Fuel Processing of Diesel for Fuel Cells

May 9, 2002

Presented by: D. A. Berry, T.H. Gardner, W. Rogers & D. Shekhawat

National Energy Technology Laboratory
Diesel Fuel Processing

Objective

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

Technical challenges

- Diesel fuel is complex and difficult to reform:
  - Deactivation of fuel reforming catalysts and fuel cell components via carbon deposition and sulfur poisoning are the principle technology barriers.
  - Diesel fuel is a complex, multi-component (>100 compounds) fuel that exhibits varying reaction pathways and kinetic rates for differing catalyst types.
- Large, complex, slow-response fuel processors problematic:
  - Several FC applications require high power density design with “fast” response and high efficiency for transient operations.
  - Hydrocarbon slip must be avoided.
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
Diesel Fuel Processing

Systems Analysis - High Efficiency Integral Combustor/Reformer

Goals:
- Maximize Thermal Integration
- Flexible System Startup
Diesel Fuel Processing

Systems Analysis - External Post Anode Combustor

800 C SECA APU

Air Compressor → Air Preheater → AutoThermal Reformer → Desulfurizer Sorbent Bed → Combustor

Fuel Pump → Steam Generator → Exhaust Condenser

Water Pump

800 C SECA APU: Fuel Cell Stack → Anode 800 C → 650 C Fuel Cell Stack Cathode

800 C

Norsk Energi Teknologisk Laboratorium (NETL)
# Diesel Fuel Processing

*Systems Analysis - Effect of Heat Integration*

<table>
<thead>
<tr>
<th></th>
<th>Shared Heat</th>
<th>Non-Shared Heat</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel (kg/hr)</strong></td>
<td>0.834</td>
<td>0.834</td>
</tr>
<tr>
<td><strong>Air – Stoichs In</strong></td>
<td>5</td>
<td>5.2</td>
</tr>
<tr>
<td><strong>ATR F/A Ratio</strong></td>
<td>9</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Steam/C Ratio</strong></td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>50.21</td>
<td>42.39</td>
</tr>
<tr>
<td><strong>Net Power</strong></td>
<td>5.0</td>
<td>4.221</td>
</tr>
<tr>
<td><strong>ATR Temperature</strong></td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td><strong>FC Temperature</strong></td>
<td>865</td>
<td>813</td>
</tr>
</tbody>
</table>
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

Steam/C Ratio
O2/C Ratio
H2 Molar Flow (kmol/hr)

CO Molar Flow (kmol/hr)

Steam/C Ratio
O2/C Ratio

NETL
Diesel Fuel Processing

*CFD Modeling - Approach*

- Develop a ATR model in Fluent
  - Fuel atomization and vaporization
  - Partial oxidation of diesel fuel
  - Combustion of anode exhaust gas
  - Steam reforming of diesel fuel

- 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
ATR Model Prototype Geometry

- Outer Diameter = 6 in.
- Inner Diameter = 2 in.
- Length = 12 in.

Anode Exhaust
Combustor

ATR Region
ATR Model Prototype Geometry

ATR Region

Anode Exhaust

Combustor

Length = 6 in.

Catalytic Steam Reforming

Fuel Spray Vaporization and POX
ATR Model Inlet Conditions

Fuel Spray
C₈H₁₈
0.2 g/s

Nozzle Air
21% Vol. O₂
79% Vol. N₂
0.2 g/s
650°C/923K

Steam
0.18 g/s

Anode Exhaust
5% Vol. H₂
3% Vol. CO
21% Vol. CO₂
36% Vol. H₂O
35% Vol. N₂
1.6 g/s
800°C/1073K

Cathode Exhaust
18% Vol. O₂
82% Vol. N₂
0.2 g/s
650°C/923K

Descriptor - include initials /org#/date
ATR Model Results

Temperature (K)
ATR Model Results

H₂ Mole Fraction

CO Mole Fraction
## Diesel Fuel Processing

### Reaction Rate Determination - Modeling Approaches

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

<table>
<thead>
<tr>
<th>Level 2</th>
<th>Mechanism Based Lumping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Psuedo-homogeneous phase</td>
<td></td>
</tr>
<tr>
<td>Based on psuedo-species lumped together based on the elucidation of a detailed mechanism</td>
<td></td>
</tr>
<tr>
<td>Requires a knowledge of process chemistry</td>
<td></td>
</tr>
<tr>
<td>Must possess the analytical ability to measure the psuedo-species only</td>
<td></td>
</tr>
<tr>
<td>Suitable for process simulators, e.g. ASPEN, ChemCad</td>
<td></td>
</tr>
<tr>
<td>Predicts transient response, hydrocarbon slip, coking and catalyst deactivation</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level 3</th>
<th>Structure Oriented Lumping</th>
</tr>
</thead>
<tbody>
<tr>
<td>State of the art in complex mixture modeling</td>
<td></td>
</tr>
<tr>
<td>Closely resembles pure mechanistic approach</td>
<td></td>
</tr>
<tr>
<td>Involves lumping isomers only</td>
<td></td>
</tr>
<tr>
<td>Requires a knowledge of process chemistry needed, expensive analytically</td>
<td></td>
</tr>
<tr>
<td>Detailed kinetic studies needed for the development of lumps</td>
<td></td>
</tr>
<tr>
<td>Suitable for CFD packages, e.g. Fluent</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level 4</th>
<th>Mechanistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure mechanistic approach</td>
<td></td>
</tr>
<tr>
<td>Detailed kinetic studies of single components and their mixtures</td>
<td></td>
</tr>
<tr>
<td>Development of experimental procedures to evaluate process chemistry</td>
<td></td>
</tr>
<tr>
<td>Knowledge of catalyst properties needed</td>
<td></td>
</tr>
<tr>
<td>Requires spectroscopic method</td>
<td></td>
</tr>
<tr>
<td>Predicts transient response, hydrocarbon slip, coking and catalyst deactivation based on fundamentals</td>
<td></td>
</tr>
</tbody>
</table>
Diesel Fuel Processing

Reaction Rate Determination - Complex Reaction Network

- Paraffins
  - \(-R\)_n
  \(\text{O}_2/\text{H}_2\text{O}\)

- Olefins
  - \(-R\)_n

- Aromatics
  - \(-R\)_n
  \(\text{O}_2/\text{H}_2\text{O}\)

- Naphthenes
  - \(-R\)_n
  \(\text{O}_2/\text{H}_2\text{O}\)

\[ \text{C} \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 \]
Diesel Fuel Processing
2002 Accomplishments

- Diesel-based 5-kWe fuel cell APU system with >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