

SOLID OXIDE

PLANAR AND TUBULAR SOLID OXIDE FUEL CELLS

Dynamic Simulation Approach

Modular Approach:

Individual simulation modules for each fuel cell type

- Tubular SOFC
- Planar SOFC
- MCFC
- PEM

Reformer module

Gas turbine module (compressor and turbine sub-modules)

Combustor module

Catalytic oxidizer module

Heat exchanger module

Humidifier module

Condenser module

Pumps, valves, regulators, plumbing, and other balance of plant (BOP)

Standardized Framework For Dynamic Modeling & Controls

- Collaboration between Control group (Prof. F. Jabbari) and Dynamic Simulation (Prof. S. Samuelsen, J. Brouwer, ...)
- MATLAB and Simulink™ Framework Chosen
- User friendly package by MathWorks (Matlab)
- Flexibility
 - Prepackaged modules
 - Object oriented
 - Easy to learn and use
 - Hardware extensible
 - Transferable to other software
- Natural for adding controls development and power electronics

Previous Module Development

Reformer, SOFC, MCFC, PEM, Gas Turbine

General Model Assumptions

- 1D process flow
- Well-stirred within nodal volume
- Slow pressure transients



Fuel Cell Assumptions

- H₂ electrochemically oxidized only
- CO consumed via water-gas shift
- Shift always at equilibrium (constraint)
- Equipotential: $V_{\text{cell}} = V_{\text{node } 1} = V_{\text{node } n}$

Dynamic Model Basic Equations

$$C = \frac{P}{R_u T}$$

Equation of State

Mass Conservation Equations

$$V \frac{dC_j}{dt} = \dot{N}_{in,j} - \dot{N}_j + r_j$$



$$VC \frac{d\mathbf{X}}{dt} = \dot{N}_{in} (\mathbf{X}_{in} - \mathbf{X}) - \mathbf{X} \sum r_j + \mathbf{R}$$

- Calculates changes in mole fraction based on inlet molar flows and reaction rates

Dynamic Model Basic Equations

Energy Conservation

Molar Flow Through Electrolyte (Fuel Cell Only)

$$\frac{d}{dt} (CC_{v,molar} T) = (\dot{N}h)_{in} - \dot{N}h + (\dot{N}h)_{solid \rightarrow gas}$$

- Gaseous $+ (\text{heat transfer}) + (\text{heat of reaction})$

Molar Flow Through Electrolyte (Fuel Cell Only)

$$\frac{d}{dt} (\rho C_{mass} T) = (\dot{N}h)_{gas1 \rightarrow solid} - (\dot{N}h)_{solid \rightarrow gas2}$$

- Solid $+ (\text{heat transfer}) + (\text{heat of reaction})$

Heat Transfer

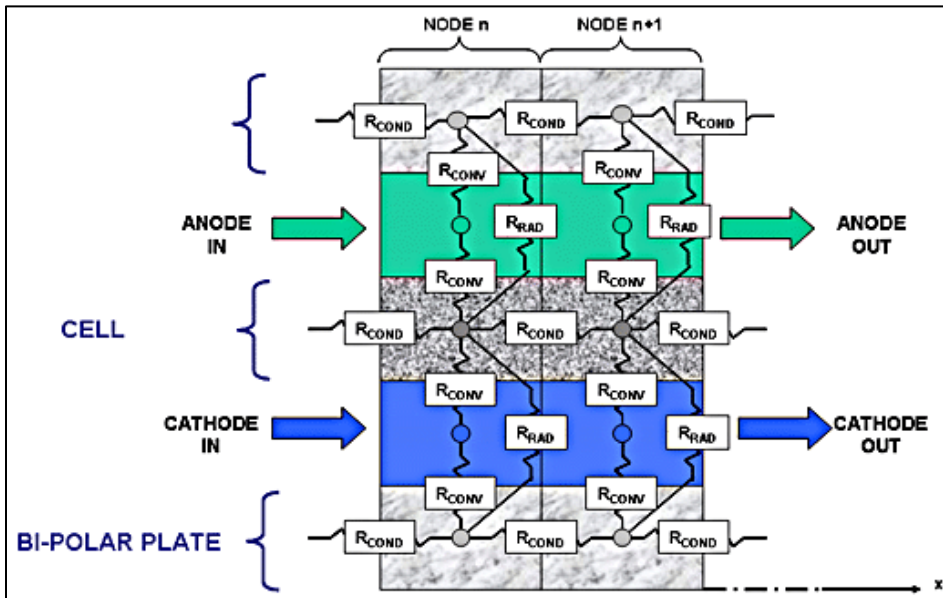
- Conduction
- Axially from node to node through solids
- Between nodal materials (bipolar plates, electrodes, ...)

Convection

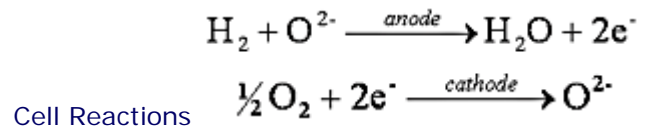
- Between surfaces and gases
- Based on Nusselt number

Radiation

- From surface to surface
- Geometry is an issue
- Concentric cylinders: TSOFC
- Parallel planes: PSOFC
- Other: combustor, reformer



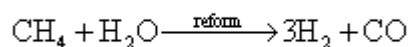
Solid Oxide Fuel Cell Electrochemistry



$$\text{Nerst Potential} \quad E = E_0 + \frac{R_s T}{2F} \ln \left(\frac{\chi_{\text{H}_2} \chi_{\text{O}_2}^{1/2}}{\chi_{\text{H}_2\text{O}}} P_{\text{CATHODE}}^{1/2} \right)$$

- Ideal operating voltage with respect to partial pressures of cell reactants

Steam Reformation – Occurs in Reformer and Fuel Cells



Methane reformation reaction

- Reaction rates on nickel based catalysts:
Lee et al. (1990) and Ross et al. (1972)

$$r_{CH_4} = -kP_{CH_4}^m P_{H_2O}^n$$

From Stoichiometry...

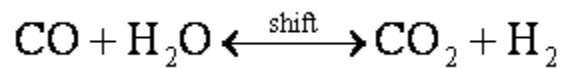
$$r_{CO} = -r_{CH_4}$$

$$r_{H_2} = -3r_{CH_4}$$

$$r_{H_2O} = r_{CH_4}$$

Water Gas Shift – Occurs in Reformers and in Fuel Cells

Shift reaction



- Reaction proceeds fast enough at elevated temperatures to assume equilibrium
- Algebraic constraint at exit of each node

$$K(T) = \frac{\chi_{CO_2} \chi_{H_2}}{\chi_{CO} \chi_{H_2O}}$$

Provides the non-electrochemical reaction source for CO₂!

Fuel Cell Operation

$$V = E - \eta_A - \eta_C - \eta_R$$

Actual operating voltage

- Polarization losses are due to kinetics, mass transport and electrical resistances

$$\eta_A = \frac{R_u T}{\alpha n F} \ln \left(\frac{i_{node}}{i_0} \right)$$

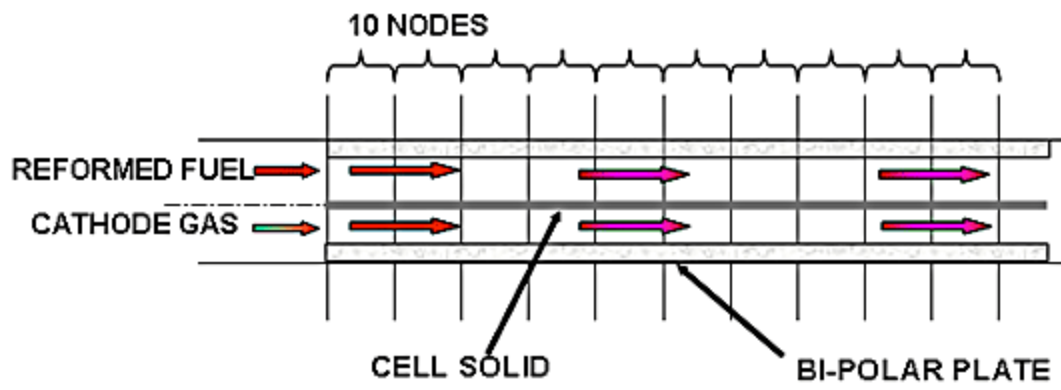
$$\eta_C = -\frac{R_u T}{n F} \ln \left(1 - \frac{i}{i_L} \right)$$

$$\eta_R = iR$$

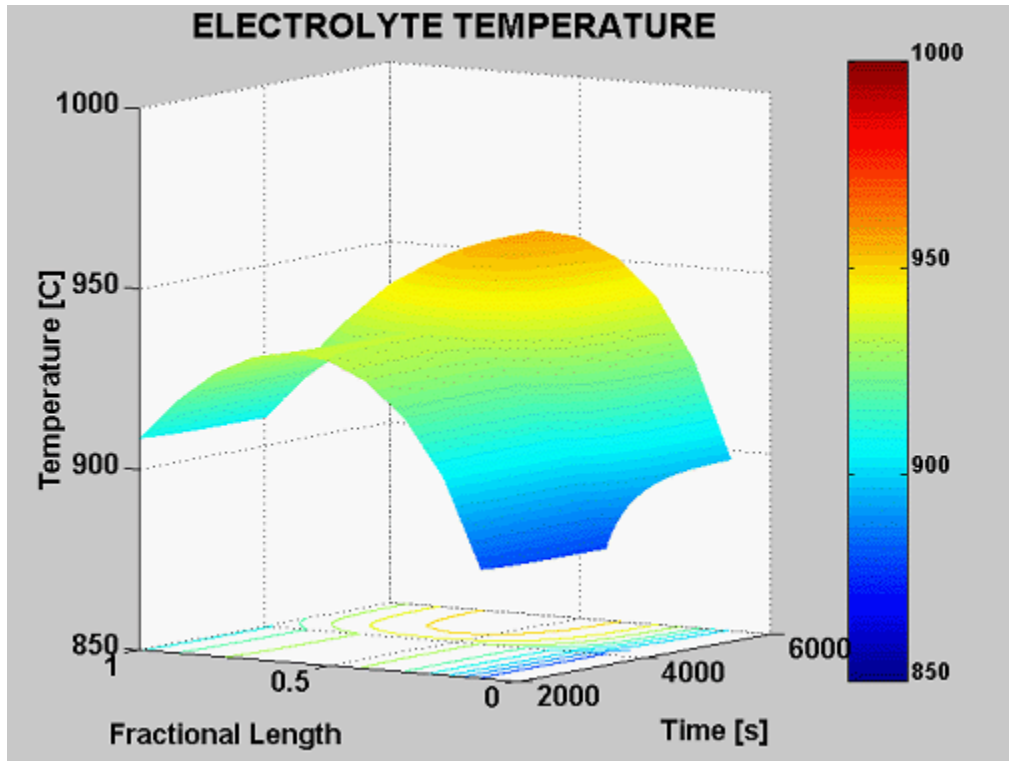
PSOFC DISCRETIZATION

10 Discrete Computational Nodes

- Anode Gas
- Cathode Gas
- Cell Solid
- Bi-Polar Plates



Sample TSOFC Outputs: 10% Load Increase

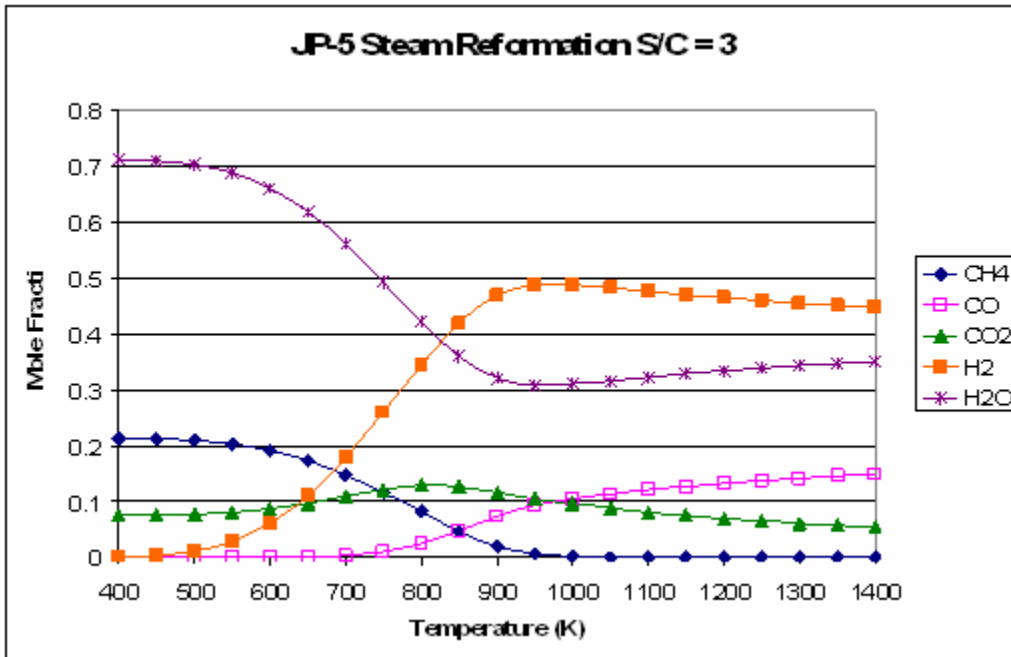


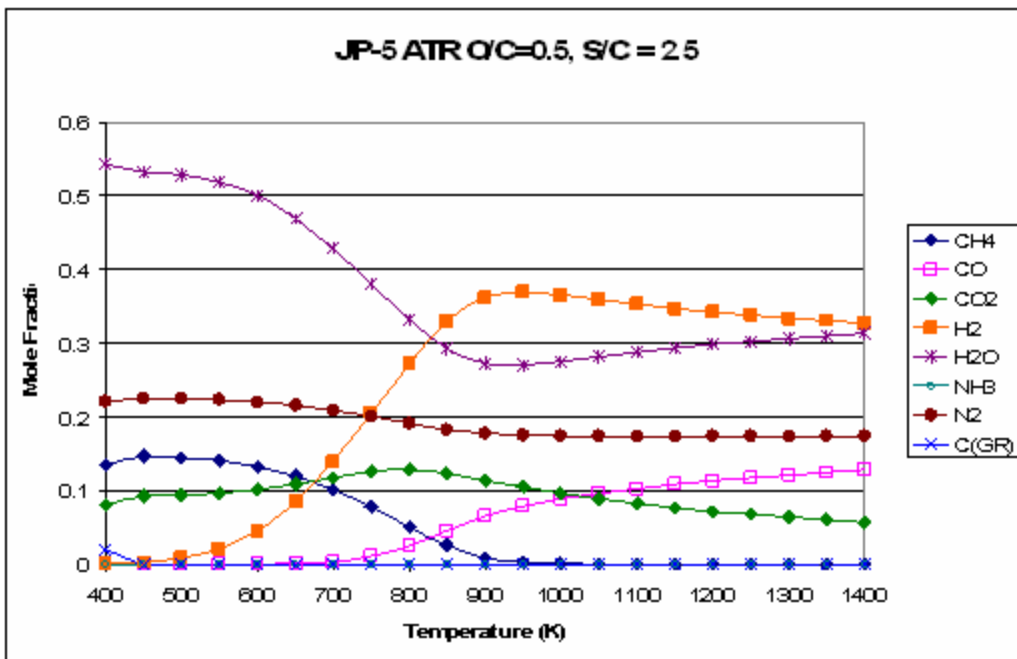
Progress and Current Status

Jet Fuel Equilibrium Results

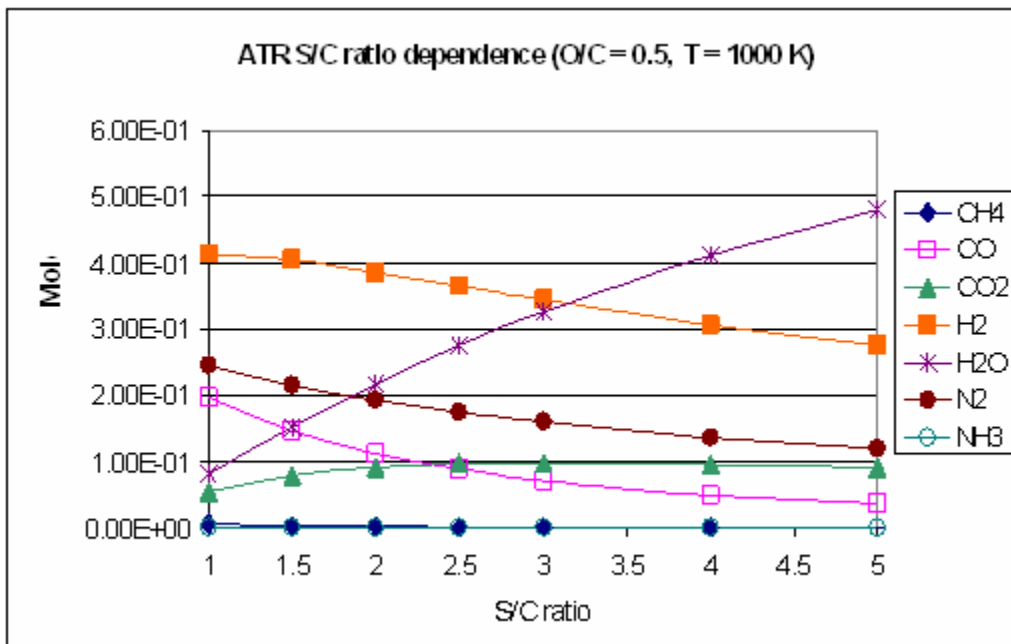
- Various Jet Fuel thermodynamic data acquired
- Commercial Aviation Fuel, Jet-A
 - C₁₁H₂₁
 - MW: 153 g/mol
 - Heat of formation (DH_{fo}): -249 kJ/mol
- Traditional Air Force Military Aviation Fuel, JP-4
 - C₁₀H_{19.4}
 - MW: 139 g/mol
 - Heat of formation (DH_{fo}): -227 kJ/mol
- Traditional Navy Military Aviation Fuel, JP-5
 - C₁₀H_{19.2}
 - MW: 139 g/mol
 - Heat of formation (DH_{fo}): -222 kJ/mol
- Standard Military Aviation Fuel, JP-8
 - C₁₂H₂₃
 - MW: 167 g/mol
 - Heat of formation (DH_{fo}): -319 kJ/mol

Jet Fuel Equilibrium Results

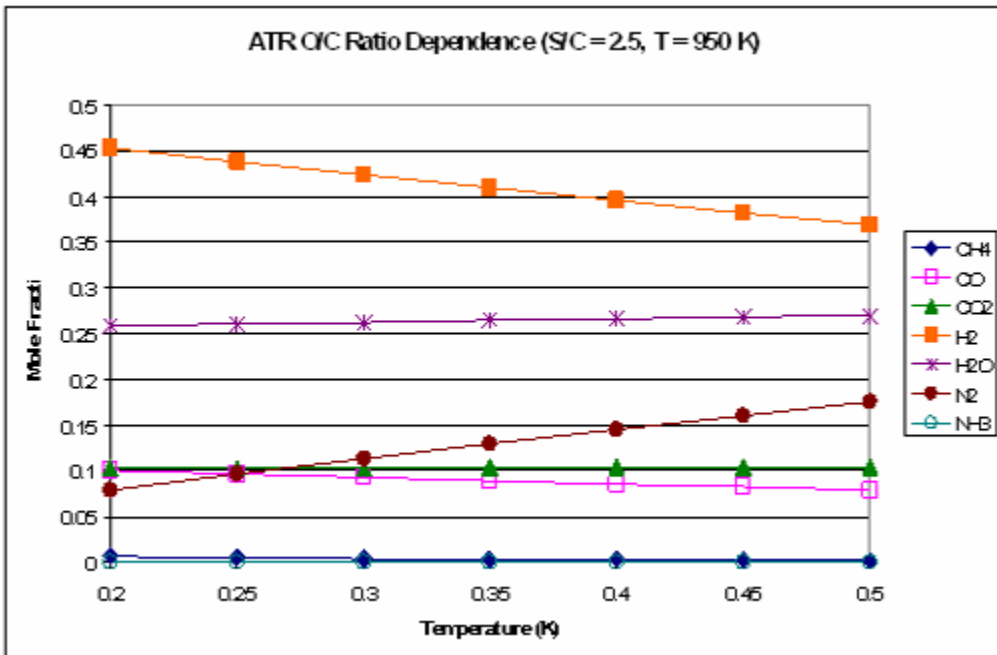
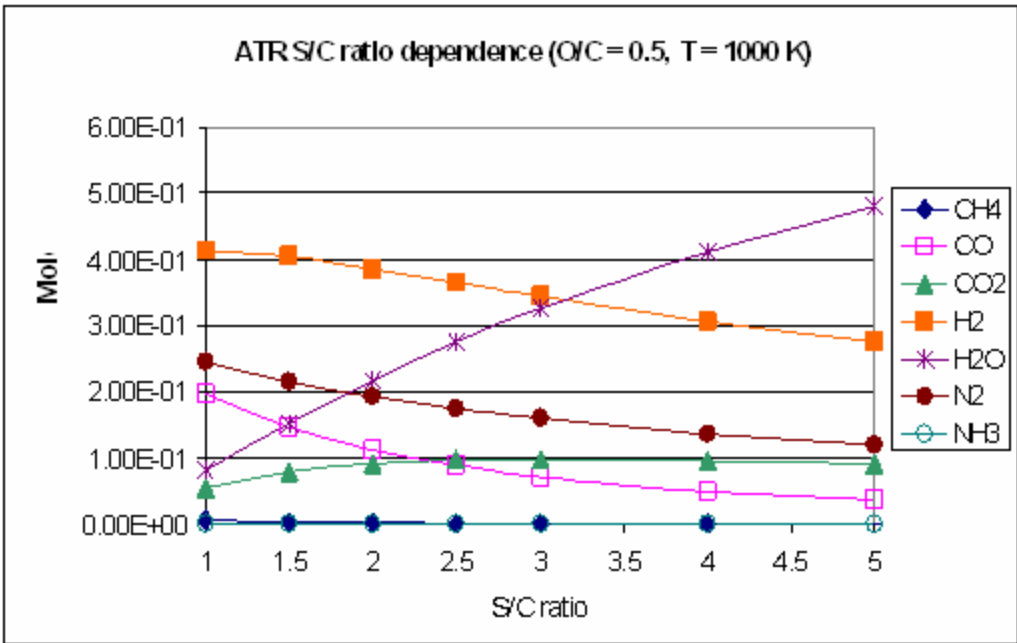




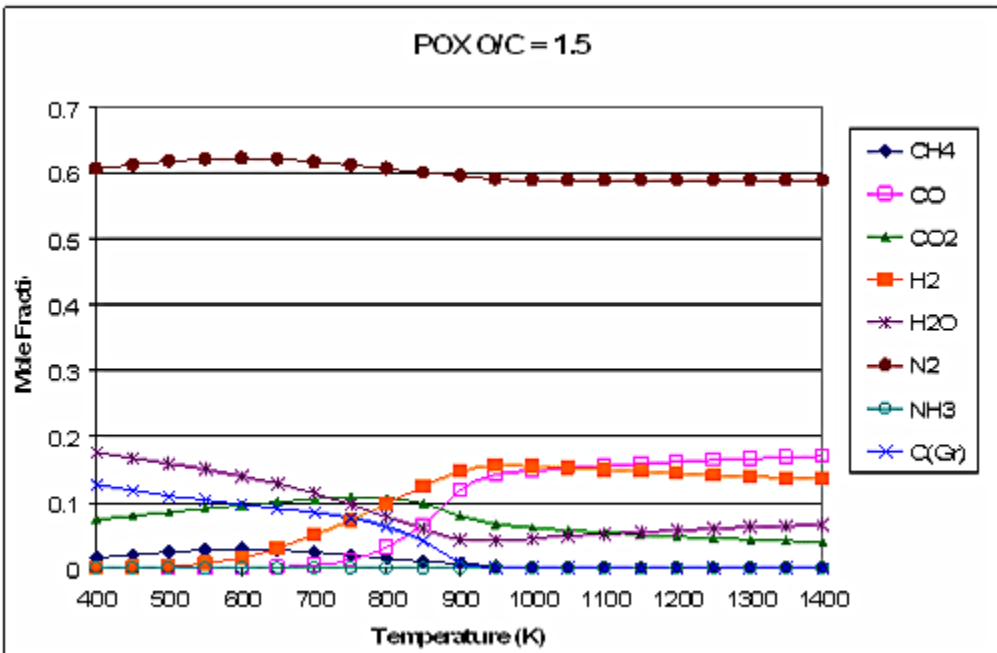
Jet Fuel Equilibrium Results – Effects of S/C



Jet Fuel Equilibrium Results – Effects of O/C



Jet Fuel Equilibrium Results – Partial Oxidation



New Module Development

Reaction Mechanism Need and Approaches

- Use Equilibrium results in look-up tables with discretized dynamic model for heat transfer, mass and momentum conservation
- Use Chemical Kinetics from a simpler hydrocarbon set
- Obtain data and/or develop simple chemical kinetic mechanism for JP-5

Must incorporate dynamic equations

- Heat transfer (conduction, convection, radiation)
- Mass (or species) conservation
- Momentum conservation
- Energy conservation

Main module development need is for the overall geometry of the NuElement Module

Dynamic JP-5 Reformer Module

Concentric Cylinders

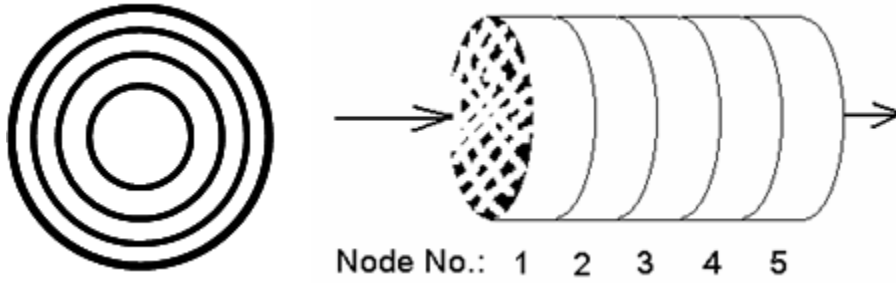
- Combustor
- Catalyst Bed
- Preheat
- Anode off-gas recycle (option)

Reformation Kinetics

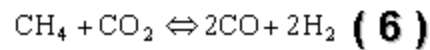
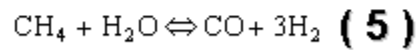
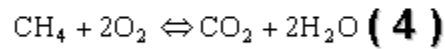
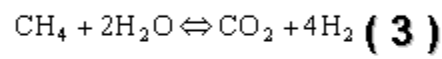
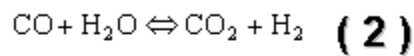
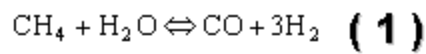


New Module Development

- Reformer Geometry (5 nodes)



- Six Step Reaction Mechanism



- Arrhenius Rate Expressions

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right)$$

$$r_1 = k_1 \left(\frac{P_{CH_4} P_{H_2O}}{P_{H_2}^{2.5}} - \frac{P_{CO} P_{H_2}^{0.5}}{K_{p1}} \right) / DEN^2$$

$$r_2 = k_2 \left(\frac{P_{CO} P_{H_2O}}{P_{H_2}} - \frac{P_{CO_2}}{K_{p2}} \right) / DEN^2$$

$$r_3 = k_3 \left(\frac{P_{CH_4} P_{H_2O}^2}{P_{H_2}^{3.5}} - \frac{P_{CO_2} P_{H_2}^{0.5}}{K_{p3}} \right) / DEN^2$$

$$r_4 = k_4 P_{CH_4} P_{O_2}$$

$$r_5 = k_5 \left(P_{CH_4} P_{H_2O} - \frac{P_{CO} P_{H_2}^3}{K_{p5}} \right)$$

$$r_6 = k_6 \left(P_{CH_4} P_{CO_2} - \frac{P_{CO}^2 P_{H_2}^2}{K_{p6}} \right)$$

$$DEN = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + K_{H_2O} P_{H_2O} / P_{H_2}$$

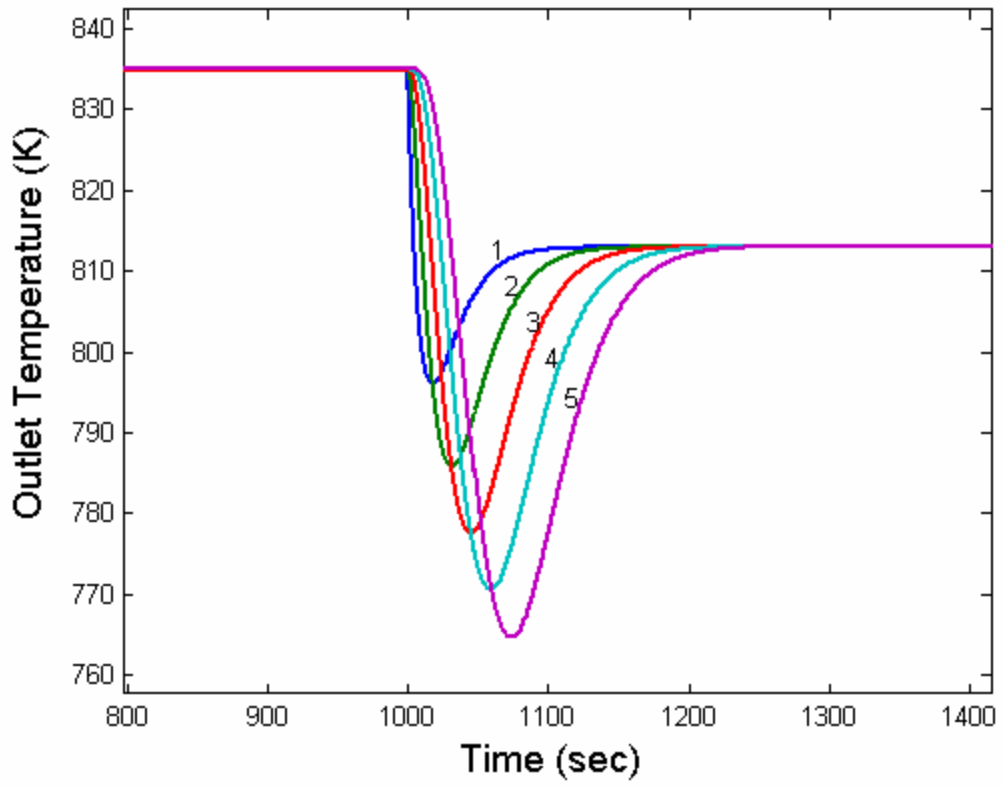
Reaction i	Activation energy E _i (kJ/mol)	Pre-exponential factor A _i
1	240.1	1.336 × 10 ¹⁵ (kmol*MPa ^(0.5) /kg _{cat} *h)
2	67.13	1.955 × 10 ⁷ (kmol/kg _{cat} *h*MPa)
3	243.9	3.22 × 10 ¹⁴ (kmol*MPa ^(0.5) /kg _{cat} *h)
4	166	1.10 (mol/g _{cat} *s*Pa ²)
5	29	4.19 × 10 ⁻⁹ (mol/g _{cat} *s*Pa ²)
6	23.7	2.42 × 10 ⁻⁹ (mol/g _{cat} *s*Pa ²)

- Reaction Equilibrium Constants

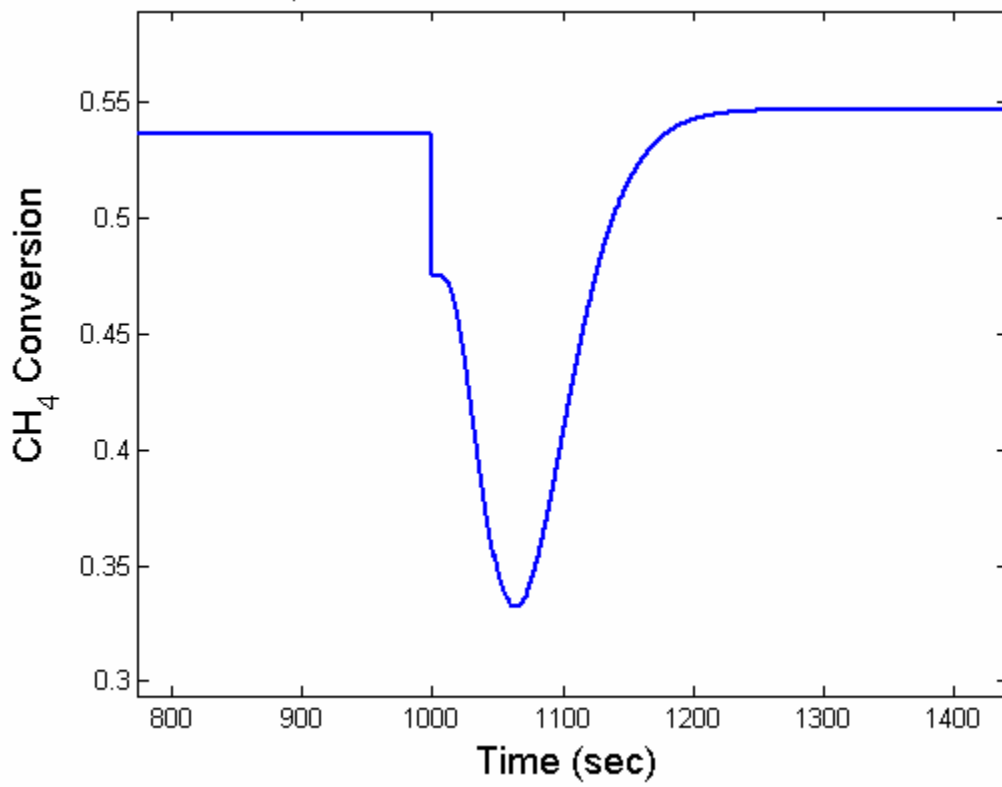
$$K_j = A_j \exp\left(-\frac{\Delta H_j}{RT}\right)$$

Equilibrium constant K _{pi}	Dimensions
K _{p1} = 1.198 × 10 ¹¹ * exp(-26830/T)	(MPa) ²
K _{p2} = 1.77 × 10 ⁻² * exp(4400/T)	(MPa) ⁰
K _{p3} = K _{p1} · K _{p2}	((MPa) ²)
K _{p5} = K _{p1}	(MPa) ²
K _{p6} = 6.780 × 10 ¹² * exp(-31230/T)	(MPa) ²

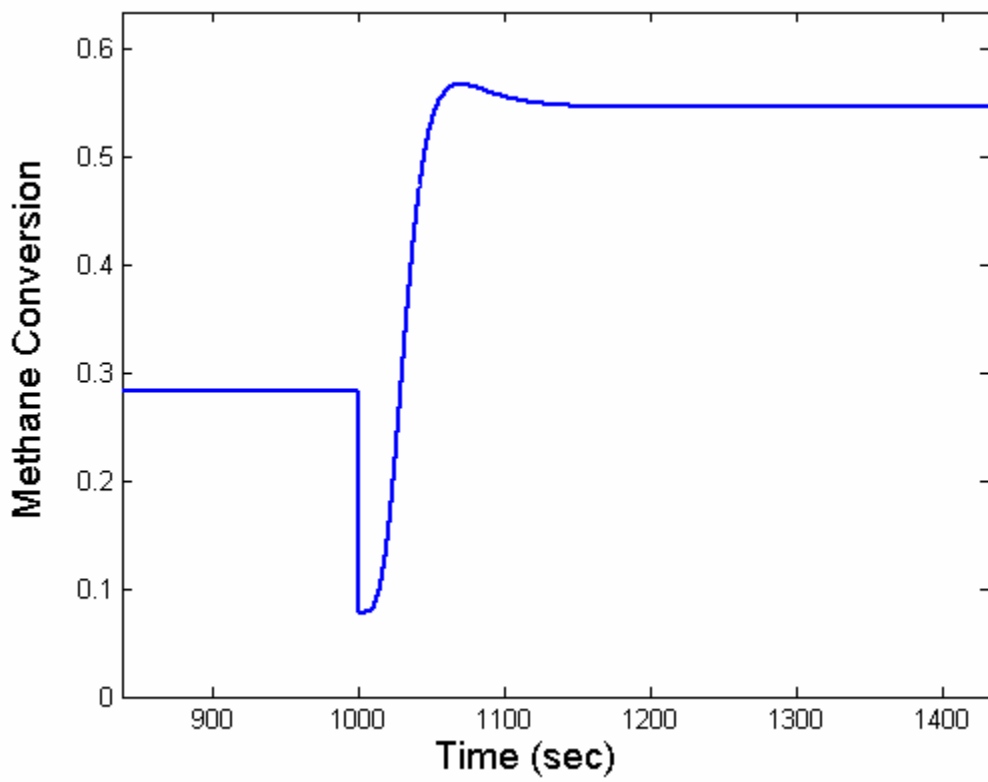
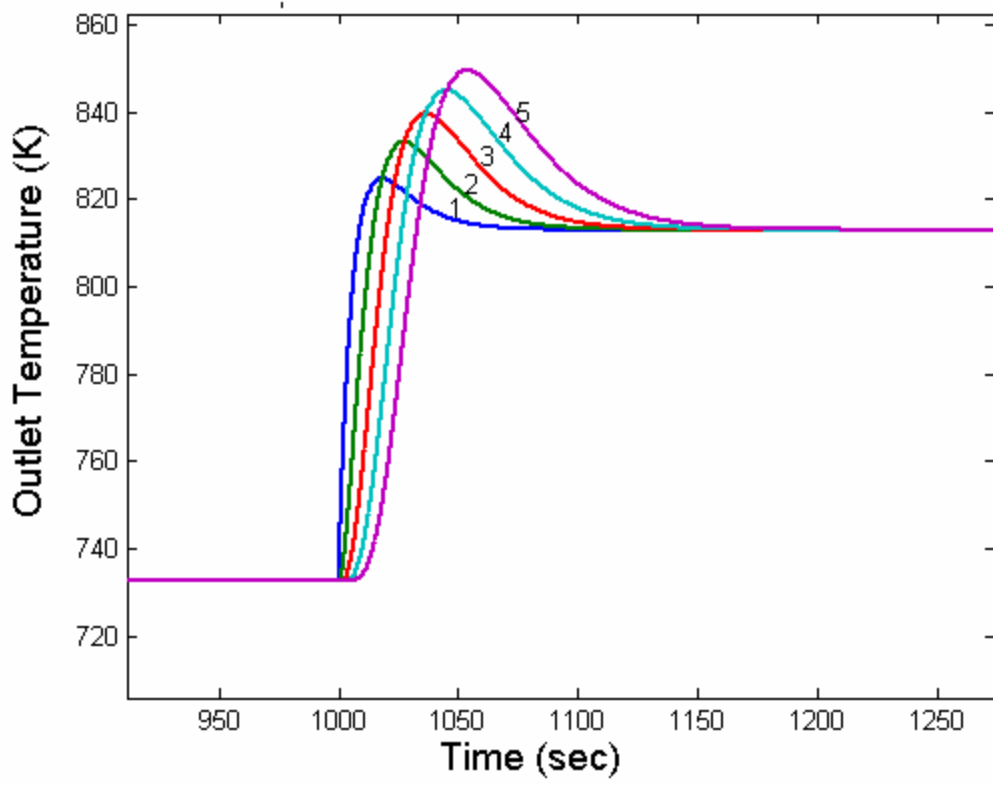
- Reformer Dynamic Simulation Results – S/C 1.0 → 1.5



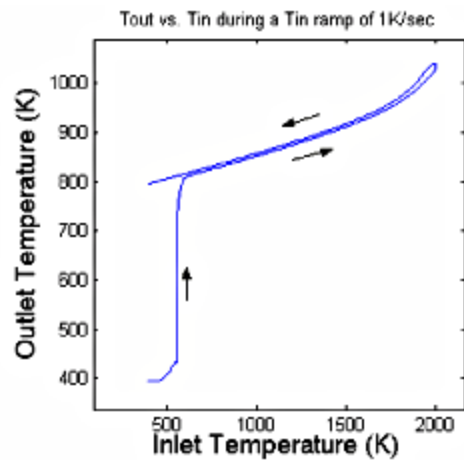
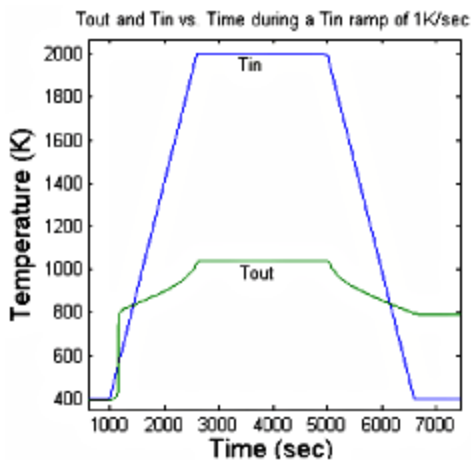
- Reformer Dynamic Simulation Results – S/C 1.0 → 1.5



- Reformer Dynamic Simulation Results – O/C 0.25 → 0.5



- Reformer Dynamic Simulation Results – Catalyst “light off”



Personnel

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Sponsors

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California Energy Commission

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