Diesel Reforming for Fuel Cell Auxiliary Power Units

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Reforming of diesel fuel can have simultaneous vehicle applications:
- **SECA application**: reforming of diesel fuel for SOFC / APU
- Reductant to catalyze NOx reduction, regeneration of particulate traps
- Hydrogen addition for high engine EGR
- Fast light-off of catalytic converter

*Our goal is to provide kinetics, carbon formation analysis, operating considerations, catalyst characterization and evaluation, design and models to SECA developers.*
Diesel Fuel Processing for APUs
Technical Issues

- **Diesel fuel is prone to pyrolysis upon vaporization**
  - Fuel/Air/Steam mixing
  - Direct fuel injection
    - Nozzle turndown and atomization quality

- **Diesel fuel is difficult to reform**
  - Reforming kinetics slow
  - Catalyst deactivation
    - Fuel sulfur content
    - Minimal hydrocarbon slip
    - Carbon formation and deposition
    - High temperatures lead to catalyst sintering

- **Water availability is minimal for transportation APUs**
  - Operation is dictated by system integration and water content
    - water suppresses carbon formation - reformer start-up an issue
Objectives and Approach

**Objectives:** Develop technology suitable for onboard reforming of diesel
- Research fundamentals (kinetics, reaction rates, models, fuel mixing)
- Quantify operation (recycle ratio, catalyst sintering, carbon formation)

**Approach:** Examine catalytic partial oxidation and steam reforming
- Modeling
  - Carbon formation equilibrium
  - Reformer operation with anode recycle
- Experimental
  - Carbon formation
  - Adiabatic reformer operation
    - Anode recycle simulation
    - Direct diesel fuel injection, SOFC anode and air mixing
    - Catalyst temperature profiles, evaluation, durability
    - Hydrocarbon breakthrough
  - Isothermal reforming and carbon formation measurements
    - Catalyst evaluation, activity measurements
    - Carbon formation rate development
Diesel Reforming
Measurements and Modeling

Adiabatic Reactor with nozzle
Window for Catalyst
Reaction Zone
Observation

Air / anode recycle
Nozzle
Catalyst (Pt/Rh)

Furnace
Iso-thermal system
• Measure kinetics
• Steam reforming / POx
• Light-off
• Carbon formation

Modeling
Equilibrium
Kinetic
Composition

Iso-thermal Microcatalyst
Fuel Cell Program
To avoid carbon formation during vaporization requires direct fuel injection

Directly inject fuel to reforming catalyst
- Commercial nozzle, control fuel pressure for fuel flow (~ 80 psi)
- Air / anode recycle (H₂ / N₂) distribute in annulus around fuel line / nozzle

Experimental results
- Operated successfully at steady state
  - Minimum fuel flow dictated by fuel distribution from nozzle
- Requires control of fuel/air preheat, limiting preheat (~ < 180 °C)
  - Prevents fuel vaporization/particulate formation

![Diagram of fuel cell operation](image)
Water Addition for Steam Reforming → SOFC Anode Recycle to Reformer

- Water required for:
  - steam reforming of fuel
  - carbon suppression
- Methods for water introduction and availability:
  - Separate water tank (tank, freezing, refilling)
  - Anode water recovery by condensation (heat ex., cond., tank, pump freezing)
  - Anode recycle to reformer (blower)

Preferred systems are water neutral
Simplest method is anode recycle to reformer
SOFC Anode Recycle Modeling

Recycling of 50% SOFC Anode Flow, S/C = 0.7

Most data presented simulates 35% recycle

Green – Fractional increase in flow caused by increasing gas volume due to recycle ratio, leads to larger reformer

<table>
<thead>
<tr>
<th>Anode Recycling Model Assumptions</th>
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<tbody>
<tr>
<td>Fuel - Diesel (C12H26)</td>
<td></td>
</tr>
<tr>
<td>Power - LHV Fuel In</td>
<td>16</td>
</tr>
<tr>
<td>O/C = 1</td>
<td>1</td>
</tr>
<tr>
<td>SOFC Conversion</td>
<td>50%</td>
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</table>

Outlet Temp at O/C = 1
S/C
Reformer Outlet Flowrate
Fractional Increase

Outlet Temperature / °C

Fractional Increase
S/C and Reformer Outlet Flowrate

Recycle Rate / %
Reforming of Diesel with SOFC Recycle

Temperature and Hydrogen / CO production

- Higher recycle reduces operating temperature
- Operation with recycle < 30 % difficult due to high operating temperatures and catalyst sintering

Pt / Rh supported catalyst
Residence time ~ 20 msec
Anode recycle simulated with H₂, N₂, H₂O
Axial Temperature Profiles during Diesel Reforming

Low-S Swedish diesel fuel

20 %
30 %
40 %

(\text{O/C} = 0.65 - 0.75)

Adjusted O/C for similar operating temperatures
Pt / Rh supported catalyst
Residence time ~ 50 msec
Anode recycle simulated with \text{H}_2, \text{N}_2, \text{H}_2\text{O}

Higher recycle ratios move oxidation downstream in reformer
Lower recycle ratios require low O/C for similar adiabatic temperature rise

Fuel Cell Program
Initial temperature profile flattens out at ~ 800 °C
Subsequent temperature profiles peak at > 850 °C and then decrease to outlet
Temperature (oxidation) profile shifts downstream following shutdown/restart cycle
Fuel Effect on Reactor Temperature Profile

Fuel composition affects the reactor front end light-off
Sulfur content and aromatic content highest in
Diesel > Gasoline > Swedish Diesel > Iso-Octane

35% recycle ratio
Adjusted O/C for similar reformer outlet temperature
Adiabatic Reformer Catalyst Surface Area
Axial and Radial Profile

BET Surface Area Distribution

Original Surface Area ~ 4.3
Isothermal Reformer Catalyst Surface Area

Large catalyst surface area loss after testing, mostly independent of temperature during isothermal diesel steam reforming.

Greater catalyst surface area loss after testing with commercial diesel fuel.

Graph: Isothermal Reactor BET Catalyst Surface Area

- Low Sulfur Diesel
- Commercial Diesel

Catalyst surface area / % fresh vs. Temperature / °C
Carbon Formation Issues

- Avoid fuel processor degradation due to carbon formation
  - Carbon formation can reduce catalyst activity, system pressure drop
  - Operation in non-equilibrium carbon formation regions
  - Low water content available for transportation diesel reforming
  - Rich start-up - Cannot avoid favorable carbon equilibrium regions
    - Water-less (Water not expected to be available at start-up)

- Catalysts
  - Various catalysts more/less prone to carbon formation

- Diesel fuels
  - Carbon formation due to pyrolysis upon vaporization

  **Carbon Formation Reactions**

  \[
  2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2 \quad \text{(Boudart Reaction)}
  \]

  \[
  \text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2 \quad \text{(CH}_4 \text{ Decomposition)}
  \]

  \[
  \text{C}_n\text{H}_{2n} \rightarrow \text{C}_n + n\text{H}_2
  \]

  Fuel pyrolysis $\rightarrow$ aromatics $\rightarrow$ PAH $\rightarrow$ C
Various forms of carbon exist
  • Different carbon forms have different thermodynamic properties

Developed chemical equilibrium code to analyze conditions for carbon formation
  • Includes 3 types of amorphous carbon
    – Operation of model in isothermal modes (adding adiabatic)
  • C++ code operates on Windows PC

Input:
  • Isothermal / Adiabatic (needs improvement for amorphous Carbon)
  • Gas phase components & concentrations
  • Equilibrium temperature, pressure, types of solid phase

Output yields (code works where carbon formation is observed)
  • Gas phase concentration, solid phase quantities
  • (Delta H reaction, outlet temperature – for adiabatic case)

Model is (will be / maybe??) available
  • no-cost, non-exclusive license
Modeling Carbon Formation Dependence for SOFC APU Recycle Ratio

Temperature for disappearance of all types of amorphous carbon as a function of SOFC anode recycle ratio

Carbon disappearance temperature as a function of steam to carbon ratio
• Quantitative carbon measurements indicate carbon made during start-up for all fuels.
• Water during start-up suppresses some carbon formation, but carbon is still formed, in smaller quantities.
• Ethanol suppresses carbon formation, while aromatics show higher carbon formation.
Isothermal Reactor
Carbon Formation Measurements

Steam Reforming

O/C = 0.0, S/C = 1.0
Peak carbon formation ~ 650 – 700 °C
Equilibrium and kinetics effects

AutoThermal Reforming

O/C = 1.0, S/C = .34
(35% Anode Recycle)
Carbon formation increases with temperature

5 hour operation
Adiabatic Reactor
Carbon Formation Measurements

AutoThermal Reforming

- Simulates 35% SOFC anode recycle
  - S/C ~ 0.34
- Average 3x higher carbon with commercial fuel than Low-S
- Carbon formation increases with increasing air (T) for commercial
- Carbon formation decreases with increasing air flow (T) for Low-S
- Carbon Formed (% fuel flow):

![Graph showing carbon formation vs. air/fuel ratio with data points for Low S Diesel and Commercial Diesel.](image)
(TGA) Thermal Gravimetric Analysis of catalyst after carbon formation measurements in isothermal reactor

Catalyst weight change after carbon formation measurements in the isothermal reactor

Carbon removal is about 0.4% catalyst weight

Carbon is not typically ‘bound’ to catalyst surface (for noble metal catalysts / with oxide supports)
**Activation energy for carbon formation:**

\[ r_{\text{carbon}} = k \exp(-\frac{E_a}{RT}) \]

Iso-thermal steam reforming (S/C = 1.0)
- commercial diesel: 86.8 kJ/mol
- low-S diesel fuel: 134.2 kJ/mol

Iso-thermal ATR (O/C = 1.0, S/C = 0.34)
- (Simulating 35% recycle)
- commercial diesel: 97.9 kJ/mol
- low-S diesel fuel: 72.4 kJ/mol

Literature values for carbon formation of 118 kJ/mol (CO\(_2\) reforming of CH\(_4\) over Ni/Al\(_2\)O\(_3\) catalysts)

**Carbon from fuel that ends up as carbon**

<table>
<thead>
<tr>
<th></th>
<th>Iso-thermal ATR</th>
<th>Iso-thermal SR</th>
<th>Adiabatic ATR</th>
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</thead>
<tbody>
<tr>
<td>Low-S Diesel</td>
<td>0.13%</td>
<td>0.22%</td>
<td>0.03%</td>
</tr>
<tr>
<td>Commercial Diesel</td>
<td>0.12%</td>
<td>0.21%</td>
<td>0.09%</td>
</tr>
<tr>
<td>Low-S ATR scales to</td>
<td>3.1 kg Carbon (10,000 hrs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.4 kg Carbon (40,000 hrs)</td>
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Summary/Findings

- **Direct fuel injection via fuel nozzle**
  - Control of fuel temperature critical
    - Prevent fuel vaporization, fuel pyrolysis / clogging of nozzle
  - Turndown can be limited by the nozzle fuel distribution

- **Reformer operation with SOFC anode recycle**
  - High adiabatic temperatures at low recycle rates
    - Leads to catalyst sintering
    - Limits light-off of reformer
  - Increasing recycle rates moves oxidation downstream in reformer
  - High recycle increases reformer size, parasitic losses
  - Operation at 30 – 40 % recycle rate

- **Carbon Formation**
  - Equilibrium carbon formation modeling
  - Carbon formation measurements show kinetic and equilibrium effects
  - Higher carbon formation during adiabatic operation with commercial diesel compared with low-S diesel
  - Carbon formation primarily not adherent to catalyst surface
Future Activities
Experimental

- Carbon formation
  - Quantify as a function of catalyst, recycle ratio
  - Define diesel components contributing to high carbon formation rates
  - Examine additive effects on carbon formation (EtOH)
  - Stand-alone startup & consideration to avoid C formation
  - Develop carbon removal/catalyst regeneration schemes

- Catalyst sintering and deactivation
  - Characterize durability – catalyst sintering
  - Develop reformer operational profiles that limit catalyst sintering
  - Stabilize active catalyst particles

- Durability and hydrocarbon breakthrough on SOFC
  - Incorporate SOFC ‘button’ cell operating on reformate

- Sulfur effect on reforming kinetics and carbon formation
Future Activities
Modeling & Technology Transfer

➤ Modeling
  • Improve carbon formation model
    – Incorporate enthalpies of other carbon species (CH$_{0.2}$) and sulfur
    – Improve robustness of code
    – Develop ‘user-friendly’ interface
  • Examine system effects of anode recycle
    – Efficiency and parasitics

➤ Technology Transfer
  • Dissemination of results via publications and presentations
    – AIChE, ACS, SECA meetings and reports
  • Make carbon formation model available for SECA teams
    – (effort ongoing for 6 months)