2003 NETL Onsite Merit Review

Development of Predictive Models for Diesel-Based Fuel Processors

National Energy Technology Laboratory

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Diesel Fuel Processing

R&D Goal and Objectives

- ***GOAL: Develop fundamental understanding and technology*** in diesel fuel reforming for the production of hydrogen and support the development of auxiliary power units (APUs) in commercial diesel truck transport as being sponsored by EERE's Hydrogen, Fuel Cells, and Infrastructure Technologies (HFC&IT) Program.

- ***OBJECTIVE: Develop a predictive model / methodology*** for diesel fuel reforming and provide ***necessary tools and information*** to fuel cell/fuel reforming developers and system integrators for ***technology development, performance optimization, and system control.***

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Technical Issues / Challenges

- **Diesel fuel is complex and difficult to reform :**
    - Diesel fuel is a complex, multi-component (>100 compounds) sulfur-containing fuel that exhibits varying reaction pathways and kinetic rates for differing fuels and catalyst types.
    - Deactivation of fuel reforming catalysts and fuel cell components via carbon deposition and sulfur poisoning are the principle technology barriers.
    - Improper reactant mixing in the reformer can lead to hot spots and carbon deposition.
- **System integration can be a significant challenge:**
    - Reformer integration with fuel cell system requires desulfurization, water management, and thermal considerations.
    - Certain FC applications may require high power density design with “fast” response and high efficiency for both steady-state and transient operations.
    - Hydrocarbon slip must be avoided to provide fuel cell with a clean synthesis gas.

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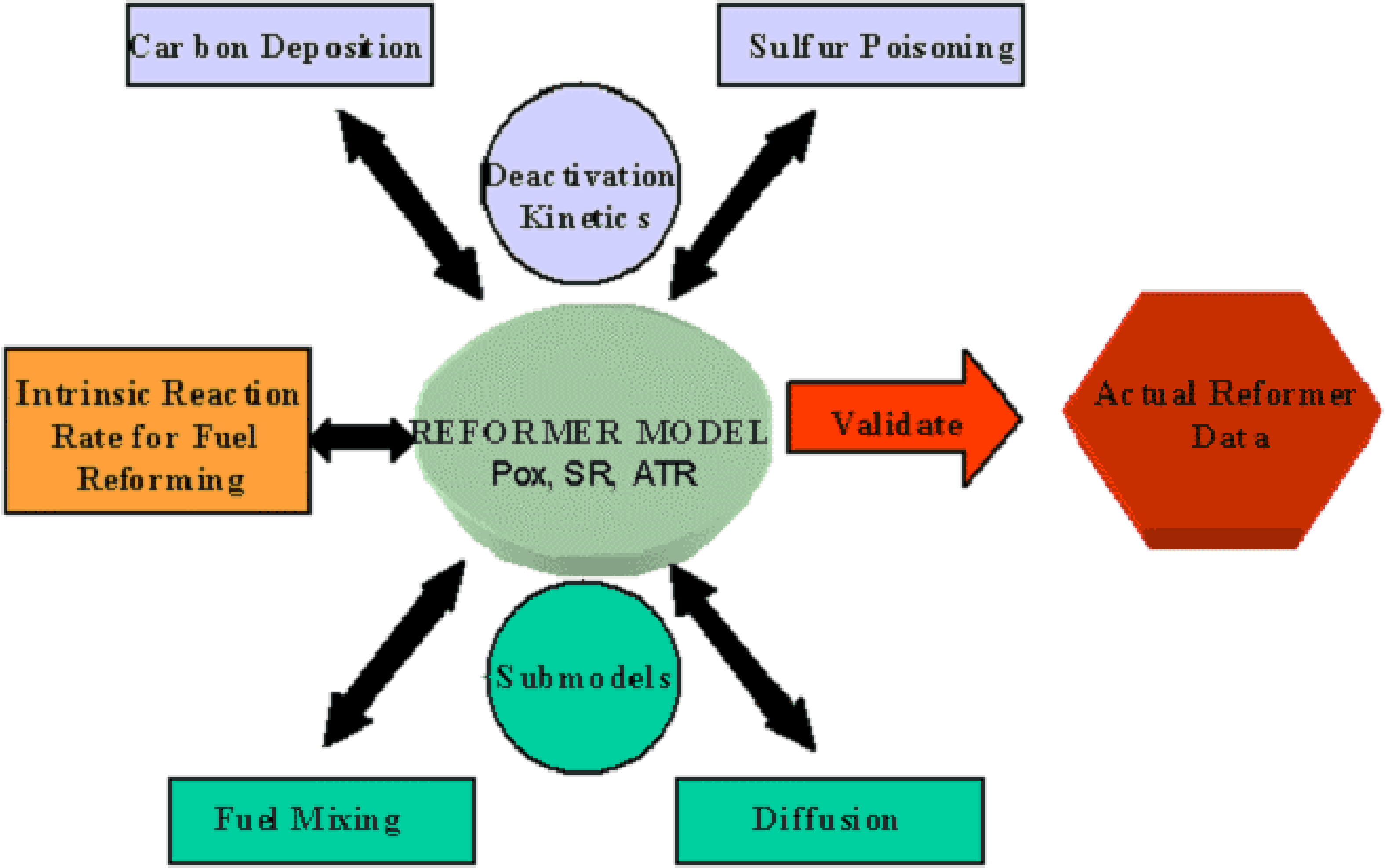
Applicability to Fuel Cell APU Commercialization

- Diesel-based fuel cell APUs are considered a significant high volume market for SOFC's.
- Fundamental understanding of diesel reforming and general methodology for kinetic rate determination would be very beneficial to catalyst developers. May extend to hydrocarbon fuels in general.
- A validated CFD model would be useful to fuel reforming developers and system integrators to predict steady-state and transient performance, develop control strategies, maximize efficiency, and minimize cost.

Reformer Model Needs



Carbon Deposition

Sulfur Poisoning

Deactivation Kinetics

Intrinsic Reaction Rate for Fuel Reforming

REFORMER MODEL
Pox, SR, ATR

Validate

Actual Reformer Data

Submodels

Fuel Mixing

Diffusion

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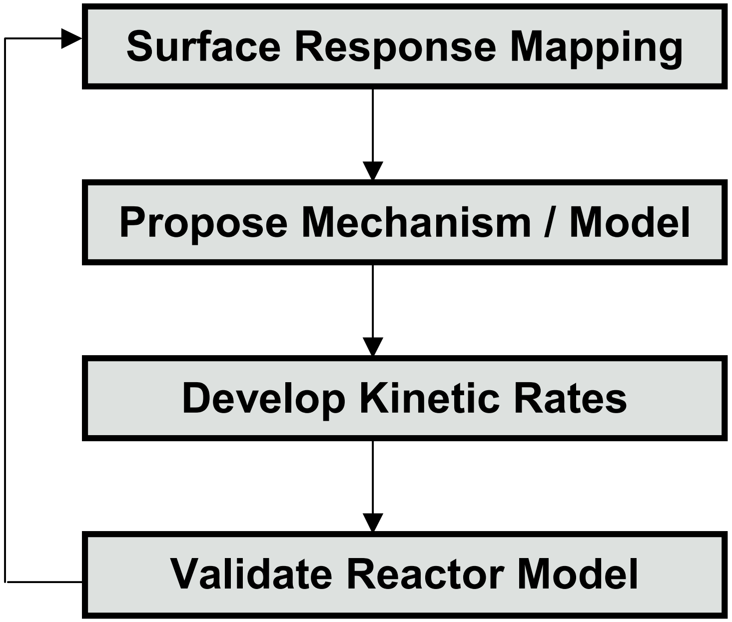
General Modeling Approach

- **Response surface methodology**
  - Process parameter optimization study for the diesel ATR
  - Elucidation of complex chemical networks for the diesel ATR
- **Propose mechanism / model**
- **Develop kinetic rates**
  - Carry out kinetic measurements
    - Representative model compounds: single component & surrogate fuel mixtures
    - Real diesel
- **Validate model**
  - Experimental data



Surface Response Mapping

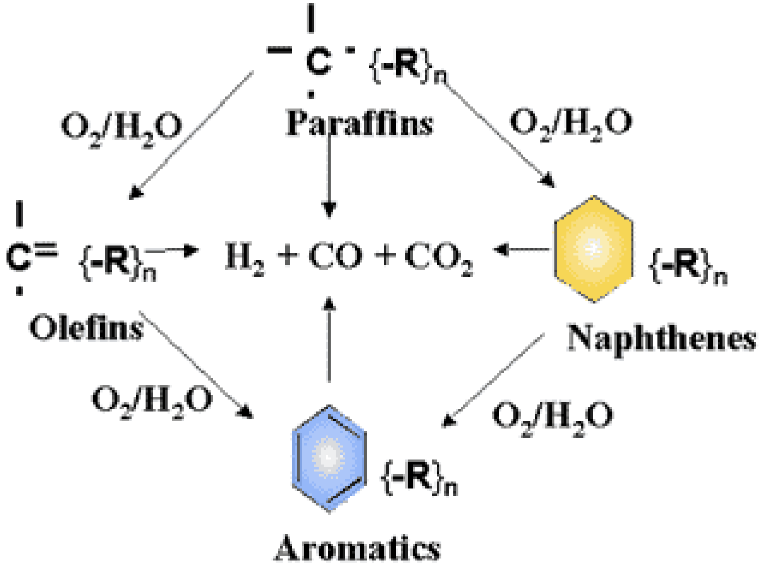
Propose Mechanism / Model

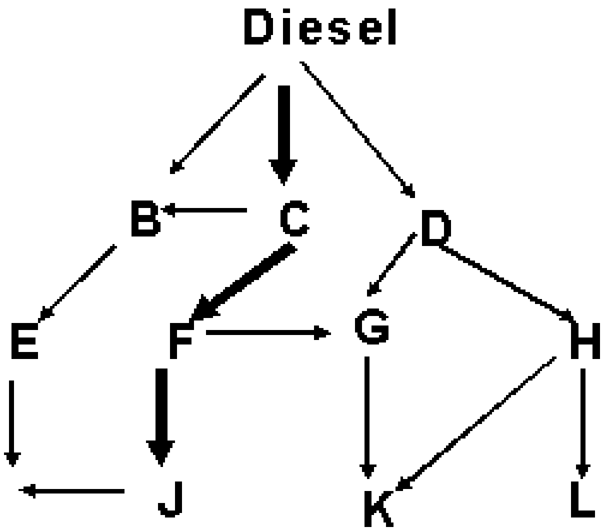
Develop Kinetic Rates

Validate Reactor Model

ATR Kinetic Modeling

- Dominant reaction pathways to be elucidated
- Assessment of kinetic parameters





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Response Surface Mapping

- **Response Surface Methodology (RSM)**
  - A statistical tool used to map characteristic responses (e.g. selectivity, yield, conversion, carbon buildup, etc.) to input variables (O_2/C, H_2O/C, temp. and hydrocarbon type) over a defined region
    - Results in a deeper understanding of the reaction system and the interaction of parameters that affect the development of predictive models
    - Provides data that can validate kinetic models and proposed reaction pathways
  - Determination of operating conditions to achieve a desired specifications
    - Maximum CO and H_2 selectivity
    - Minimize carbon deposition
    - Minimize hydrocarbon slip

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Diesel Fuel Composition – what to test?

- **Diesel Fuel Analysis**
  - Diesel fuel is a complex, multi-component mixture of paraffinic, aromatic and naphthenic hydrocarbons in the range of (C_7-C_{26})
    - An exponential increase in the number of hydrocarbon isomers with increasing carbon number makes compound identification difficult
      - Hydrocarbon compound classification may be made based on hydrogen deficiency, C_nH_{2n+z}
    - GC-FID/MSD – Dual detector system: simultaneous flame ionization detection and mass spectrometry (soft chemical ionization to avoid molecular fragmentation of heavy hydrocarbons)
    - Representative model compounds selected from each major homologous class present in diesel fuel include:
      - Parrafin: n-Tetradecane
      - Aromatic: 1-Methylnapthalene
      - Naphthene: Decalin

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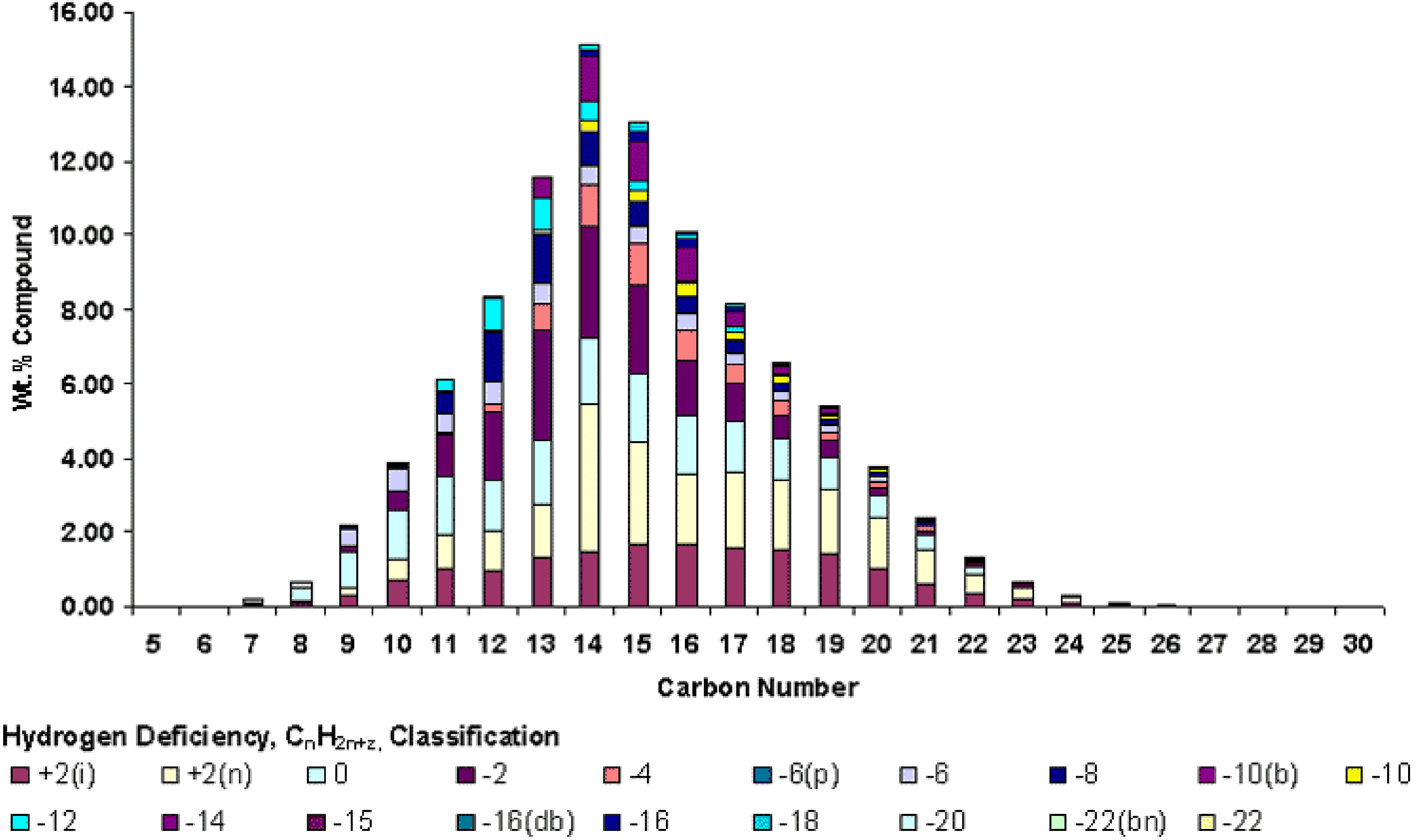
Diesel Fuel Composition – Con't.



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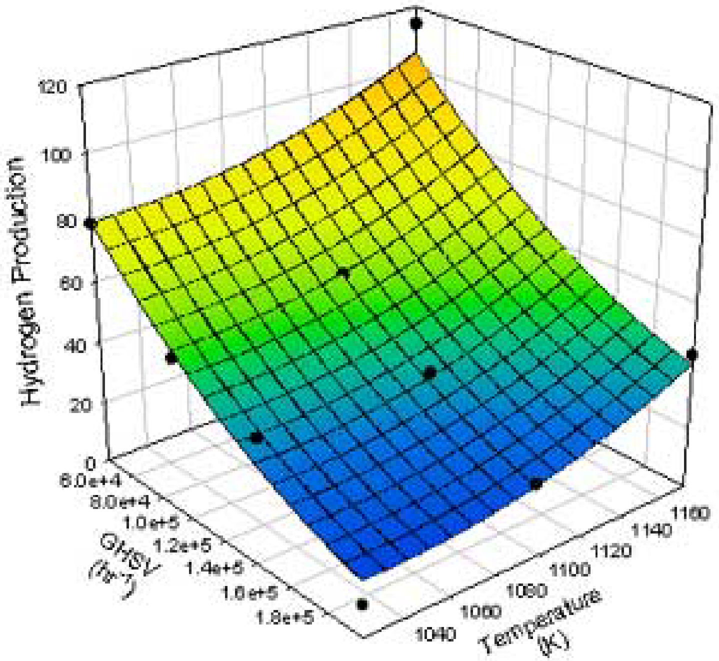
Experimental Conditions

	Paraffin	**Aromatic**	**Naphthene**
Model Compound	n-Tetradecane	1-methyl naphthalene	Decalin
O_2/C	0 - 0.5	0 - 0.5	0 - 0.5
H_2O/C	0 - 1.5	0 - 1.5	0 - 1.5
T (°C)	750 – 900	750 – 850	750 - 850
GHSV (h^{-1})	50,000 - 200,000	22,000 - 66,000	50,000 - 150,000

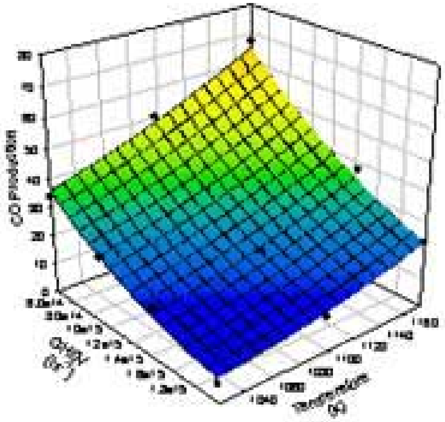
ATR of n-Tetradecane (O_2/C=0.3, S/C=1.5)

Hydrogen Production

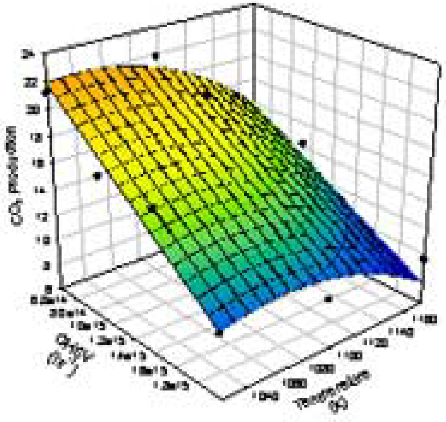


- Reverse WGS reaction dominates at higher T
- Olefins and aromatics produced at higher SV and lower T
- Naphthenes not observed

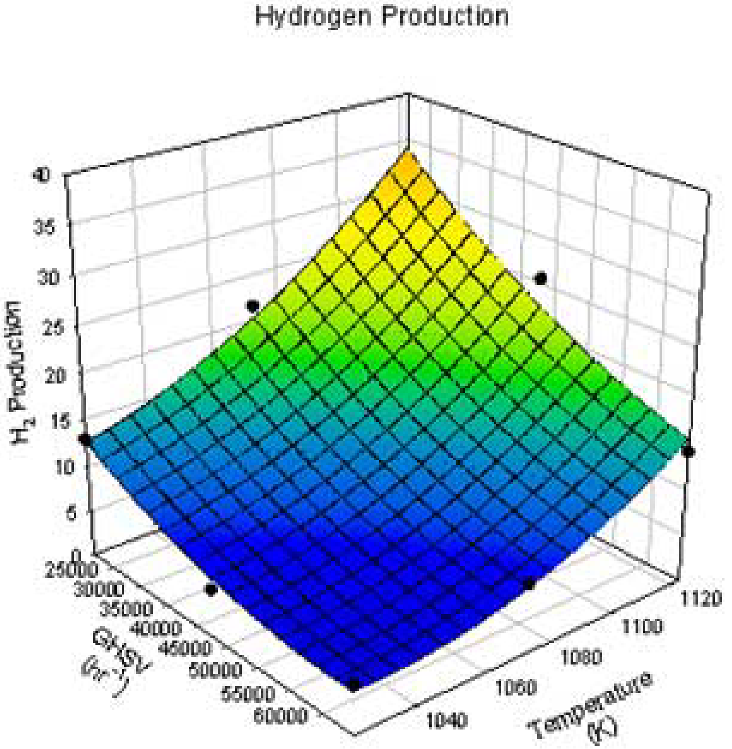
Carbon Monoxide Production

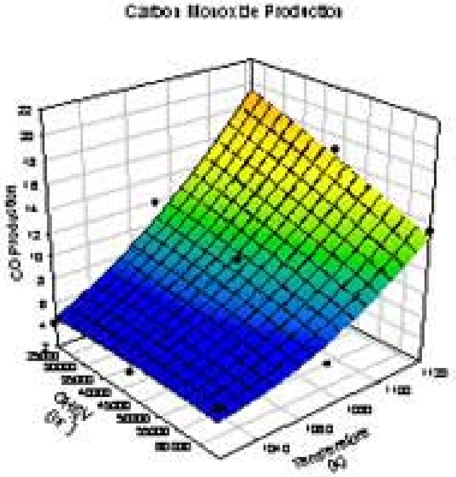


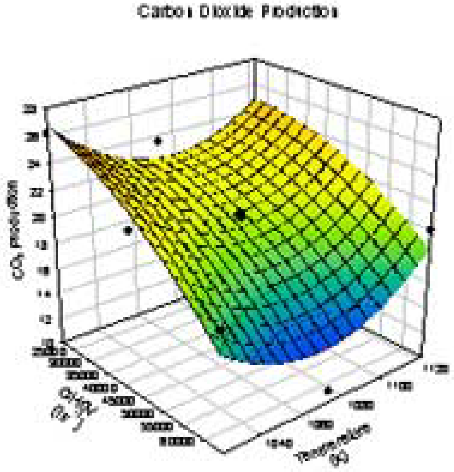
Carbon Dioxide Production



ATR of 1-Methylnaphthalene (O_2/C=0.3, S/C=1.5)

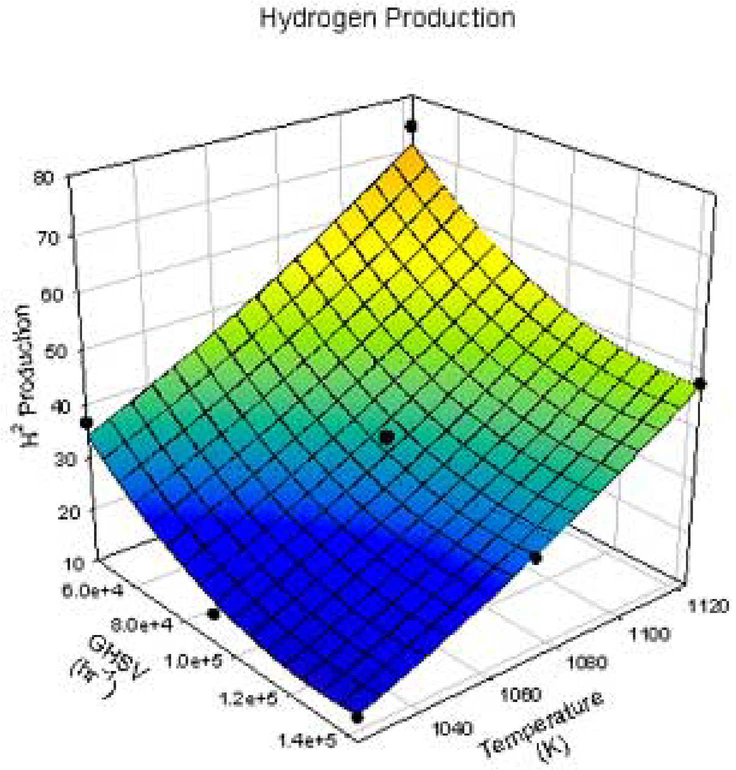


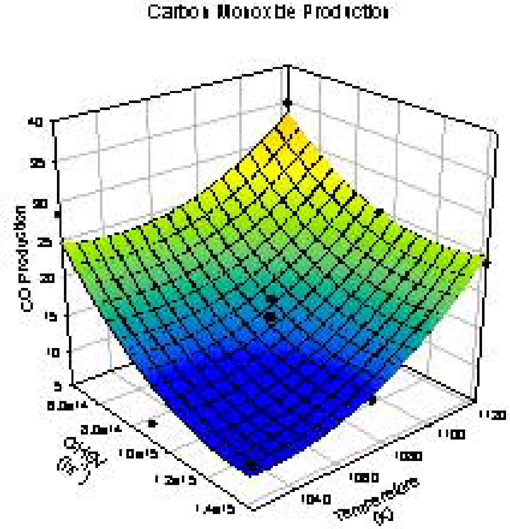


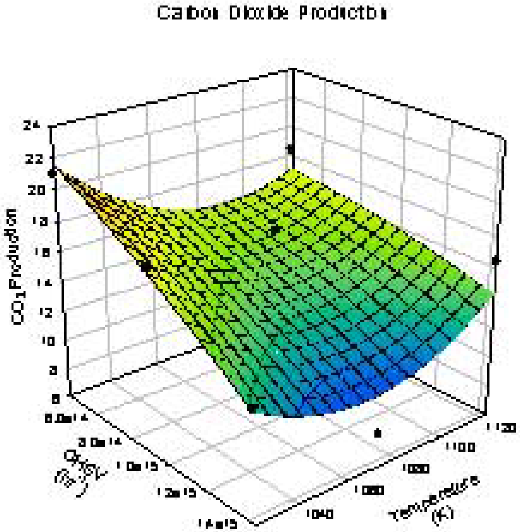


-Reforming rate increases significantly with increasing SV and T
-Slow reforming rate relative to paraffines and naphthenes
-Fast carbon deposition rate
-Naphthenes not observed
-Small concentrations of lower olefins observed
-Methane is the main paraffin formed

ATR of Decalin (O_2/C=0.3, S/C=1.5)

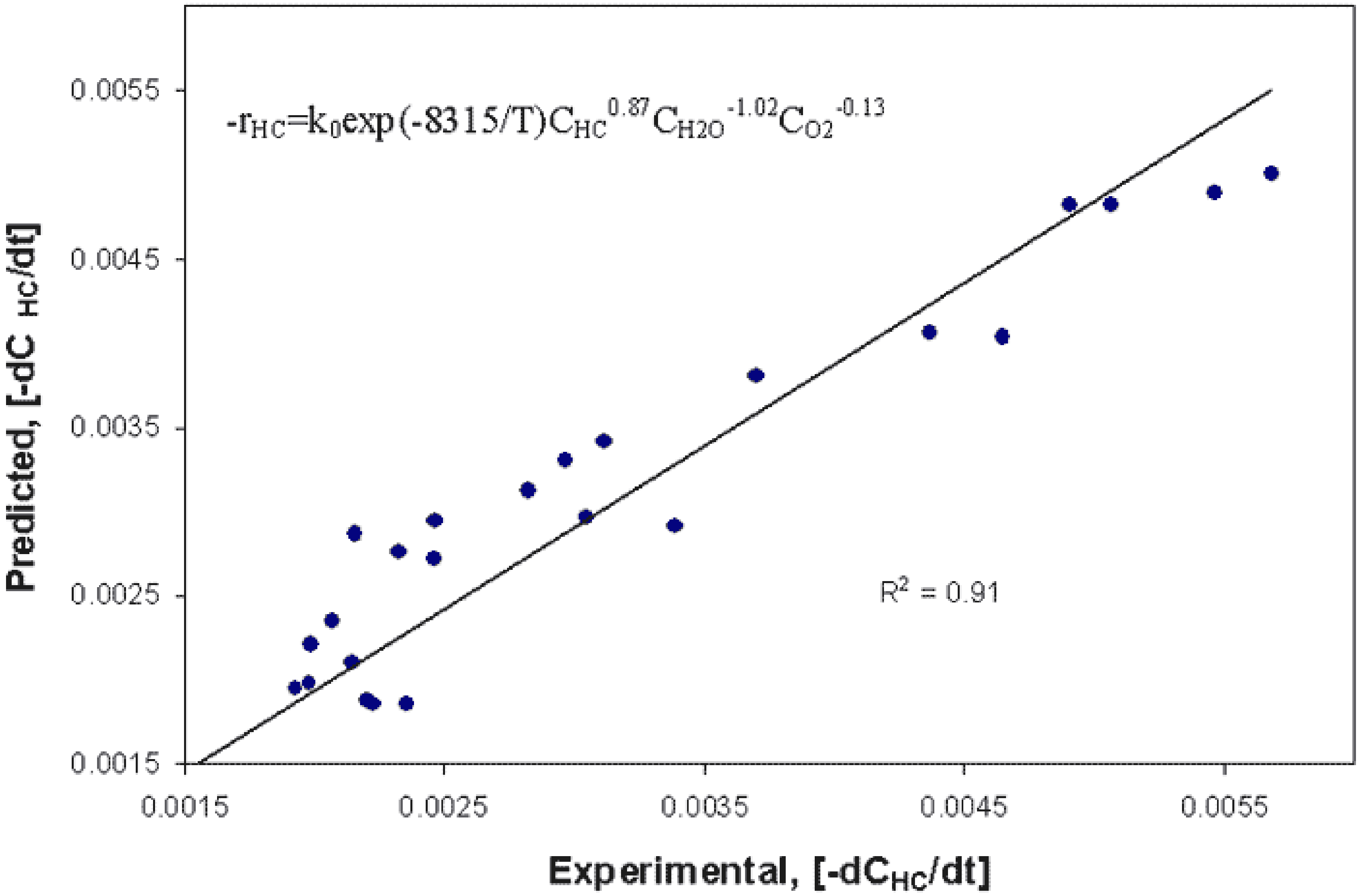

Hydrogen Production


Carbon Monoxide Production


Carbon Dioxide Production

-Aromatics, paraffines, olefins observed in product
-Higher aromatic content in product

Experimental Vs Predicted Values for Diesel ATR on Pt/Al_2O_3



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Conclusions / Accomplishments

- Tested three model compounds from the major representative functional groups in diesel fuel
- Developed surface response maps for steam reforming, partial oxidation and ATR over Pt catalysts for single component fuels
- Liquid product distribution varied with the type of reforming performed
- Higher olefins as well as aromatics content in product from ATR/SR/POX of paraffines at lower SV and higher T
- Significant coking observed from reforming (ATR/POX/ SR) of aromatics and naphthenes at higher T (~900 C)
  - Results in high pressure drops
- Quadratic fit of data from RSM was excellent (>90%)
- Reforming rate at the same conditions
  - Aromatics << Naphthenes < Paraffines
- $H_2/CO/CO_2$ production
  - Moles of ($H_2/CO/CO_2$) produced*100/moles of carbon fed
- Developed lumped parameter “power-law” ATR model

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Future Plans/Collaboration/Tech Transfer

- **Continue Surface Response Mapping :**
  - Evaluate other fuel compounds within a classification to examine if similar reforming behavior exists
  - Conduct combinatorial fuel compound studies
- **Develop Kinetic Submodels**
  - From response mapping, develop intrinsic reaction models for particular catalyst types
  - Continue collaboration/funding with Las Alamos National Laboratory LANL) to provide carbon deactivation kinetics
  - Continue collaboration with Argonne National Laboratory (ANL) to obtain experimental reactor performance data to validate reaction models and provide for fuel reactant mixing modeling capability suitable for CFD modeling codes.
- **Technology Transfer**
  - Continue dissemination of project results through EERE program reviews and FE SECA program reviews to principle developers such as Delphi Automotive, GE/Honeywell, Siemens-Westinghouse, and Cummings/McDermott.