production in 2004
 - + Expected to triple by 2014
- **Natural gas, coal**
 - First convert to syngas
 - Then syngas to Fischer-Tropsch liquids and/or alcohols
 - + FT liquids low in sulfur and aromatics (high quality diesel)
 - > Flight-tested in B-52
 - + Alcohols have disadvantage of lower energy density
- **Biomass**
 - Ethanol
 - Biodiesel or green diesel
 - Syngas to FT or alcohols
- **Oil shale**
 - Thermal treatment yields oil comparable to conventional crude
 - Timeframe for development uncertain
- **Impact on performance and emissions?**



Summary/Outlook

- Encouraging results obtained with detailed mechanisms for gas-phase reactions of conventional fuels
 - Detailed models provided the understanding required to manipulate the chemistry to improve performance and reduce emissions
- Research needed to apply similar approach to alternative fuels:
 - Additional rule development
 - Identification of appropriate surrogate mixtures
 - Mechanism generation for surrogate mixtures
 - More efficient mechanism reduction
 - More efficient integration algorithms
- Big advantage to be able to build on previous research on conventional hydrocarbon fuels

