2002 SECA CORE REVIEW

Fuel Processing of Diesel for Fuel Cells

National Energy Technology Laboratory

June 19, 2002

David A. Berry, Todd H. Gardner, Robert James, William Rogers, and Dushyant Shekhawat

Diesel Fuel Processing
Technical Issues Addressed

- **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.

- **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.

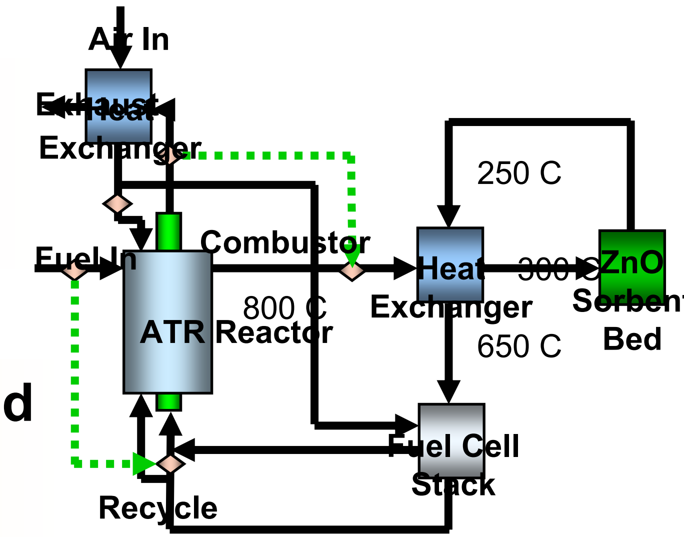
Diesel Fuel Processing

R&D Objectives

- ***Develop fundamental understanding*** of diesel fuel processing and provide ***necessary tools and information*** to fuel cell/fuel process developers and system integrators for ***technology development, performance optimization, and system control.***

Diesel Fuel Processing
Technical Approach

- Conduct Systems Analysis to Understand Reformer Integration and Operational Requirements



- Utilize CFD Models to Understand and Address Heat and Mass Transfer Issues and Reactor Performance for Steady State and Transient Analysis

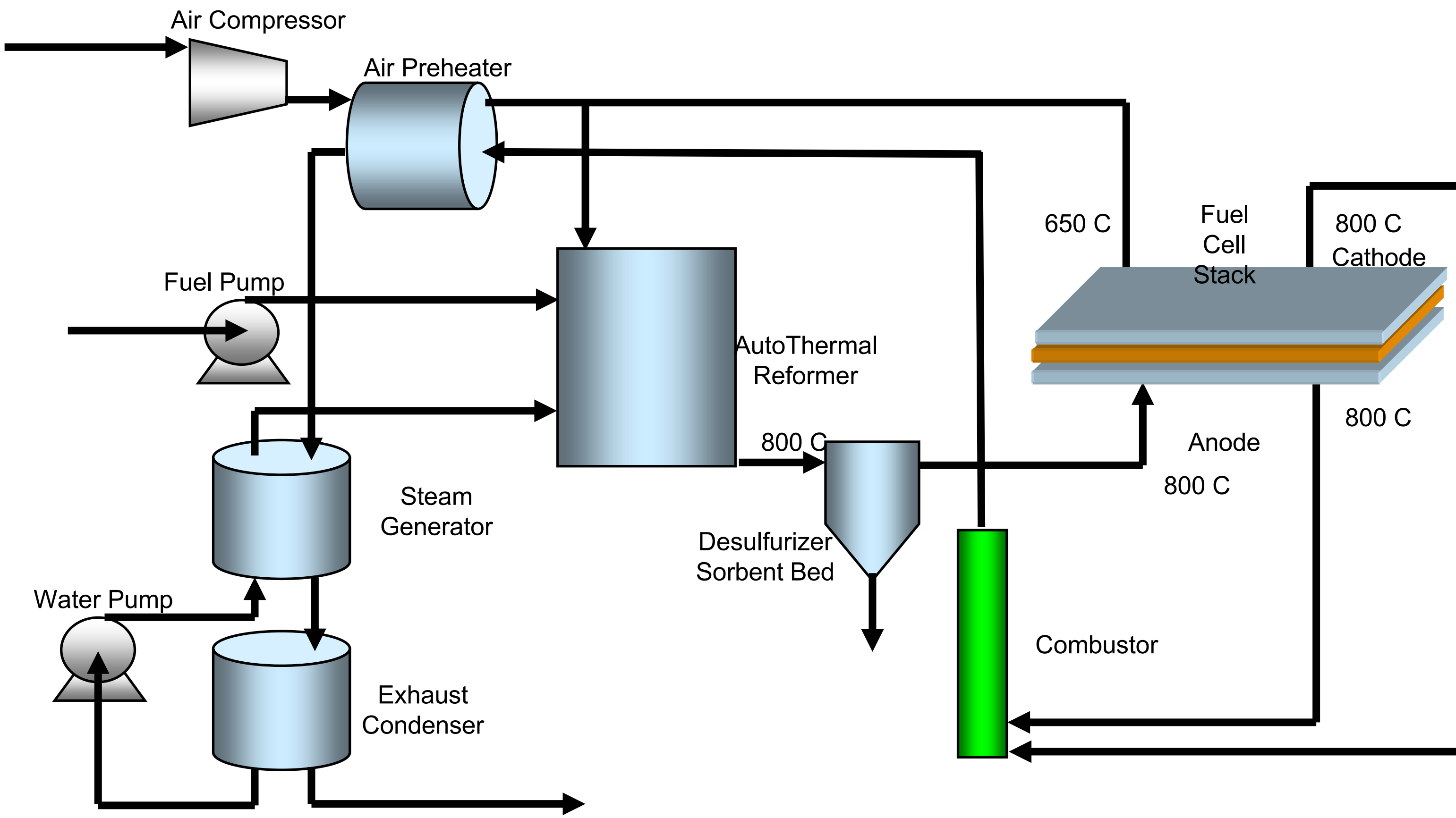
- Conduct Kinetic Rate Determination Studies in the Laboratory to Allow for Predictive Modeling and Design

NETL

Diesel Fuel Processing

Systems Analysis Results - High Efficiency Diesel Fuel Processor

800 C SECA APU

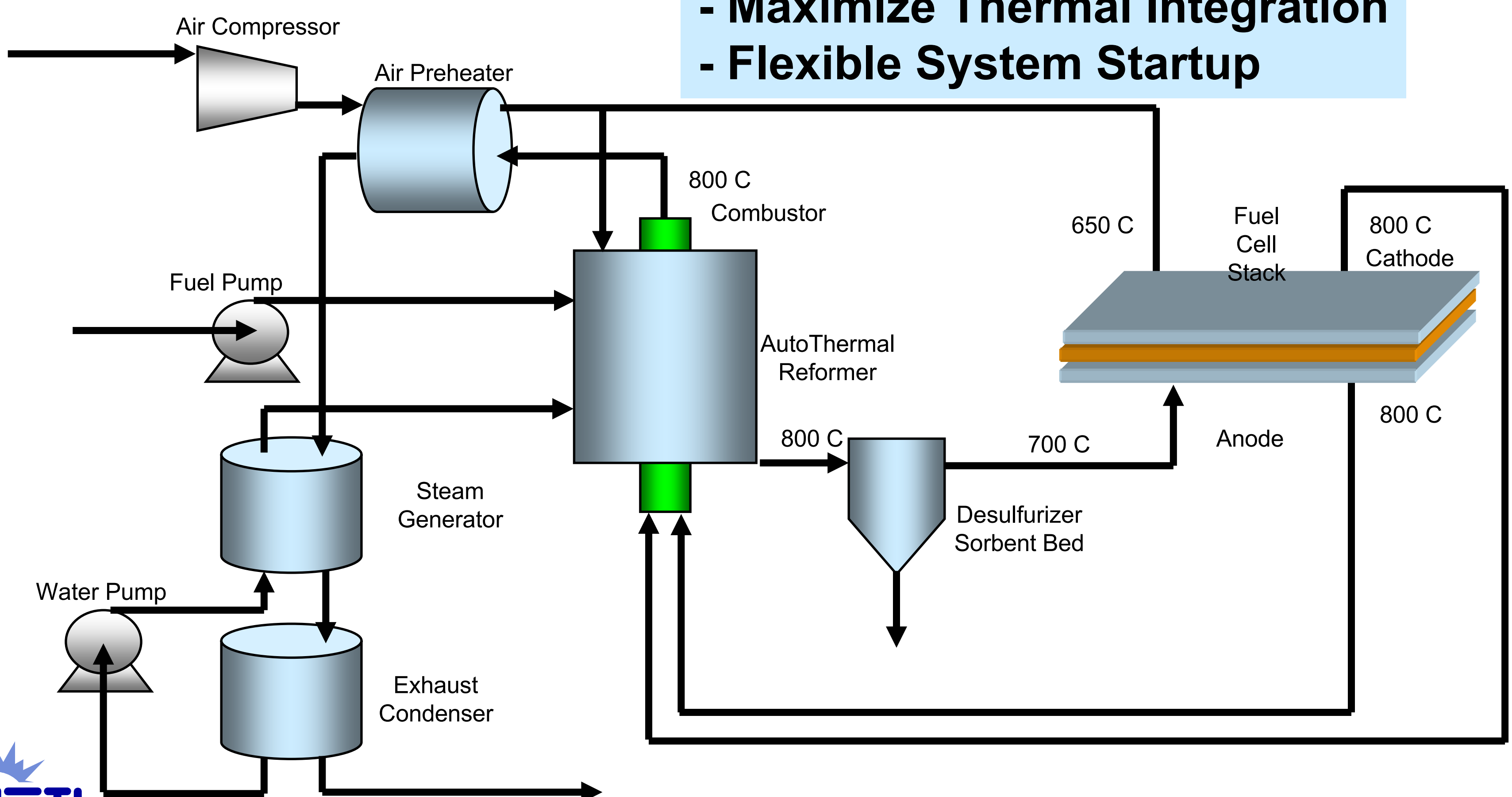


Diesel Fuel Processing

Systems Analysis Results - Integral Combustor/Reformer

800°C NETL APU

Goals:
- **Maximize Thermal Integration**
- **Flexible System Startup**



Diesel Fuel Processing

Systems Analysis Results - Effect of Heat Integration

	Shared Heat	Non-Shared Heat
Fuel (kg/hr)	0.834	0.834
Air – Stoichs In	5.5	5.2
ATR F/A Ratio	9	3.5
Steam/C Ratio	0.8	0.8
Efficiency	49.8	42.39
Net Power	5.0	4.221
ATR Temperature	800	800
FC Temperature	845	813

NETL

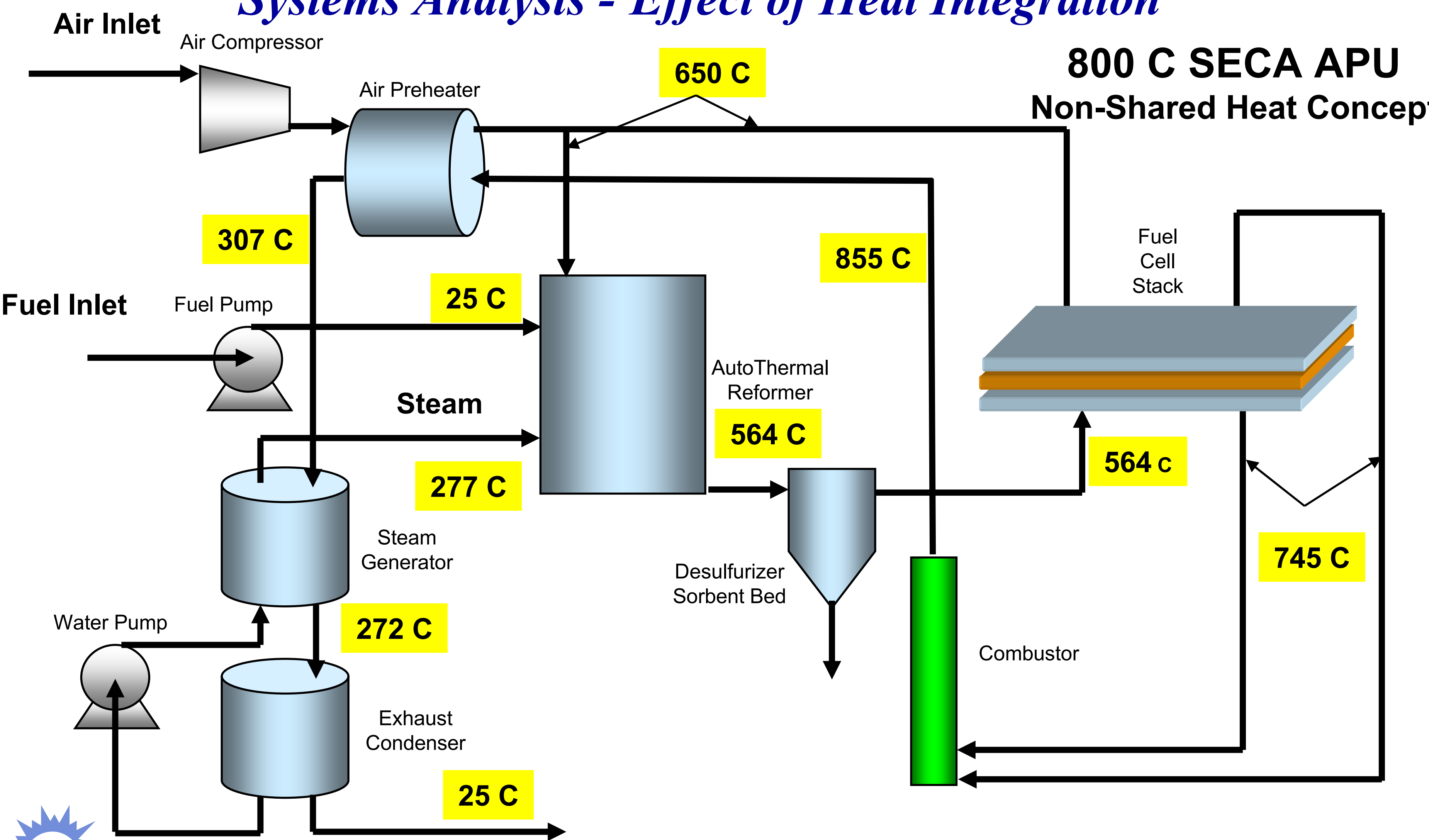
Diesel Fuel Processing

Systems Analysis - Effect of Heat Integration

	Shared Heat	Non-Shared Heat
Fuel (kg/hr)	0.834	0.834
Air – Stoichs In	5.5	5.5
ATR F/A Ratio	9	9
Steam/C Ratio	0.8	0.8
Efficiency	49.8	47.16
Net Power	5.0	4.734
ATR Temperature	800	565
FC Temperature	845	745

Diesel Fuel Processing

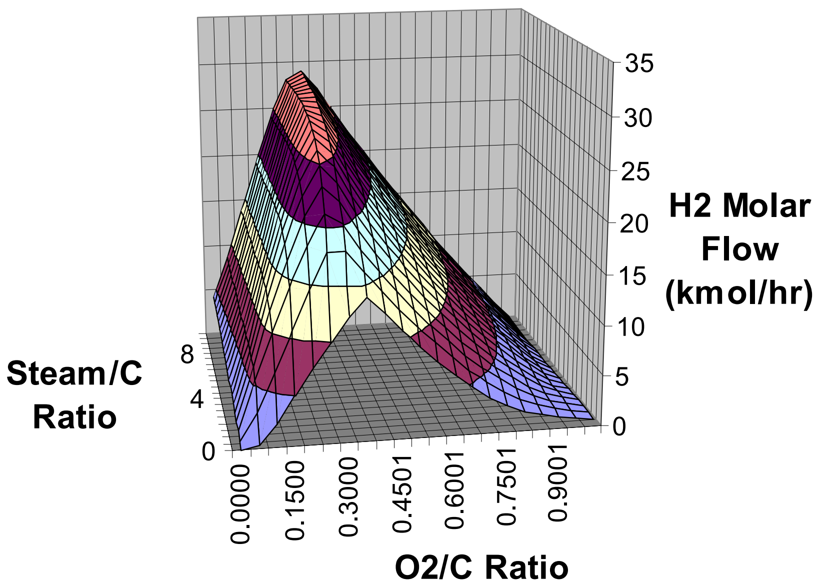
Systems Analysis - Effect of Heat Integration



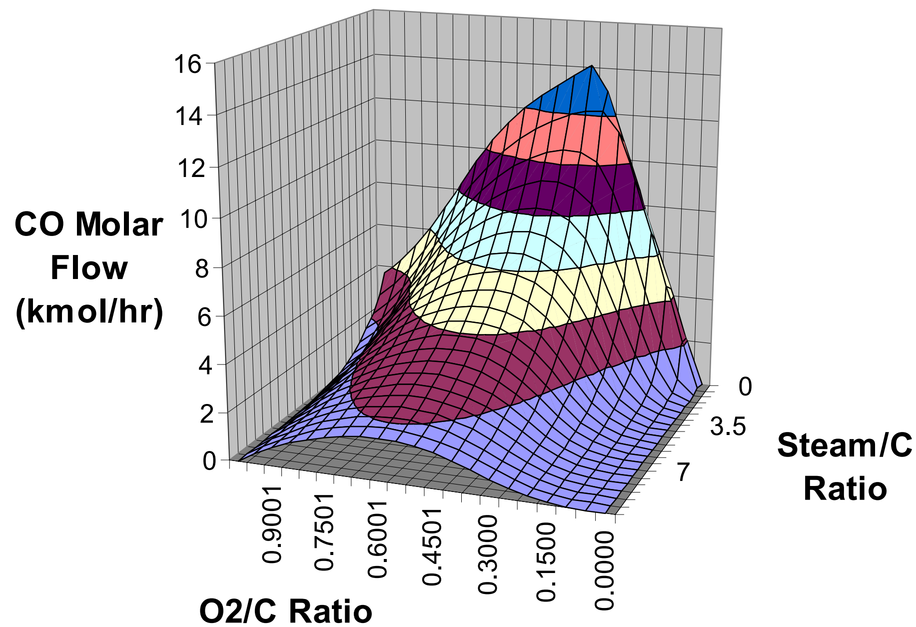
Diesel Fuel Processing

Systems Analysis - ATR Oxygen & Steam Sensitivity

H2 Molar Flow vs. O2/Steam/C Ratio



CO Molar Flow vs. O2/Steam/C Ratio



Diesel Fuel Processing

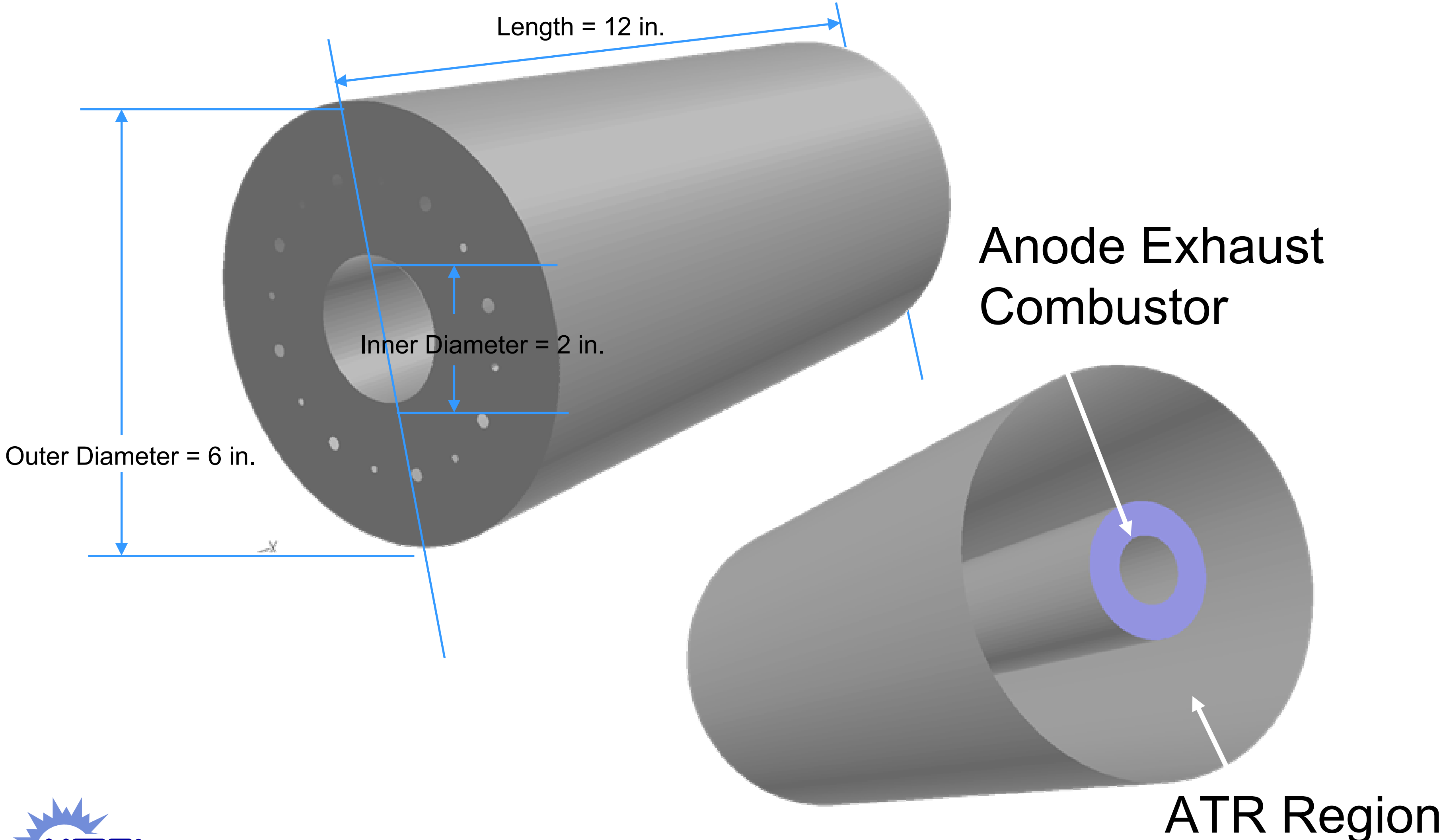
CFD Modeling - Approach

- **Develop a ATR model in Fluent**
  - Fuel atomization and vaporization
  - Partial oxidation of diesel fuel
  - Steam reforming of diesel fuel
  - Combustion of anode exhaust gas
- **Obtain reaction kinetic expressions from**
  - Catalyst manufacturer
  - Literature
  - Experiments
- **Conduct steady state simulations and validate model with ATR experimental data**
- **Conduct transient simulations**
  - Use the simulation results to study reformer performance
  - Export temperature fields into ANSYS and calculate the thermal stresses

NETL

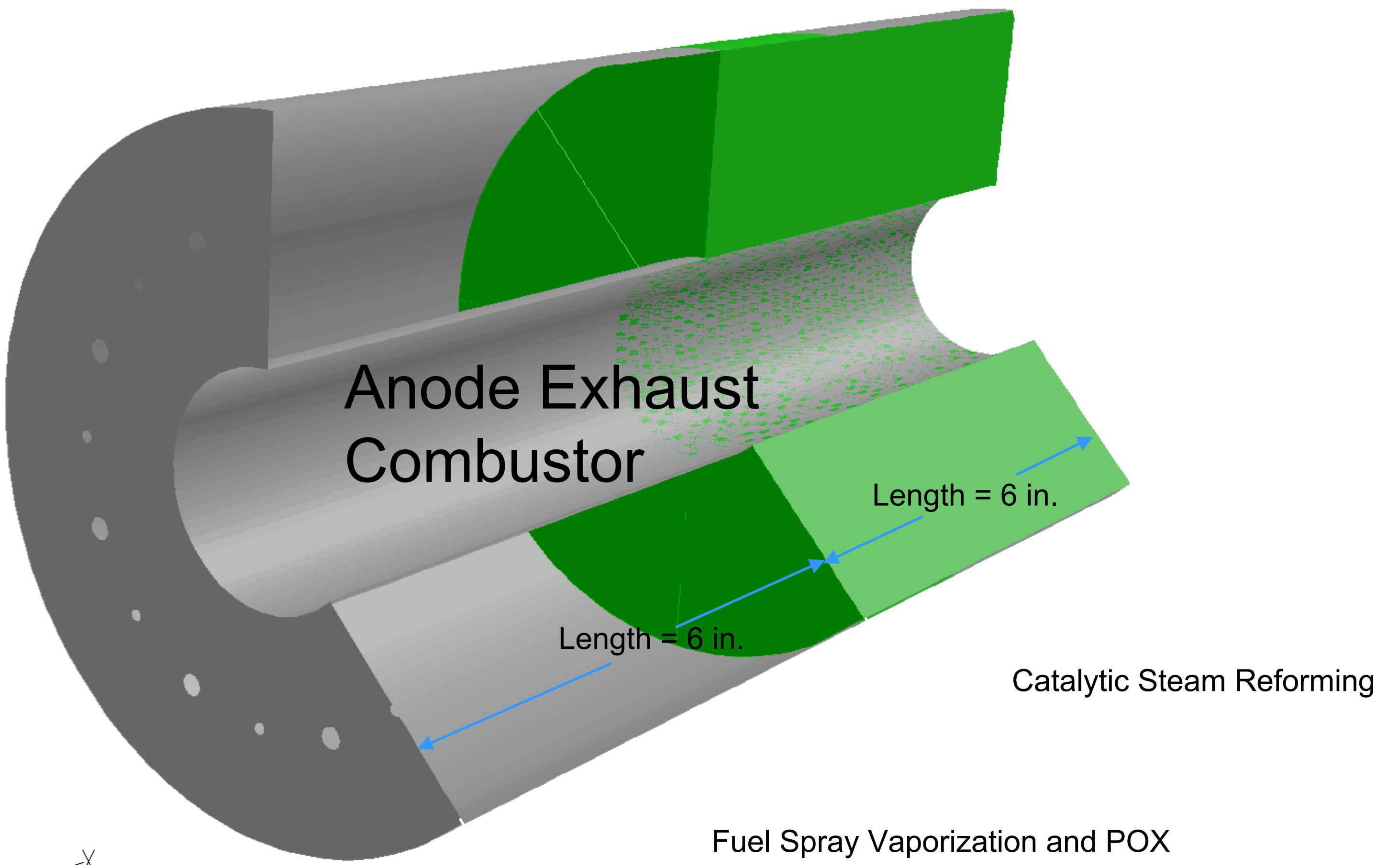
Diesel Fuel Processing

CFD Modeling Results - ATR Model Prototype Geometry

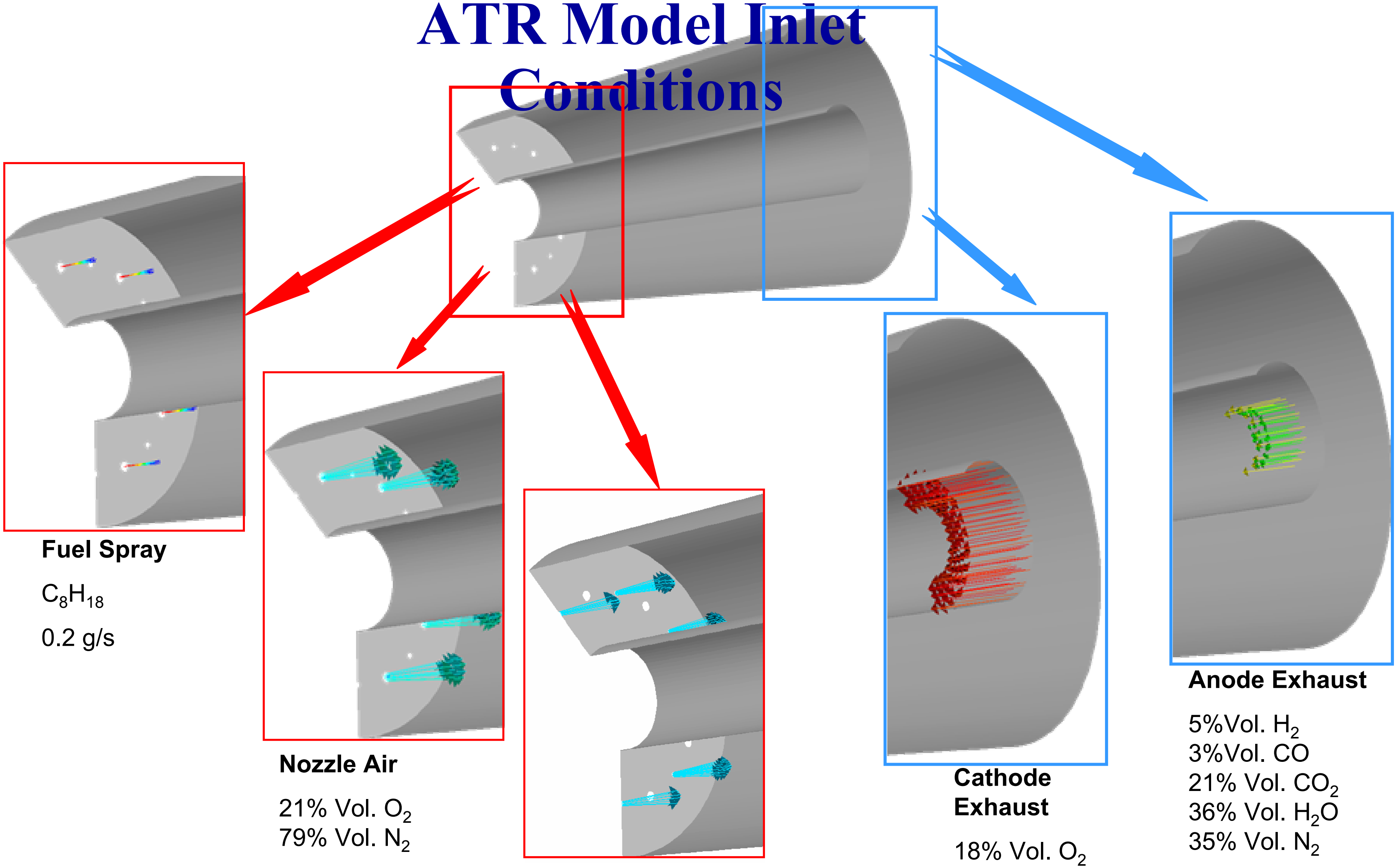


Diesel Fuel Processing

CFD Modeling Results - Reaction Zones



ATR Model Inlet Conditions



Fuel Spray

C_8H_{18}

0.2 g/s

Nozzle Air

21% Vol. O_2
79% Vol. N_2

0.2g/s

650C/923K

Steam

0.18g/s

Cathode Exhaust

18% Vol. O_2
82% Vol. N_2
0.2g/s
650C/923K

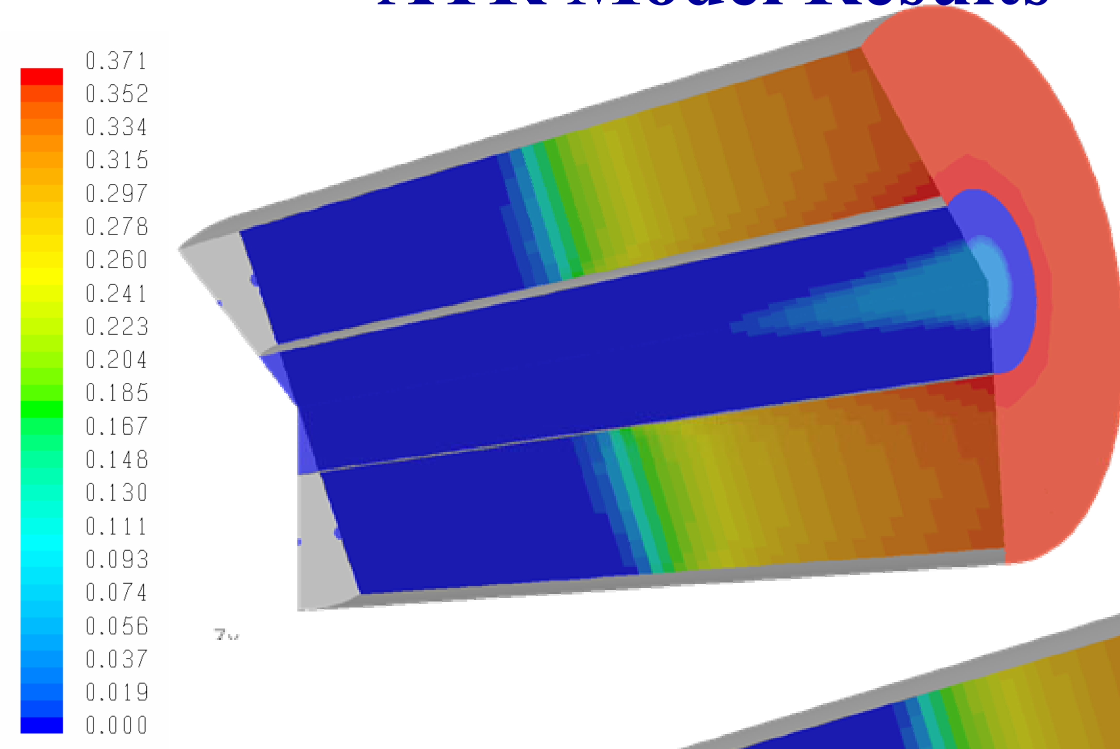
Anode Exhaust

5%Vol. H_2
3%Vol. CO
21% Vol. CO_2
36% Vol. H_2O
35% Vol. N_2

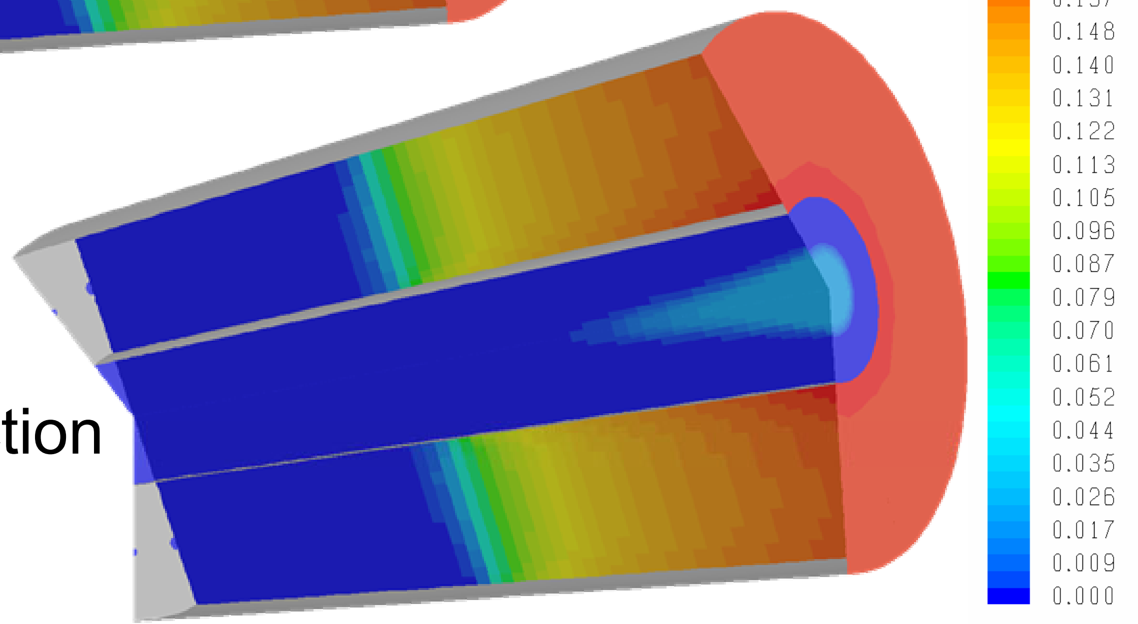
1.6g/s

800C/1073K

ATR Model Results



H_2 Mole Fraction



CO Mole Fraction

Diesel Fuel Processing

Reaction Rate Determination - Modeling Approaches

Level 1
Intuitative Lumping

- Lumps derived from intuition (gross identification of lumping groups), e.g. paraffins, aromatics, etc.
- Little is known regarding the exact mechanism
- Psuedo-1st order
- Psuedo-homogeneous phase
- Easy to develop, inexpensive
- Suitable for process simulators, e.g. ASPEN, ChemCad
- Predicts transient response and hydrocarbon slip

Level 2
Mechanism Based Lumping

- Psuedo-homogeneous phase
- Based on psuedo-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 psuedo-species only
- Suitable for process simulators, e.g. ASPEN, ChemCad
- Predicts transient response, hydrocarbon slip, coking and catalyst deactivation

Level 3
Structure Oriented Lumping

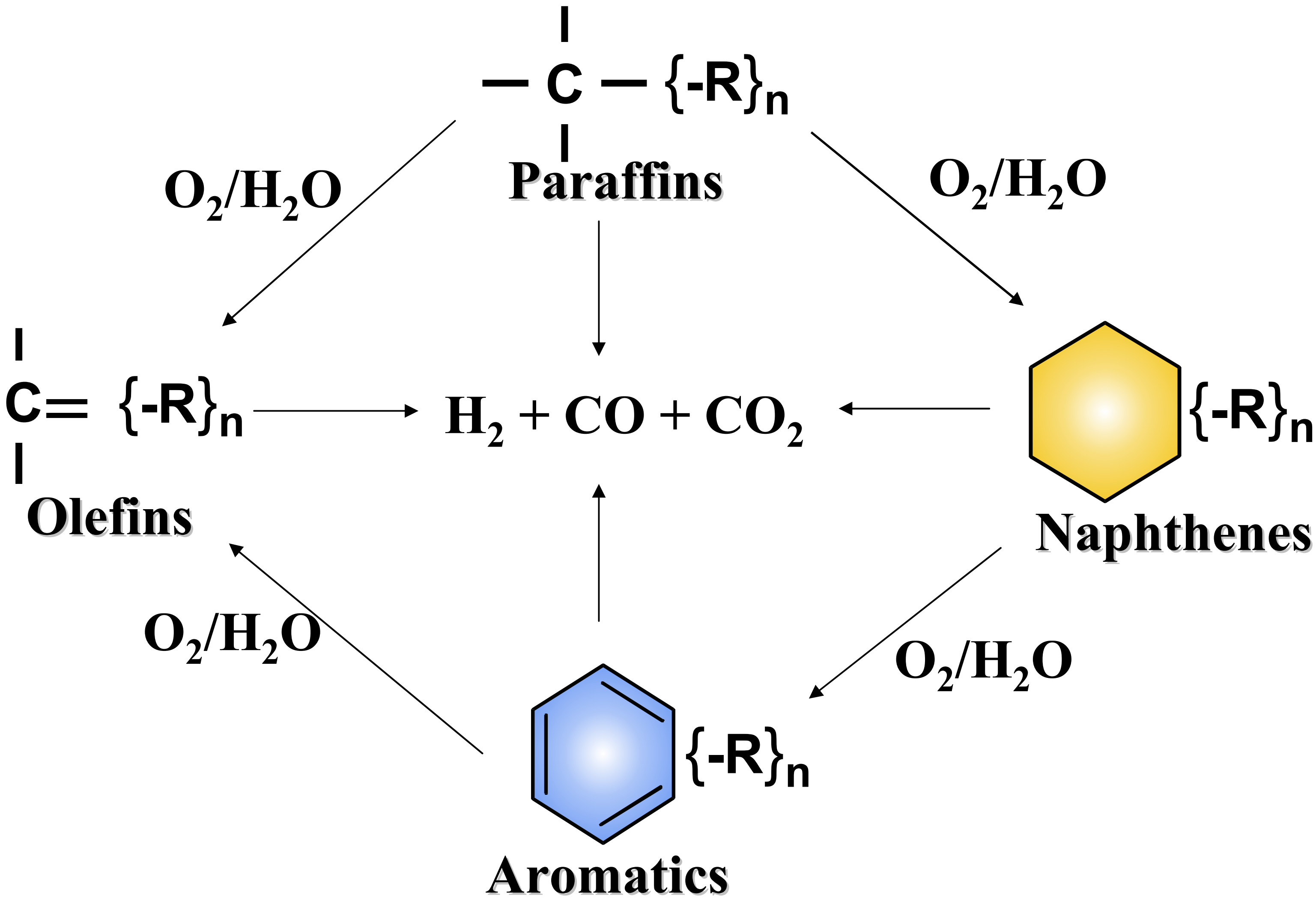
- State of the art in complex mixture modeling
- Closely resembles pure mechanistic approach
- Involves lumping isomers only
- Detailed knowledge of process chemistry needed, expensive analytically
- Detailed kinetic studies needed for the development of lumps
- Suitable for CFD packages, e.g. Fluent

Level 4
Mechanistic

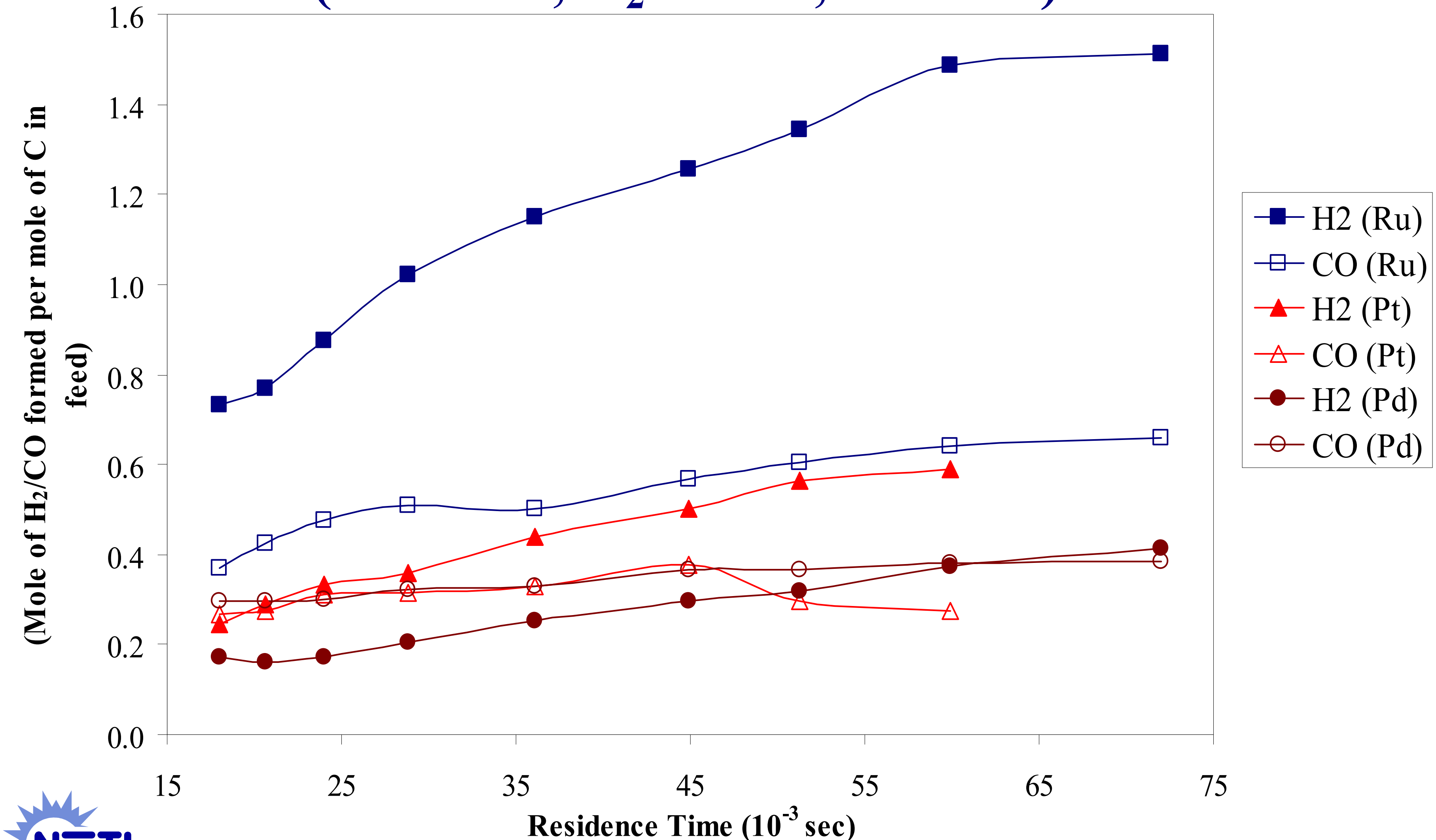
- Pure mechanistic approach
- Detailed kinetic studies of single components and their mixtures
- Development of experimental procedures to evaluate process chemistry
- Knowledge of catalyst properties needed
- Requires spectroscopic method
- Predicts transient response, hydrocarbon slip, coking and catalyst deactivation based on fundamentals

Diesel Fuel Processing

Reaction Rate Determination - Complex Reaction Network

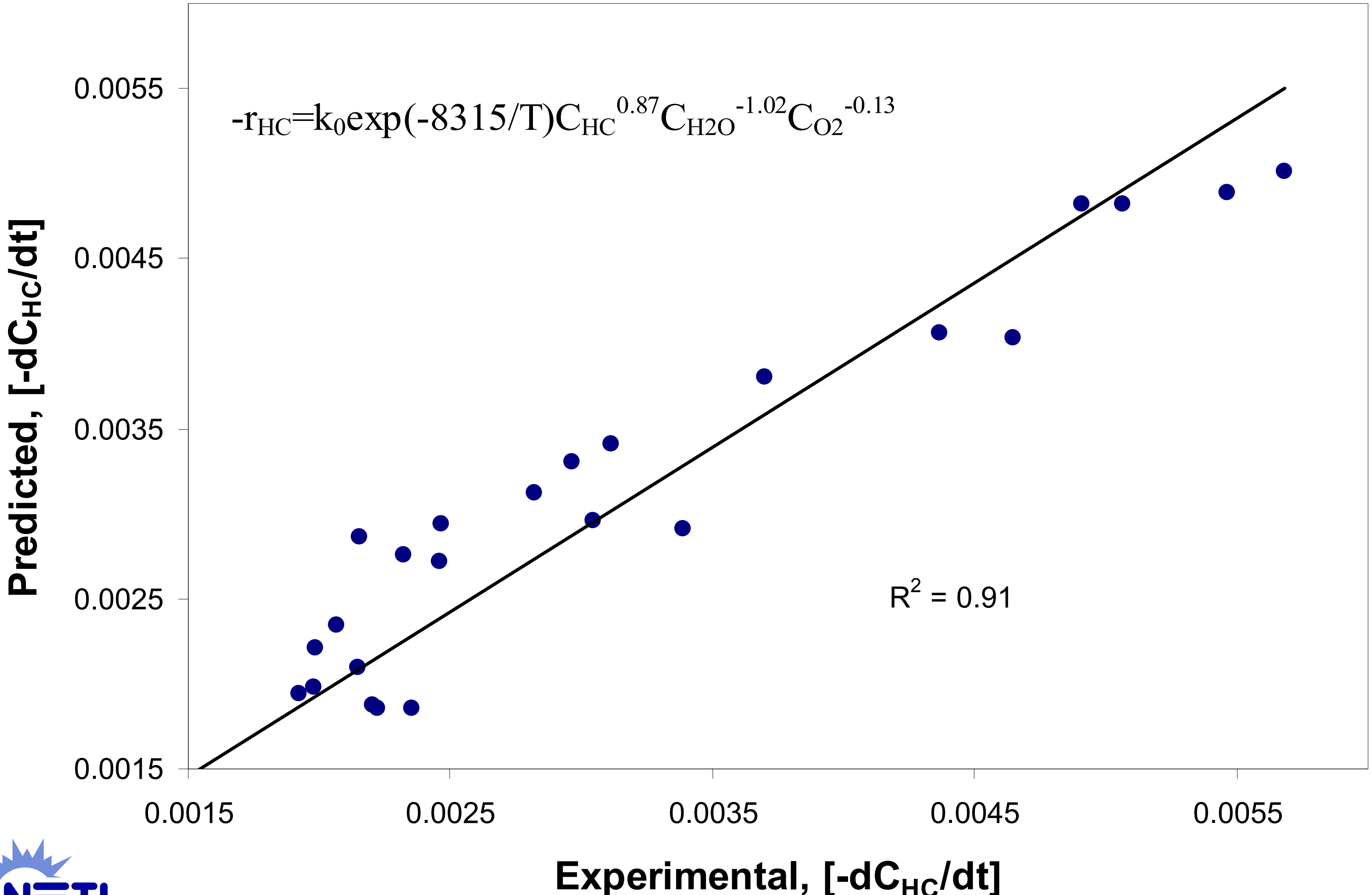


Product Distribution from ATR of Diesel (T=850 C, O_2/C=0.3, S/C=1.5)



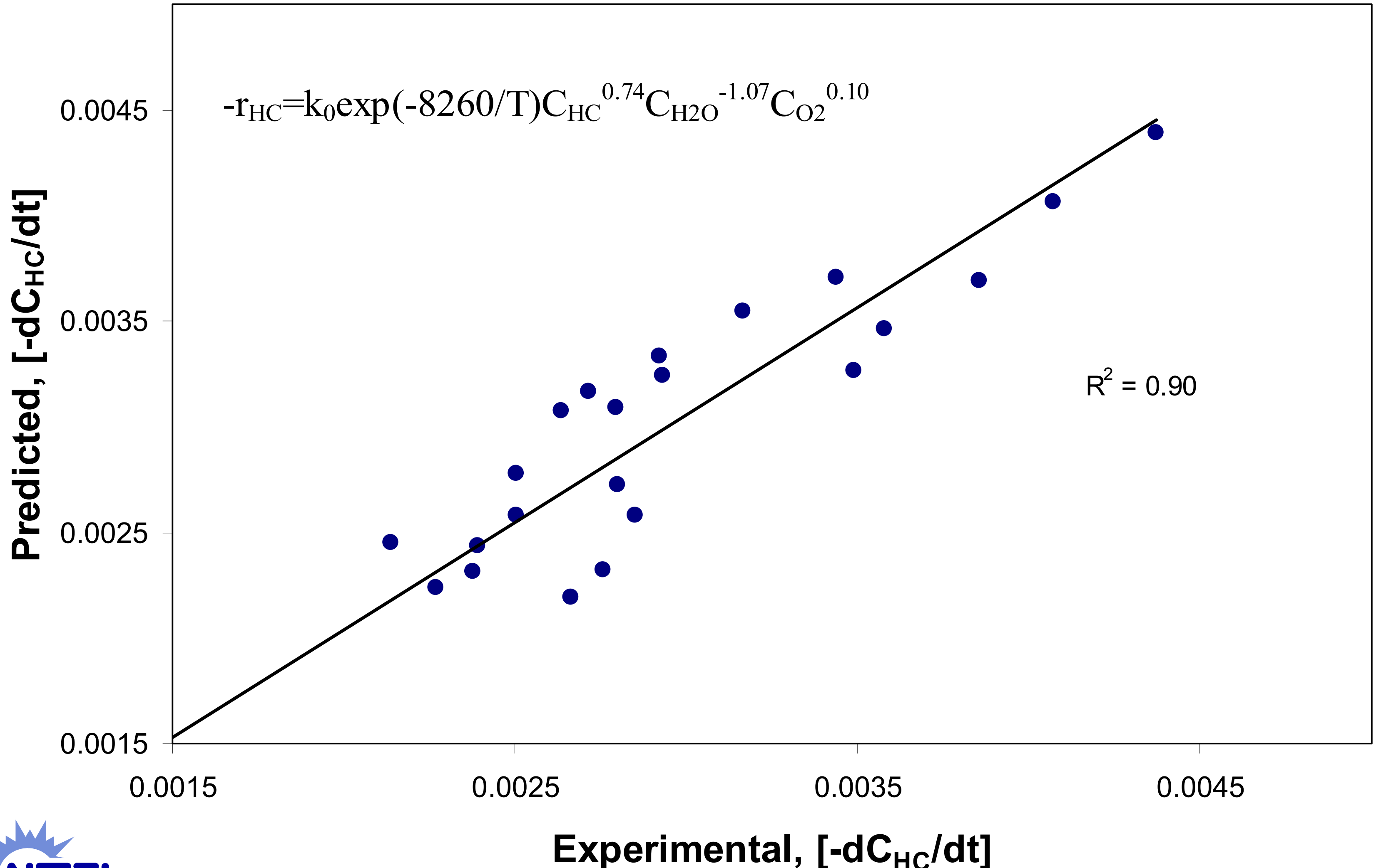
Diesel Fuel Processing

Experimental Vs Predicted Values for Diesel ATR on Pt/Al_2O_3



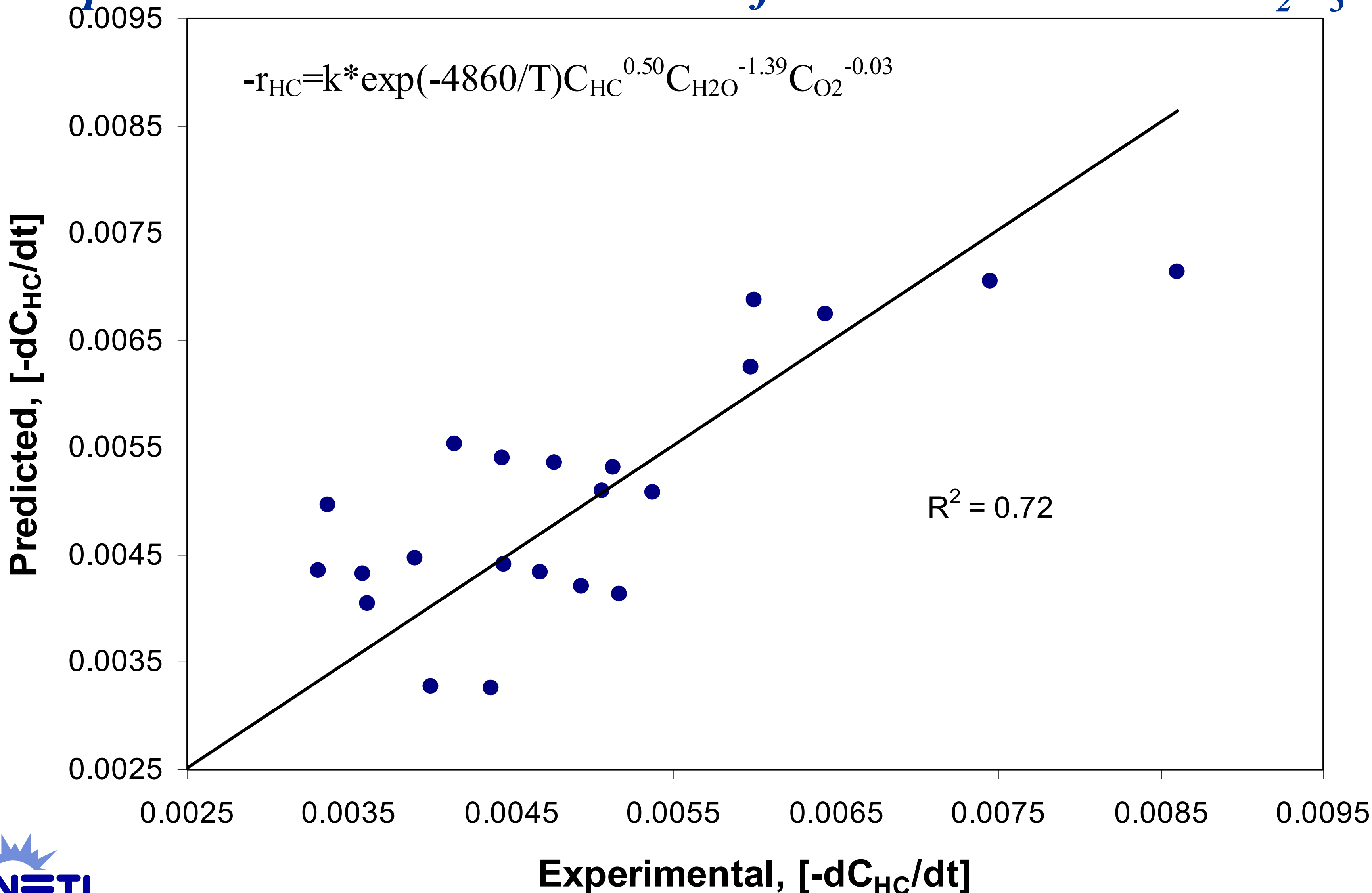
Diesel Fuel Processing

Experimental Vs Predicted Values for Diesel ATR on Pd/Al_2O_3



Diesel Fuel Processing

Experimental Vs Predicted Values for Diesel ATR on Ru/Al_2O_3



Diesel Fuel Processing
2002 Results Accomplishments

- **Diesel-based 5-kWe fuel cell APU system with 45% - 50% electrical conversion efficiency identified**

- **A prototype CFD model including all the key elements of ATR has been developed**
  - Developed a model that accounts for fuel atomization and vaporization, partial oxidation, steam gasification, and anode exhaust gas combustion
  - Tested the convergence behavior of the model

- **Laboratory Kinetic Experiments Conducted**
  - Tested Pt, Pd, and Ru catalysts
  - Initial rate measurements made for hexadecane and diesel fuel

Diesel Fuel Processing
Applicability to SOFC Commercialization

- Diesel-based 5-kWe 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.

Diesel Fuel Processing

Future Plan

2002 **2003** 2004 **2005** **2006**

PREDICTIVE CFD MODEL DEVELOPMENT FOR DIESEL REFORMING

LEVEL 1 KINETIC MODEL DEVELOPMENT - Validate

LEVEL 2 KINETIC MODEL DEVELOPMENT - Validate

LEVEL 3 KINETIC MODEL DEVELOPMENT

DEVELOP KINETIC RATE METHODOLOGY

CONDUCT DESIGN & EVALUATION OF DIESEL REFORMING TECHNOLOGY