

2003 SECA CORE TECHNOLOGY REVIEW



Fuel Reforming Kinetics for Diesel-Based Fuel Cell Reformers

National Energy Technology Laboratory

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Diesel Fuel Processing

R&D Goal and Objectives

GOAL:

- *Provide kinetic reaction rate and process information* of diesel fuel reforming to support the development of auxiliary power units (APUs) in commercial diesel truck transport and other related applications as being sponsored by NETL's SECA Fuel Cell Program

OBJECTIVE:

- Correlate fuel reforming rates versus process conditions, and catalyst type for individual, and combined diesel constituents (surrogate diesel fuel).



Diesel Fuel Processing

Technical Issues / Challenges

- **Diesel fuel is complex and difficult to reform :**
 - Multi-component (>100 compounds) fuel that exhibits varying reaction pathways and kinetic rates.
 - Deactivation of fuel reforming catalysts and fuel cell anodes via carbon deposition and sulfur poisoning are a major concern.
 - Improper reactant mixing can lead to hot spots and carbon deposition.
- **System integration can be a significant challenge:**
 - Reformer integration with fuel cell system requires potential desulfurization, water management, and thermal considerations.
 - Certain FC applications may require, fast start, quick response (transient), part-load operation.
 - Minimal / no hydrocarbon slip.



Diesel Fuel Processing

Applicability to Fuel Cell APU Commercialization

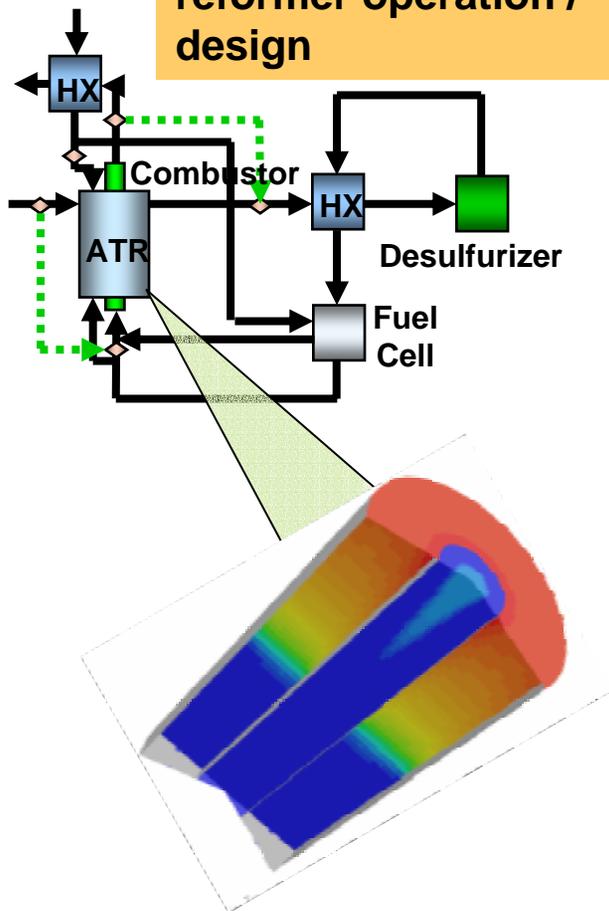
- Diesel-based fuel cell APUs are considered a significant high volume market for SOFC's.
- Fundamental understanding of diesel reforming and general methodology for kinetic rate determination would be beneficial to catalyst developers. May extend to hydrocarbon fuels in general.
- Fuel reforming kinetics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



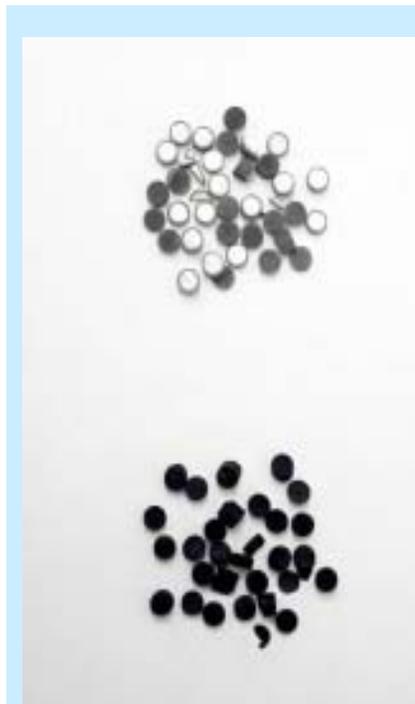
Diesel Fuel Processing

Fuel Reforming Reaction Studies – Why?

System integration & reformer operation / design

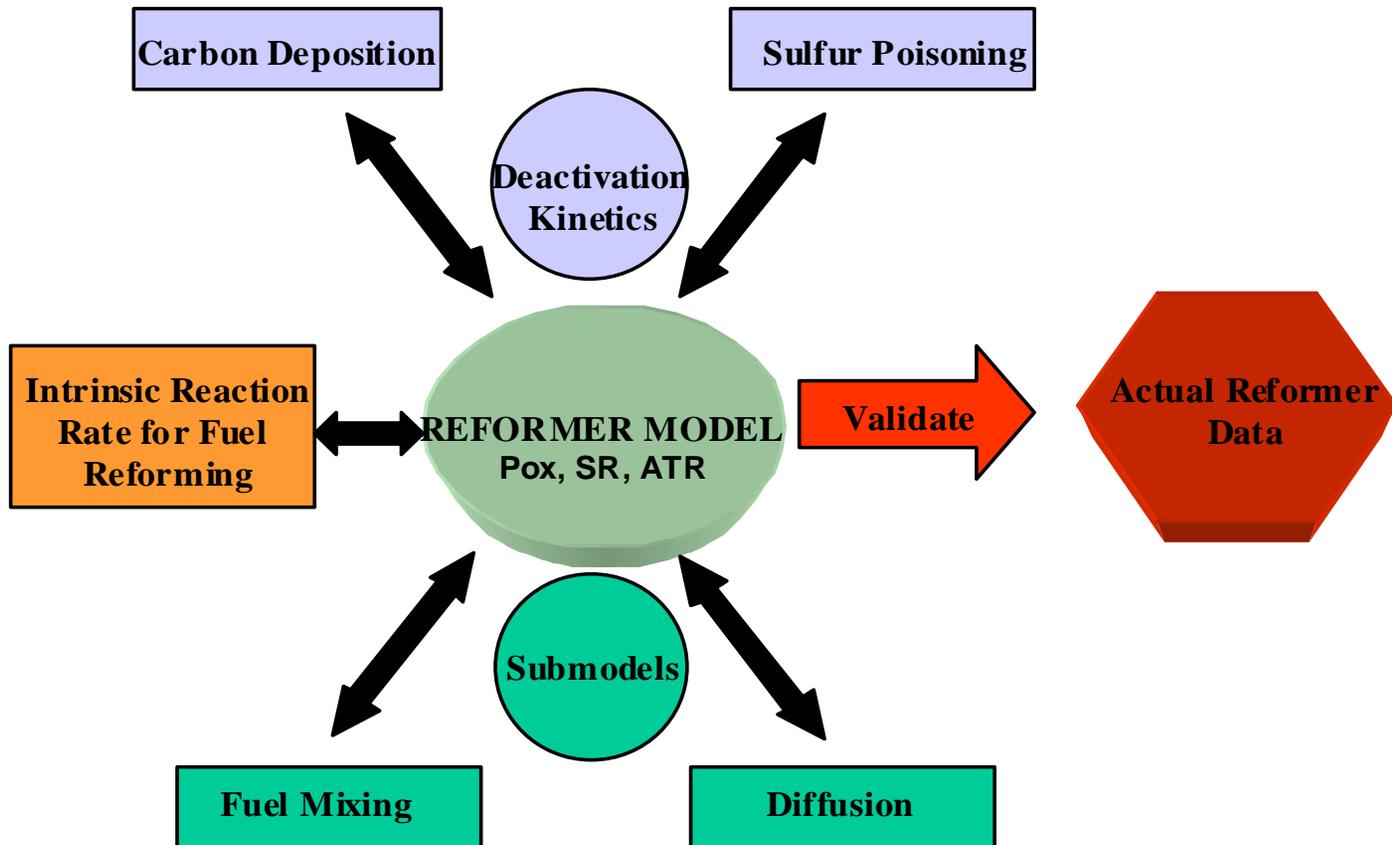


Insights for catalyst improvement & design



Reformer Model

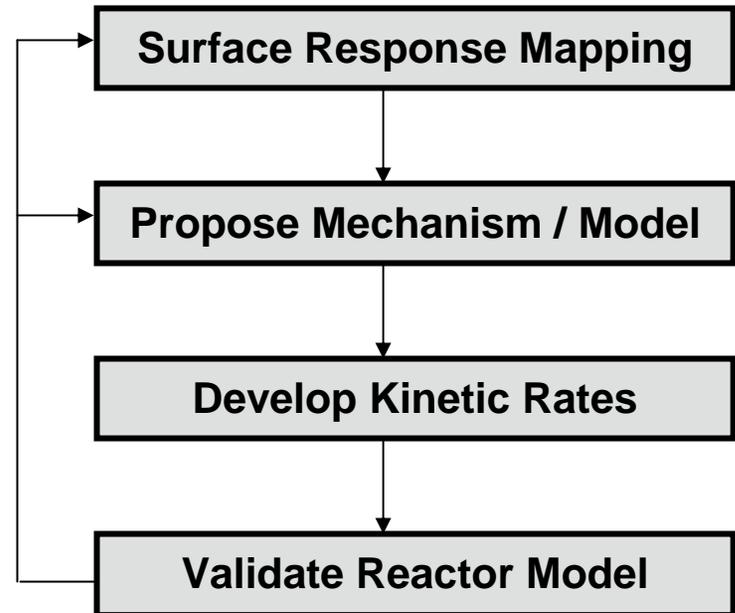
Elements for Integrated Model – Capturing Understanding



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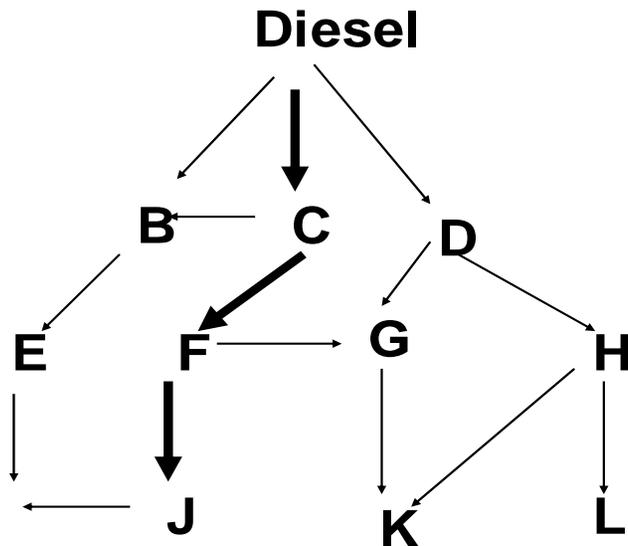
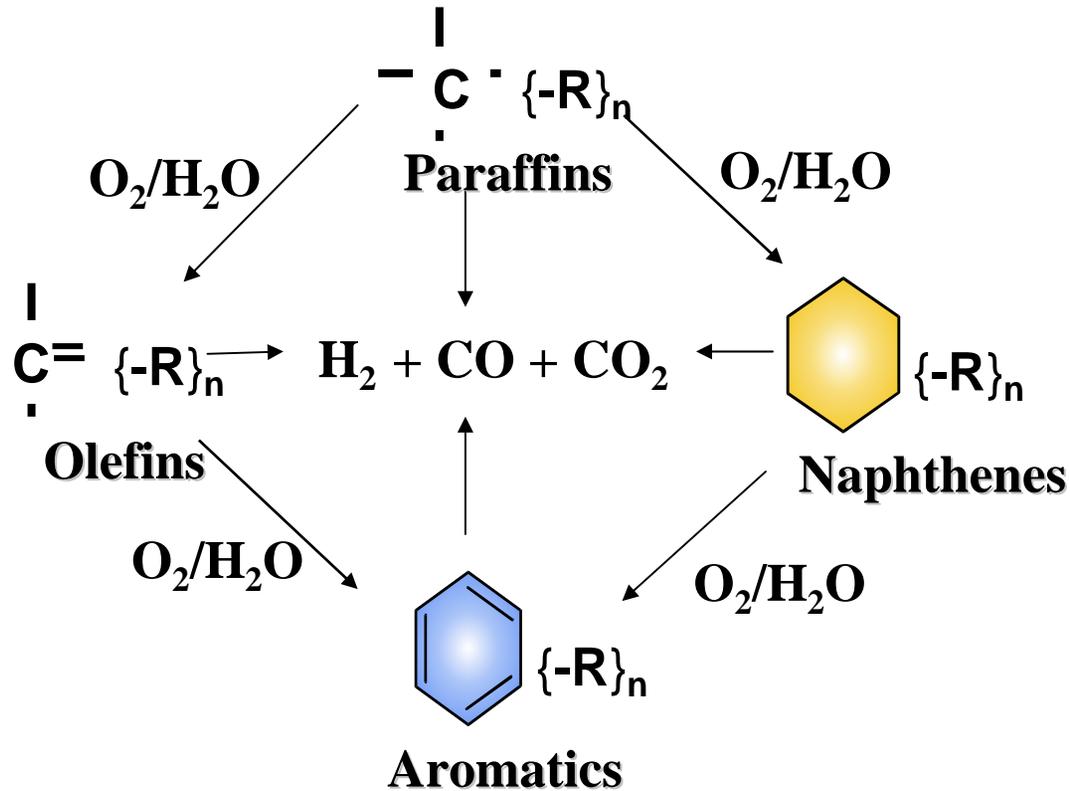
General Kinetic Modeling Approach

- **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



ATR Kinetic Modeling

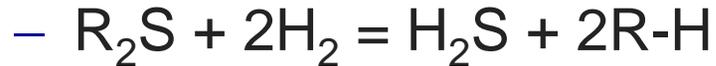
- Dominant reaction pathways to be elucidated
- Assessment of kinetic parameters



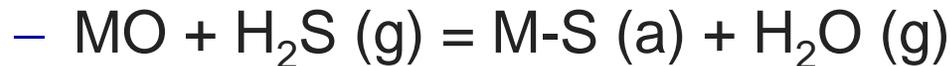
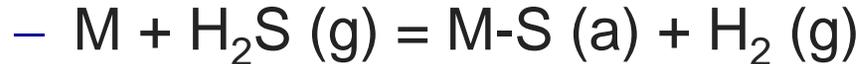
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Sulfur Poisoning

- **Organic sulfur reduction**



- **Dissociative sulfur adsorption**



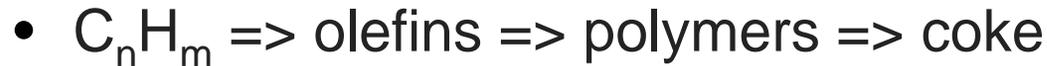
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Carbon Formation

- **Boudouard Reaction**



- **Polymerization Reaction**



- **Pyrolytic Reaction**



- **Whisker carbon formation**



Diesel Fuel Processing

Diesel Fuel Composition – what to test?

- **Diesel Fuel Analysis**

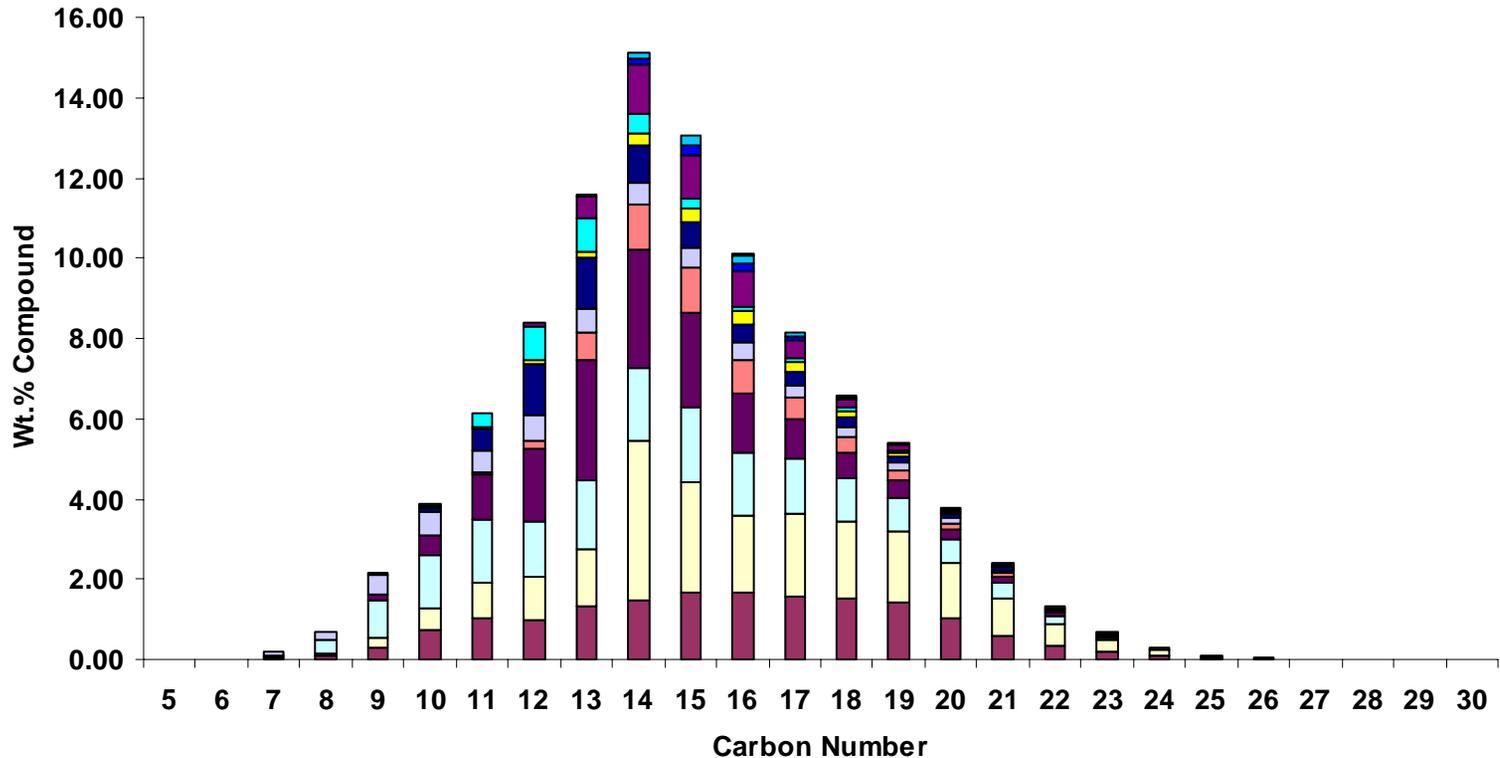
- Diesel fuel is a complex, multi-component mixture of paraffinic, aromatic and naphthenic hydrocarbons in the range of (C₇-C₂₆)

- 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:
 - Paraffin: n-Tetradecane
 - Aromatic: 1-Methylnaphthalene
 - Naphthene: Decalin



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Diesel Fuel Composition – Con't.



Hydrogen Deficiency, C_nH_{2n+z} , Classification



Diesel Fuel Processing

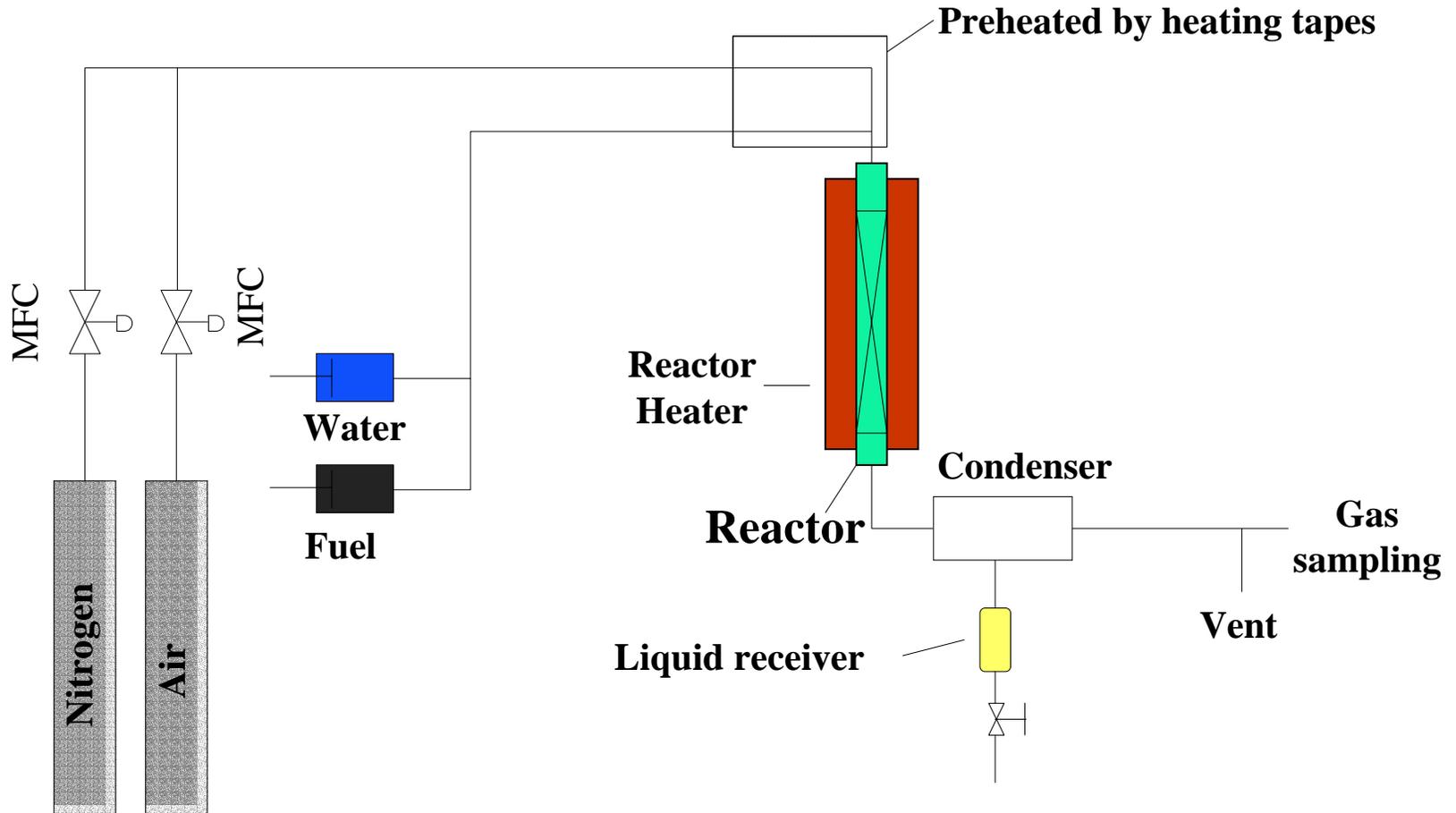
Experimental Conditions

	Paraffin	Aromatic	Naphthene
Model Compound	n-Tetradecane	1-methyl naphthalene	Decalin
O/C	0 - 1.0	0 - 1.0	0 - 1.0
H₂O/C	0 - 3	0 - 3	0 - 3
T (°C)	750 – 900	750 – 850	750 - 850
GHSV (h⁻¹)	50,000 - 200,000	22,000 - 66,000	50,000 - 150,000



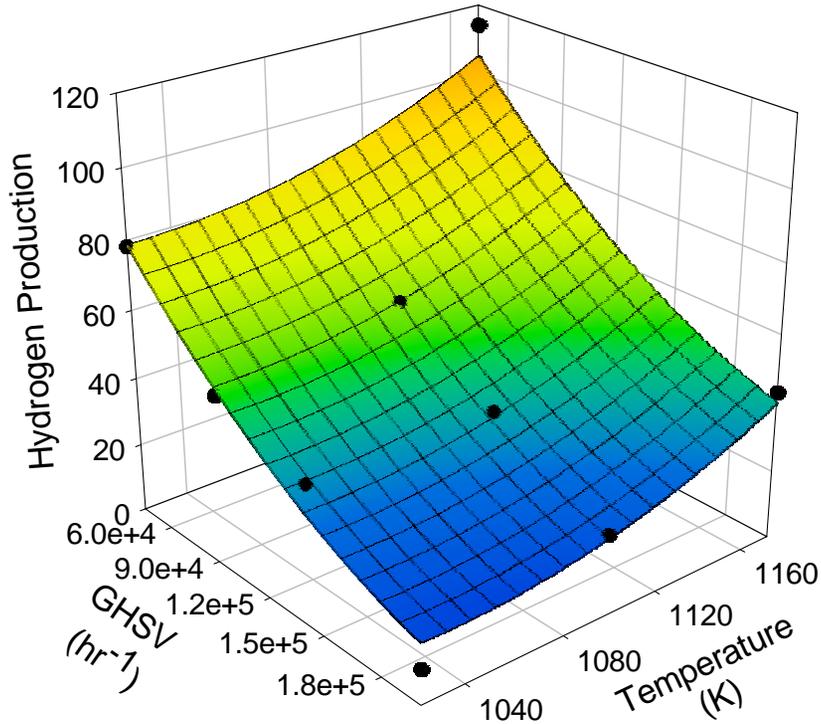
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Experimental Setup

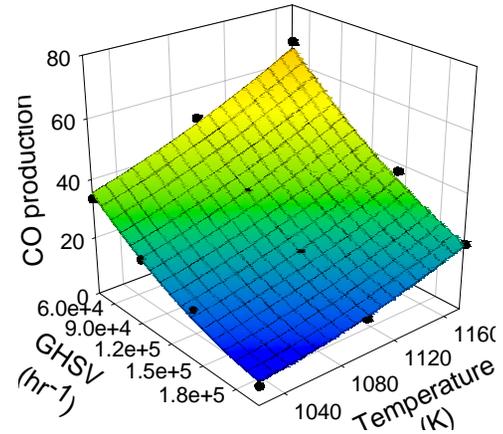


ATR of n-Tetradecane (Pt/Al_2O_3 , $O_2/C=0.3$, $S/C=1.5$)

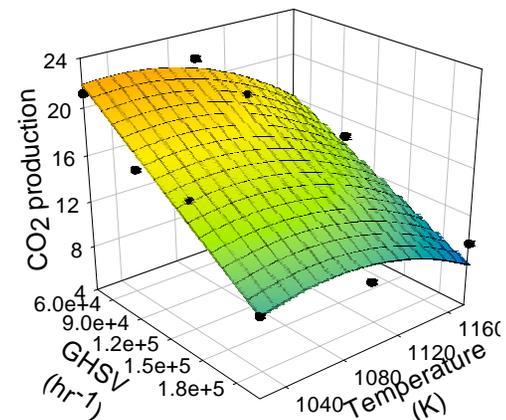
Hydrogen Production



CO Production



CO₂ Production

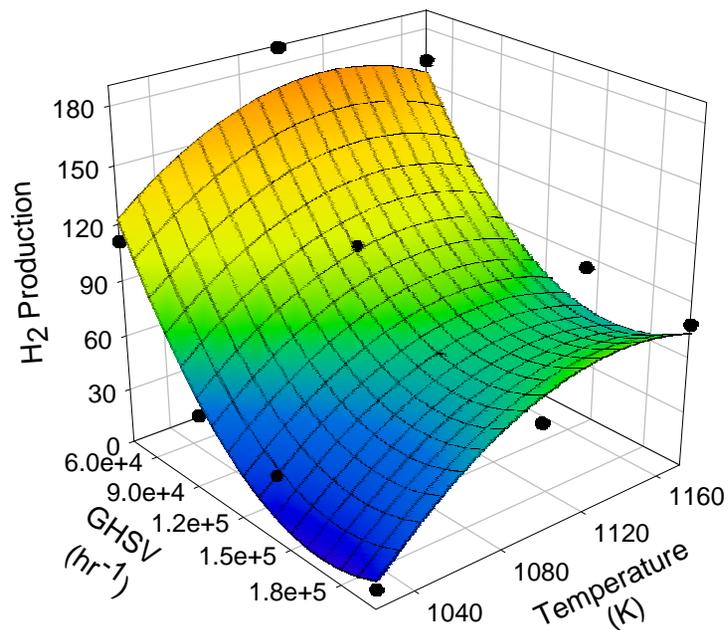


- Reverse WGS reaction dominates at higher T
- Olefins and aromatics produced at higher SV and higher T
- Naphthenes not observed

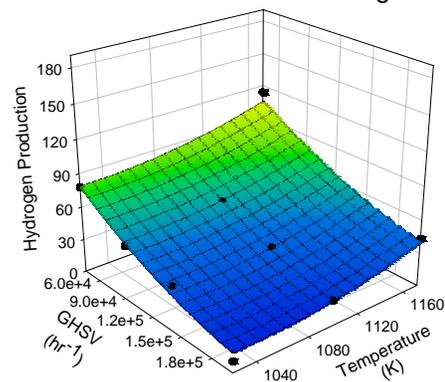


Reforming of n-Tetradecane (Pt/Al_2O_3)

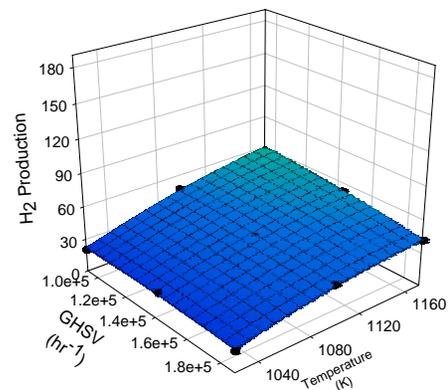
Steam Reforming



Autothermal Reforming



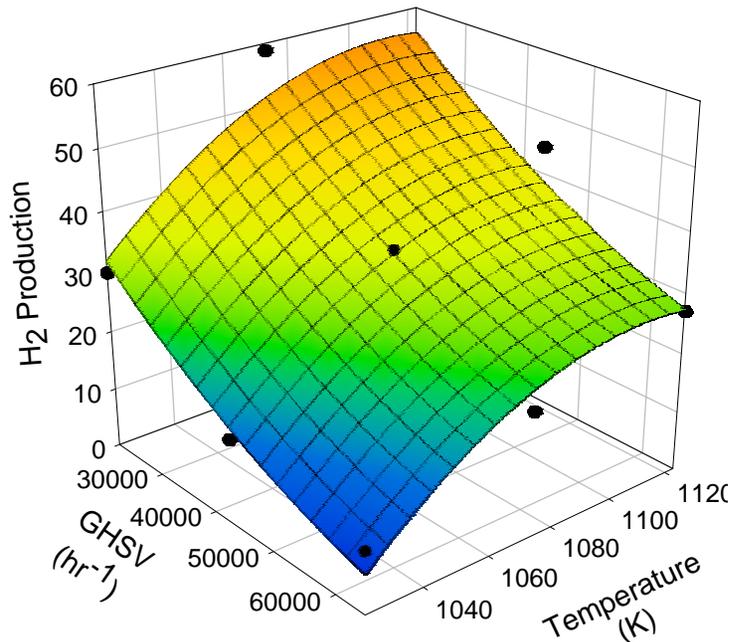
Partial Oxidation



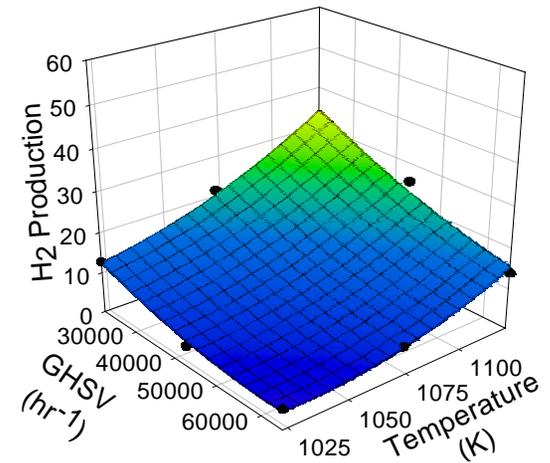
- A series of oxygenated products such as aldehydes and ketones formed from POX, particularly at higher SV and lower T

Reforming of 1-Methylnaphthalene (Pt/Al_2O_3)

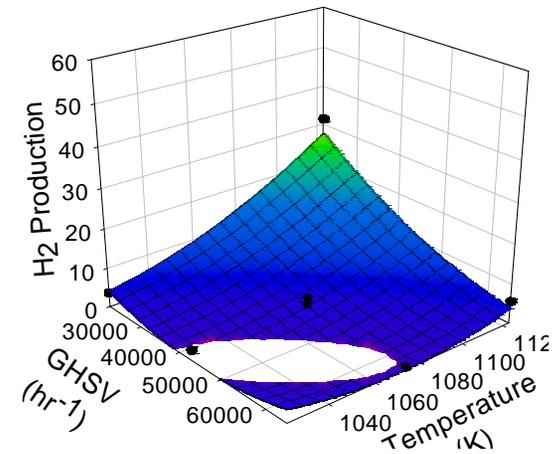
Steam Reforming



Autothermal Reforming



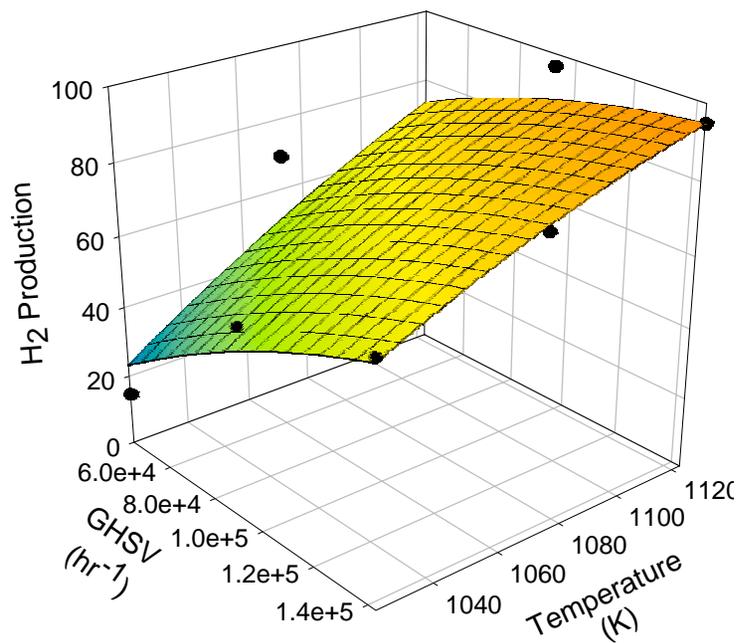
Partial Oxidation



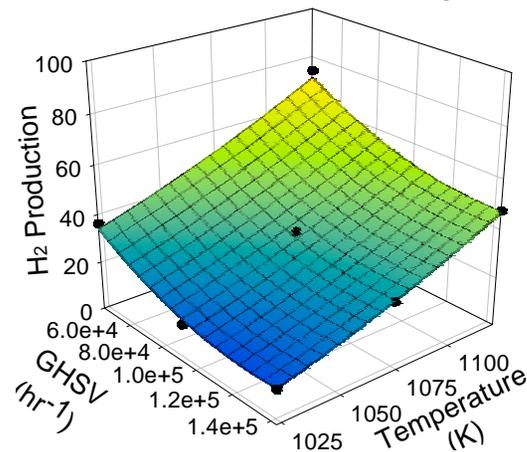
- Reforming rate increases significantly with increasing T and decreasing SV.
- Slow reforming rate relative to paraffins and naphthenes
- Fast carbon deposition rate
- Naphthenes not observed
- Small concentrations of lower olefins observed
- Methane is the main paraffin formed

Reforming of Decalin (Pt/Al_2O_3)

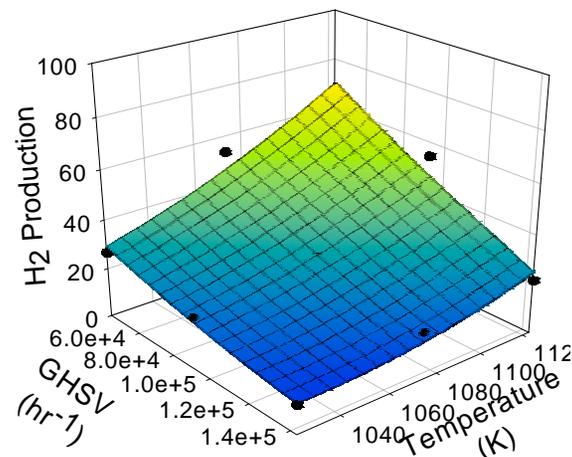
Steam Reforming



Autothermal Reforming

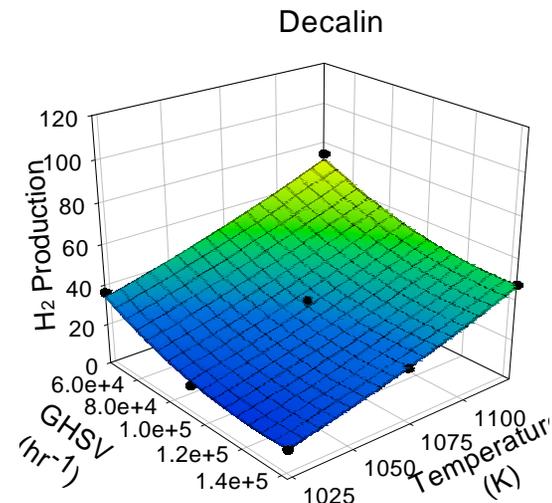
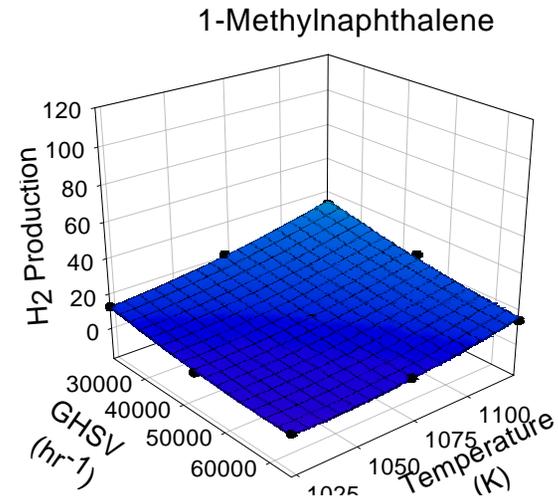
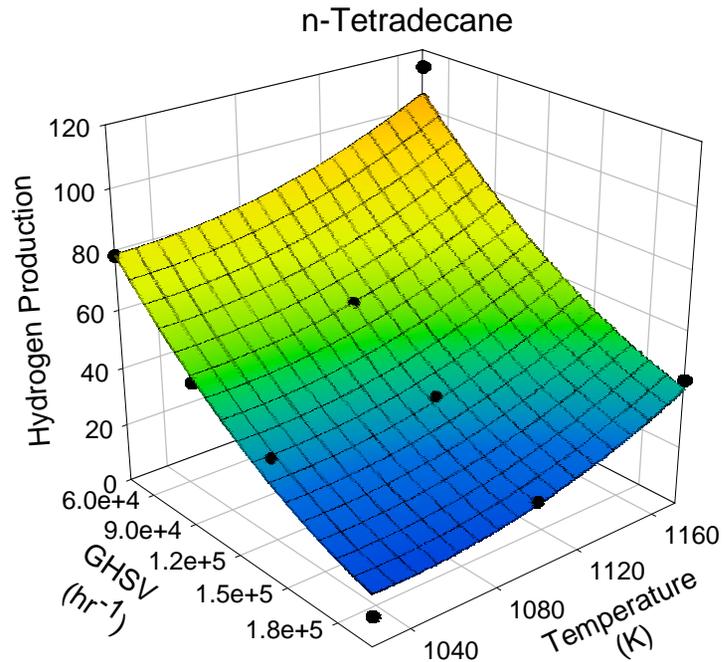


Partial Oxidation



- Aromatics, paraffins, olefins observed in product
- Higher aromatic content in product relative to reforming of tetradecane

ATR of Different Model Compounds (Pt/Al_2O_3 , $O_2/C=0.3$, $S/C=1.5$)



- Liquid product distribution varied with the type of reforming performed
- Hydrogen production rate at the same conditions
Aromatics \ll Naphthenes $<$ Paraffines

Diesel Fuel Processing

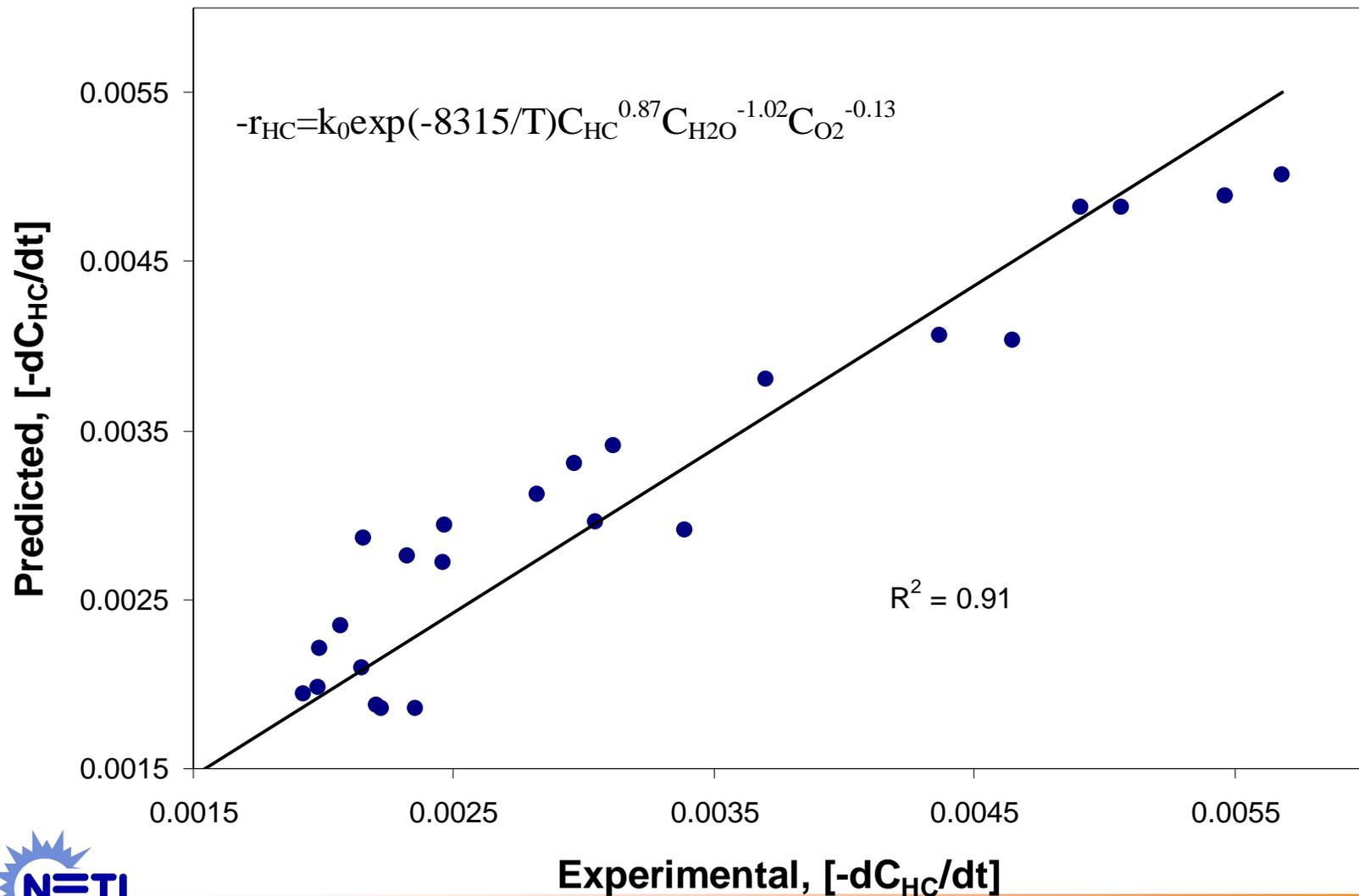
Reaction Rate Determination - Modeling Approaches

Level 1 Intuitive Lumping	Level 2 Mechanism Based Lumping	Level 3 Structure Oriented Lumping	Level 4 Mechanistic
<ul style="list-style-type: none">• Lumps derived from intuition (gross identification of lumping groups), e.g. paraffins, aromatics, etc.• Little is known regarding the exact mechanism• Pseudo-1st order• Pseudo-homogeneous phase• Easy to develop, inexpensive• Suitable for process simulators, e.g. ASPEN, ChemCad• Predicts transient response and hydrocarbon slip	<ul style="list-style-type: none">• Pseudo-homogeneous phase• Based on pseudo-species lumped together based on the elucidation of a detailed mechanism• Requires a knowledge of process chemistry• Must possess the analytical ability to measure the pseudo-species only• Suitable for process simulators, e.g. ASPEN, ChemCad• Predicts transient response, hydrocarbon slip, coking and catalyst deactivation	<ul style="list-style-type: none">• State of the art in complex mixture modeling• Closely resembles pure mechanistic approach• Involves lumping isomers only• Detailed knowledge of process chemistry needed, expensive analytically• Detailed kinetic studies needed for the development of lumps• Suitable for CFD packages, e.g. Fluent	<ul style="list-style-type: none">• Pure mechanistic approach• Detailed kinetic studies of single components and their mixtures• Development of experimental procedures to evaluate process chemistry• Knowledge of catalyst properties needed• Requires spectroscopic method• Predicts transient response, hydrocarbon slip, coking and catalyst deactivation based on fundamentals



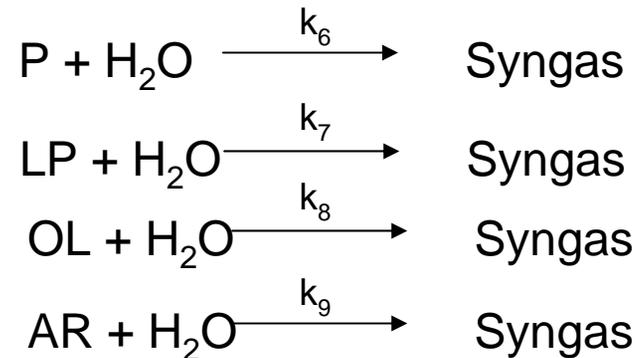
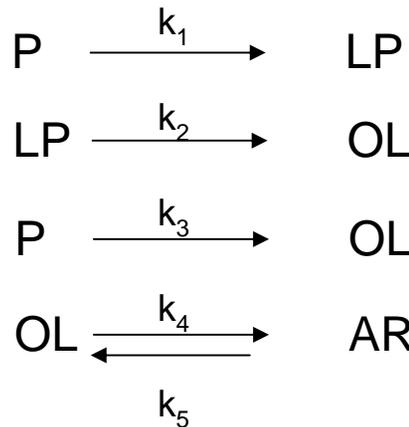
Kinetic Rate Expression for Diesel ATR on Pt/Al₂O₃

Example of Lumped Parameter Power Law Model



Analysis of Kinetic Scheme

- Paraffin Steam Reforming

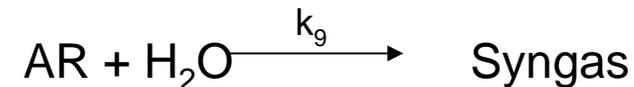
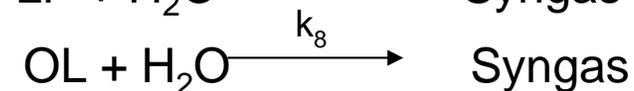
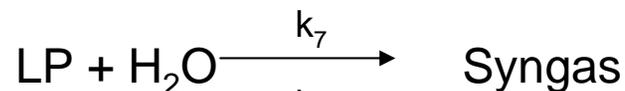
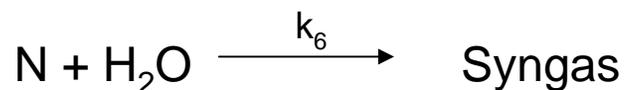
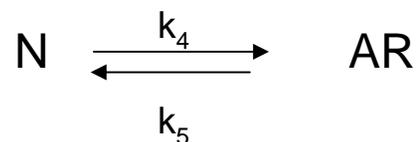
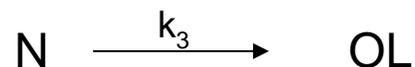
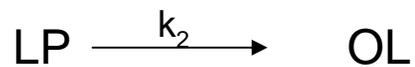
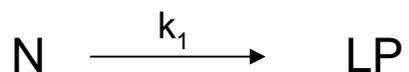


P = Paraffins
LP = Lower Paraffins
OL = Olefins
AR = Aromatics



Analysis of Kinetic Scheme

- Naphthenes Steam Reforming



P = Paraffins

LP = Lower Paraffins

OL = Olefins

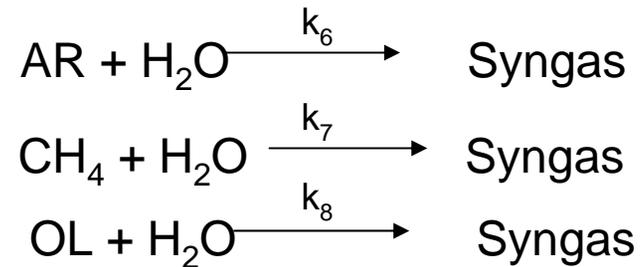
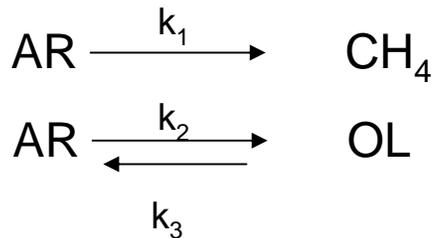
AR = Aromatics

N = Naphthenes



Analysis of Kinetic Scheme

- Aromatics Steam Reforming



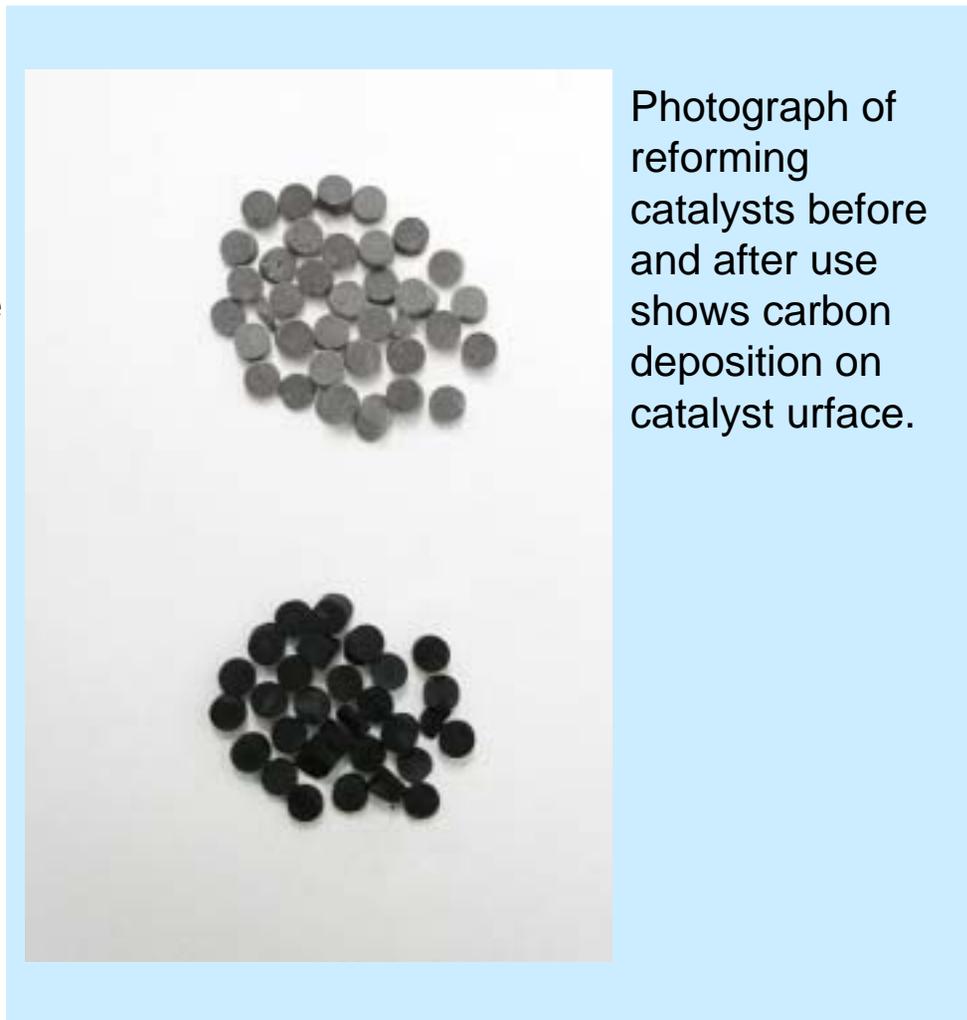
P = Paraffins
LP = Lower Paraffins
OL = Olefins
AR = Aromatics



Diesel Fuel Processing

Carbon Studies

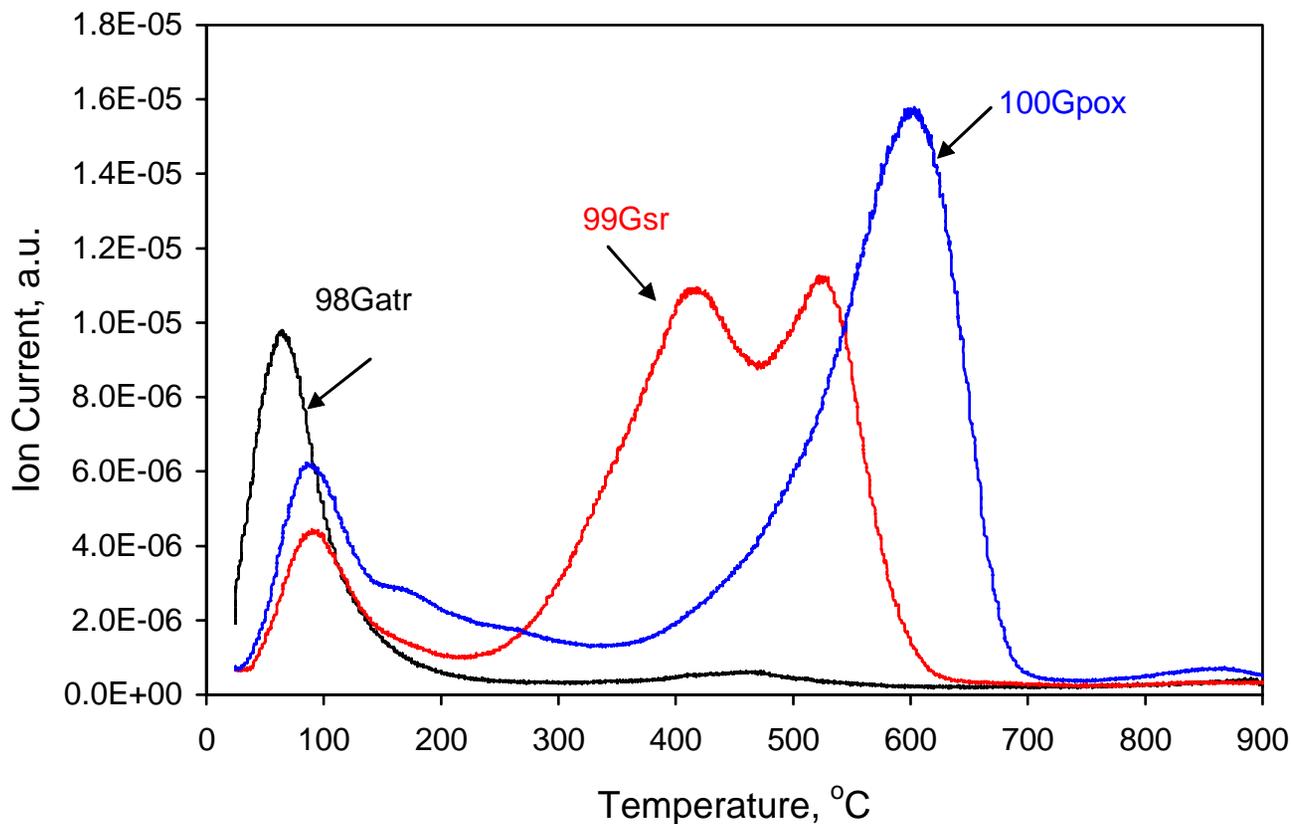
- Carbon is a fundamental barrier issue for catalytic reforming.
- Carbon formation studies were conducted to evaluate fuel type and reforming condition (SR, ATR, POx) on Pt catalyst.
- Temperature programmed oxidation (TPO) and Raman were used to analyze carbon formed on the catalyst.



Diesel Fuel Processing

Carbon Studies – Effect of Reforming Type

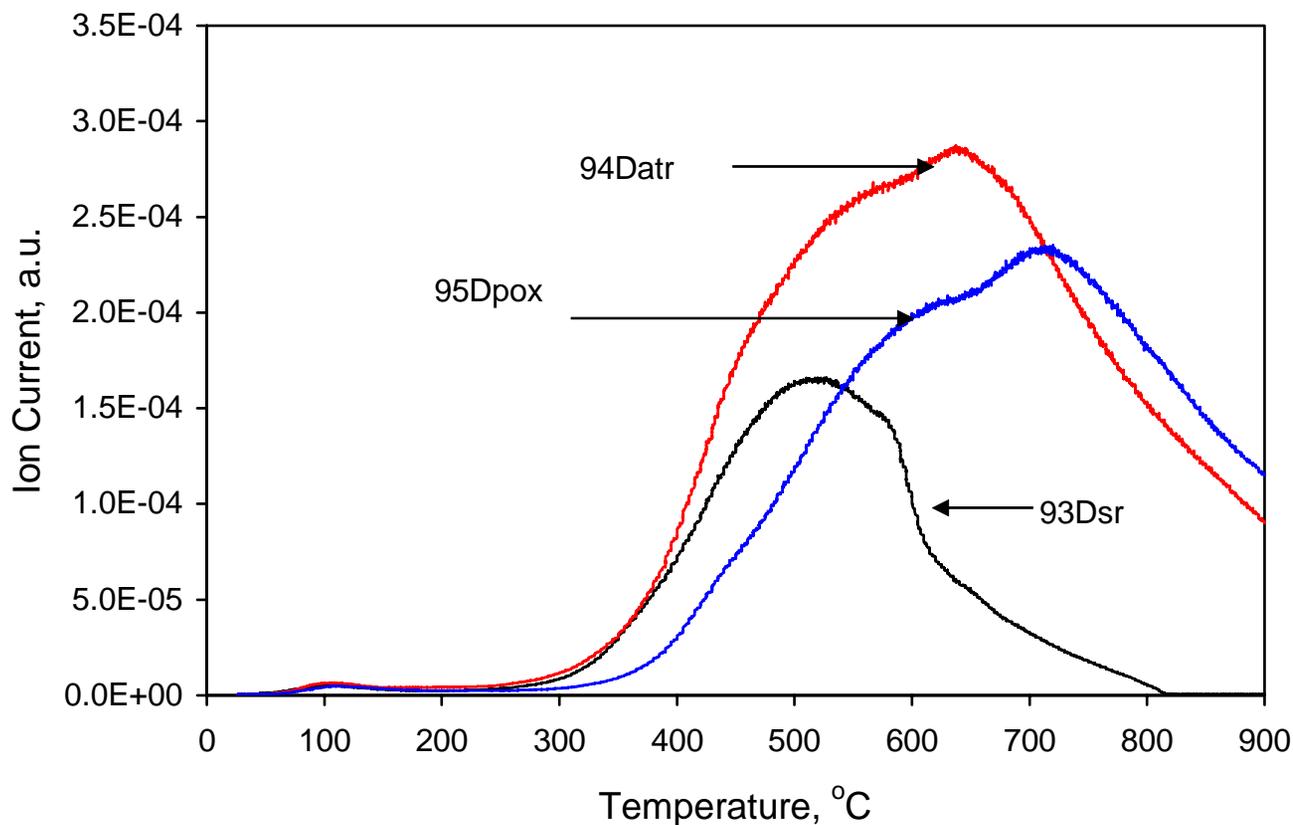
**TPO of carbon deposited on 0.5% pt/alumina, 2%O₂/He
at 40 cc/min, 20 °C/min heating rate, Decalin**



Diesel Fuel Processing

Carbon Studies – Aromatic Fuel C Different

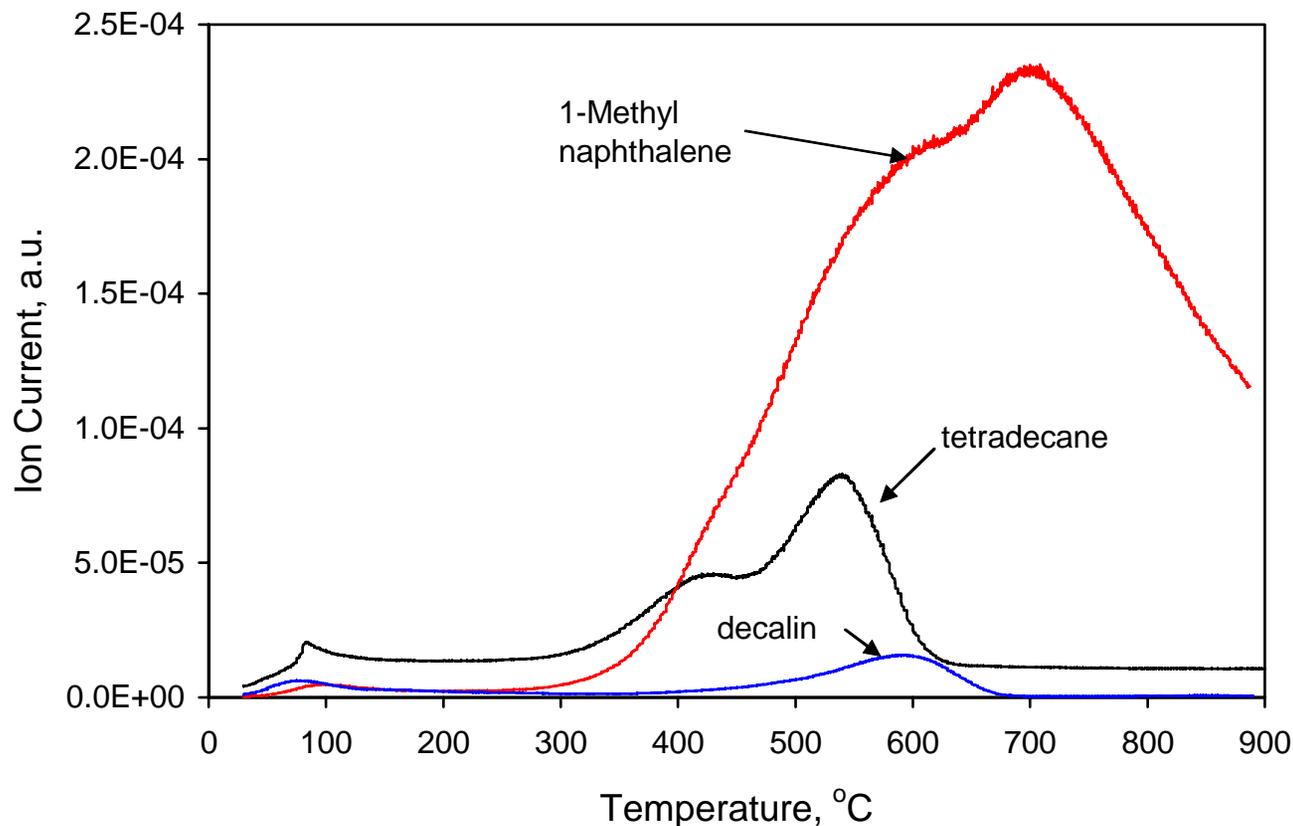
TPO of carbon deposited on 0.5%Pt/alumina, 2%O₂/ He at 40 cc/min, 20 °C/min heating rate (1-methylnaphalene)



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Carbon Studies – Effect of Fuel Type

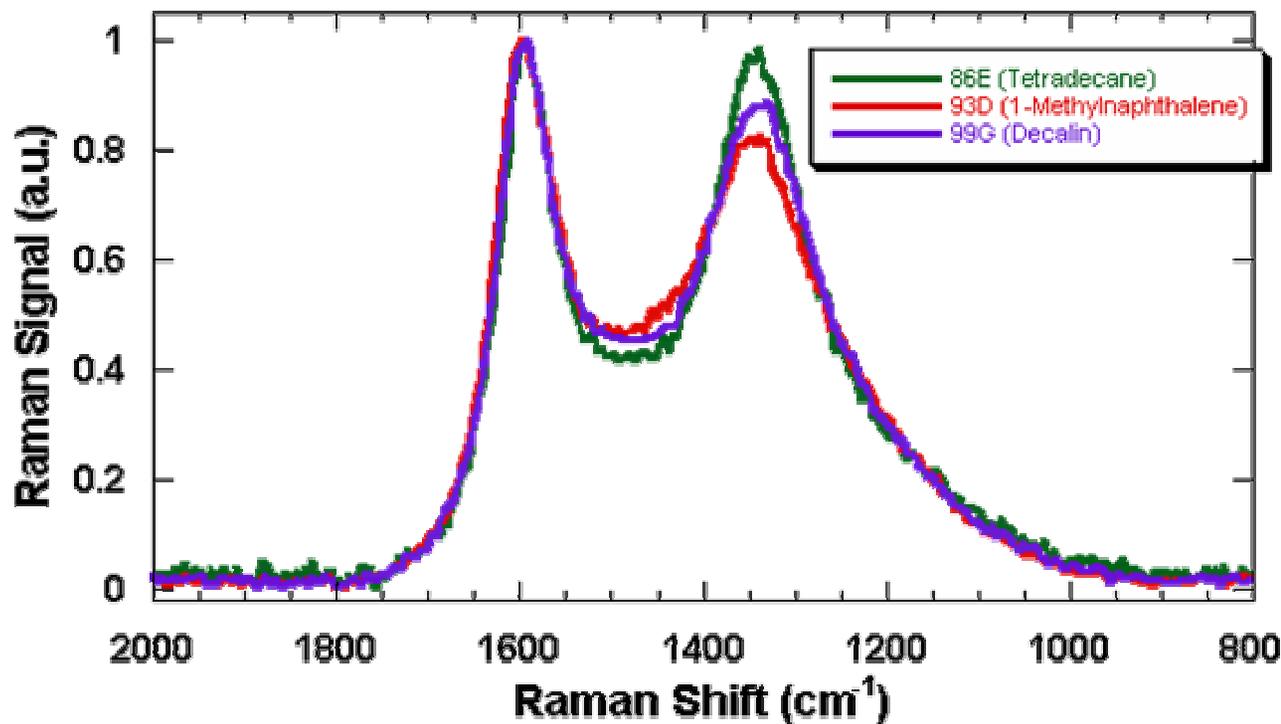
TPO of carbon deposited on 0.5%Pt/alumina (pox), 2%O₂/He at 40 cc/min, 20 °C/min heating rate



Diesel Fuel Processing

Carbon Studies – Raman Analysis

Steam Reforming with Different Feedstocks



Diesel Fuel Processing

Carbon Studies – Raman Analysis cont.

Sample ID	Process	Feedstock	Ig/Id	Crystallite Size (nm)	freq G	HWHM G	Freq D	HWHM D
83E	ATR	Tetradecane	0.4	1.7556	1589	40	1343	103
94D	ATR	1-ethylnaphthalene	0.3	1.7204	1592	39	1346	118
98G	ATR	Decalin	0	0	0	0	0	0
86E	SR	Tetradecane	0.4	1.8348	1590	37	1341	90
93D	SR	1-ethylnaphthalene	0.4	1.7776	1592	38	1348	107
99G	SR	Decalin	0.4	1.826	1591	38	1342	98
87J	POX	Tetradecane	0.3	1.7248	1589	38	1341	106
95D	POX	1-ethylnaphthalene	0.3	1.7028	1585	44	1351	128
100G	POX	Decalin	0	0	0	0	0	0



Diesel Fuel Processing

Carbon Studies – Wt % Gain

Reforming	Feed	T	SV (hr-1)	SA (m2/g)*	Carbon, wt%
ATR	Tetradecane	825	100,000	96.3	<0.5
SR	Tetradecane	825	100,000	93.9	1.38
POX	Tetradecane	825	100,000	104.7	3.13
SR	1-methylnaphthalene	800	44,000	81.5	4.35
ATR	1-methylnaphthalene	800	44,000	73.6	7.51
POX	1-methylnaphthalene	800	44,000	77.5	8.57
ATR	Decalin	800	100,000	96.0	<0.5
SR	Decalin	800	100,000	94.6	1.06
POX	Decalin	800	100,000	101.1	0.59



Diesel Fuel Processing

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 paraffins at higher 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 very good (>90%)
- Reforming rate at the same conditions
 - Aromatics << Naphthenes < Paraffins
- Assessed carbon formation as a function of reforming mode and fuel type.



Diesel Fuel Processing

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
 - Continue evaluation of carbon formation
- **Develop Kinetic Submodels**
 - Develop reaction kinetics / models for particular catalyst types
 - Continue collaboration with Las Alamos National Laboratory (LANL) to provide carbon deactivation kinetics
 - Collaborate with the national labs and fuel processing developers to obtain experimental reactor performance data to validate reaction models.
- **Technology Transfer**
 - Continue dissemination of results through publications and FE SECA program reviews to principle developers such as Acumentrics, Cummings/McDermott, Delphi Automotive, FCE, GE/Honeywell, Siemens-Westinghouse.

