Nano Miniaturization of a Hydrogen Plant

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Introduction – Brief Overview

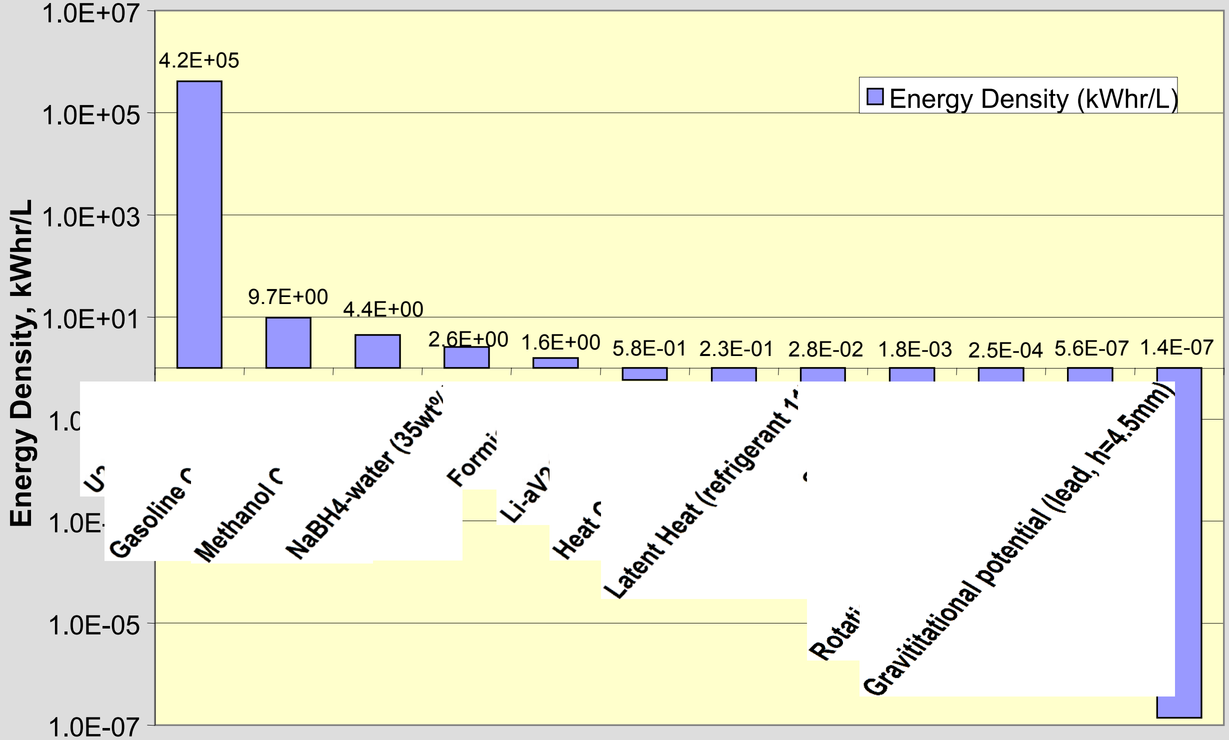
- Objective: Hydrogen production for micro power supply
- Background
  - Energy density hydrocarbons >> secondary batteries
    - Methanol = 5.6 kW_t-hr/kg, lithium-ion batteries = 0.12 kW_e-hr/kg
    - 10% efficient conversion = 4.6 times energy density increase
- Result: Micro-scale fuel processor
  - **One Billionth (10^{-9})** volume and process capacity
  - Reproduces major unit operations of a hydrogen plant
  - Fits on a dime

Microscale Reactor

- Hydrogen plant on a dime–the microreactor vision!
- New basis for engineering systems
  - Hydrogen distribution
  - Power supplies
  - Miniature products
  - Chemical labs
- Lessons learned
  - Keep it simple
  - Be flexible
  - Build and test
  - Metal can work

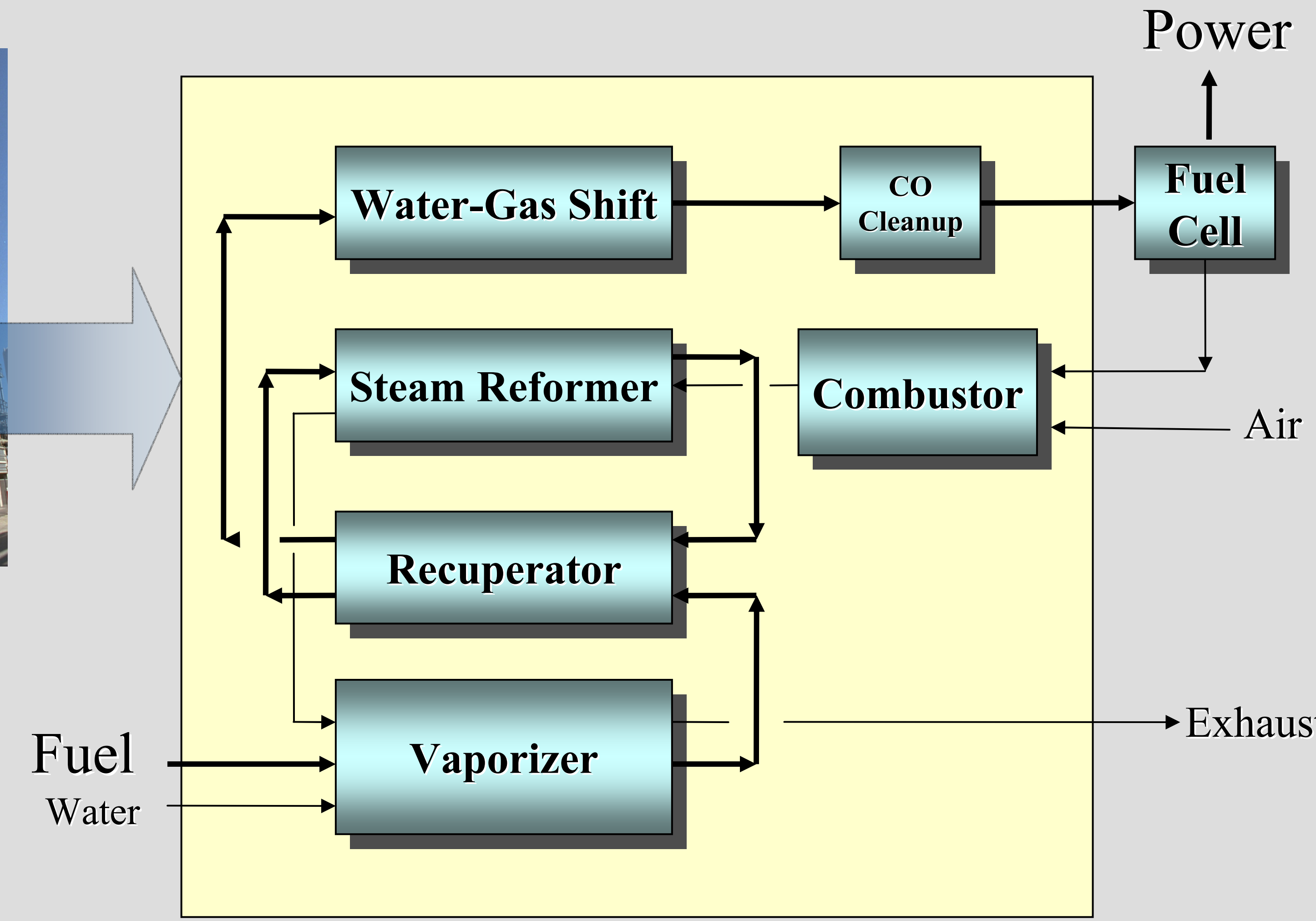
Energy Density of Some Potential Storage Devices

- Except for the battery, these storage devices will need a conversion device to make electrical power

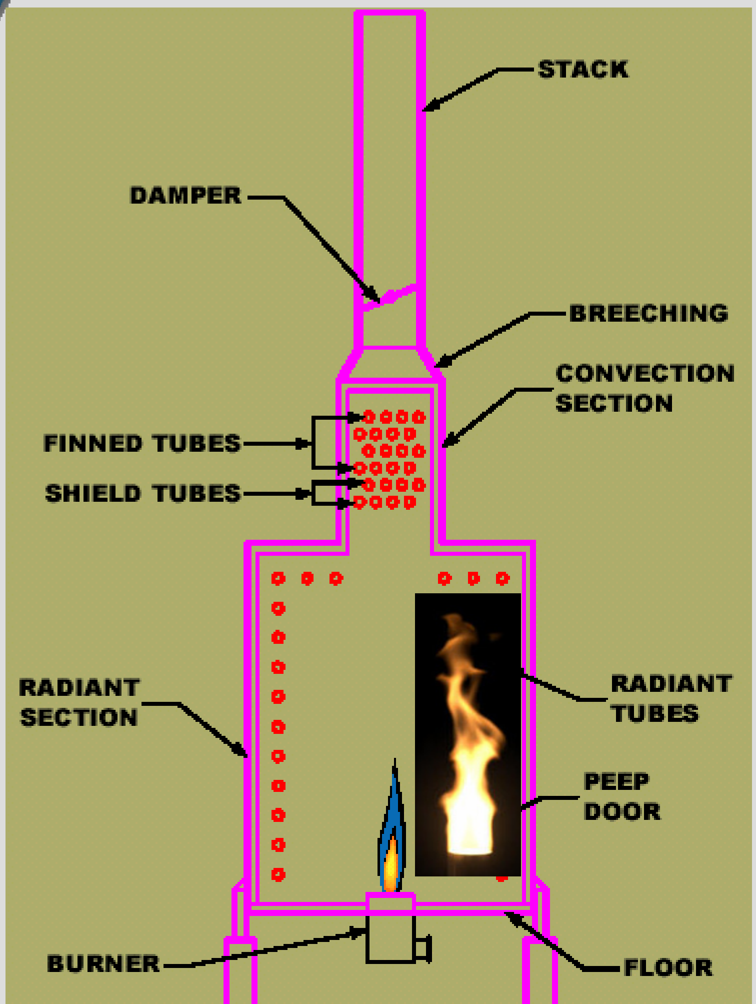


Adapted from Paul B. Koeneman et al. J. Microelectromechanical Systems vol. 6 no.4 1997 p 355

Hydrogen Production



Conventional Technology: Tube Box Heaters



How Do You Miniaturize Conventional Technology?

- Combine:
  - Chemical processing +
  - Microelectronic fabrication +
  - Nano technology

Scale-Down Approach

- Identify significant unit operations
- Identify controlling mechanisms/opportunities
  - How will scale-down affect them?
  - Does nano technology enable a new approach?
    - Reactions
    - Materials
    - Designs
- Design, build, test
  - Keep it simple – both the design and fabrication
  - Keep the end in mind
    - How will it be tested?
    - Is mass fabrication feasible?
  - Try multiple designs
- Model
- Repeat: design, build, test, model

Miniaturization Issues

Unit Op	Opportunity	Enabling Tech	Comments
Reforming reactor	- heat transfer - mass transfer - slow kinetics	- microchannel - improved catalysts	- Increase heat and mass transfer - Fast kinetics
Heat source	- quenching - T control	- catalytic combustion - microchannel	- Quenching is not an issue with - Catalytic combustion and microchannels improve T control
PSA	- CO removal	- methanation	- Thermal runaway mitigated with microchannel reactors - Passive CO removal
Heat exchanger	- thermal loss - heat transfer	- design, fuel, and material selection	- Tight unit op integration - Low-temperature reactions - Appropriate materials

Miniaturization Focus: High Efficiency/Minimize Heat Loss

- Low-temperature reactors
  - Fuel Selection
  - Catalyst
  - Reactor design
- Low volume and surface area
- Thermal integration
  - Design: put the heat only where it is needed
- Insulation
  - Material selection
  - Vacuum package?

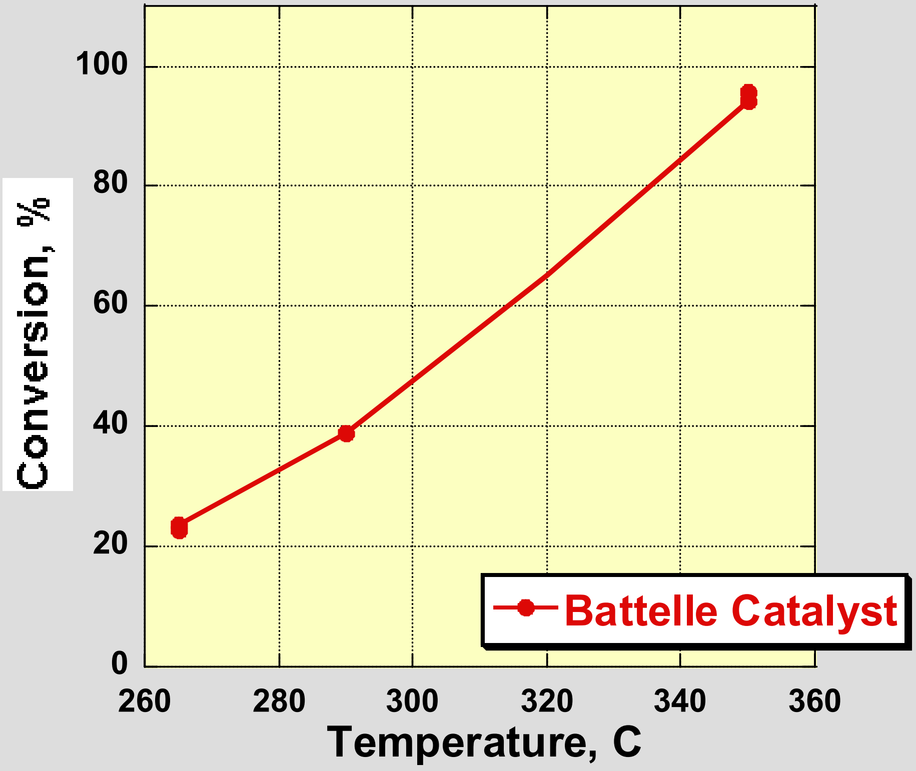
Fuel Selection

- Methanol mix has a low reforming T and high energy density

Fuel	Reaction T (°C)	Specific Energy (pure)	Specific Energy (mix)
Methanol	250-350	5.6 kW_t-hr/kg	1:1 S:C ~3.2 kW_t-hr/kg
C8-C12 hydrocarbon	650-800	12.5 kW_t-hr/kg	2:1 S:C ~3 kW_t-hr/kg
Methanol	DMFC	5.6 kW_t-hr/kg	3M 0.55 kW_t-hr/kg
Formic Acid	Direct FA FC	1.6 kW_t-hr/kg	10M 0.55 kW_t-hr/kg

Methanol-Specific Battelle Catalyst

- Reactor Conditions
  - Atmospheric pressure
  - Temperature 260-350°C
- **24,000-50,000 hr^{-1} GHSV**
- Catalyst Life >1000 hr
- Non-pyrophoric
- Typical Composition (dry gas)
  - **H_2 = 72-74%**
  - **CO_2 = 24-26%**
  - **CO = <1%**
  - **Equilibrium CO at 350°C = 5.4%**



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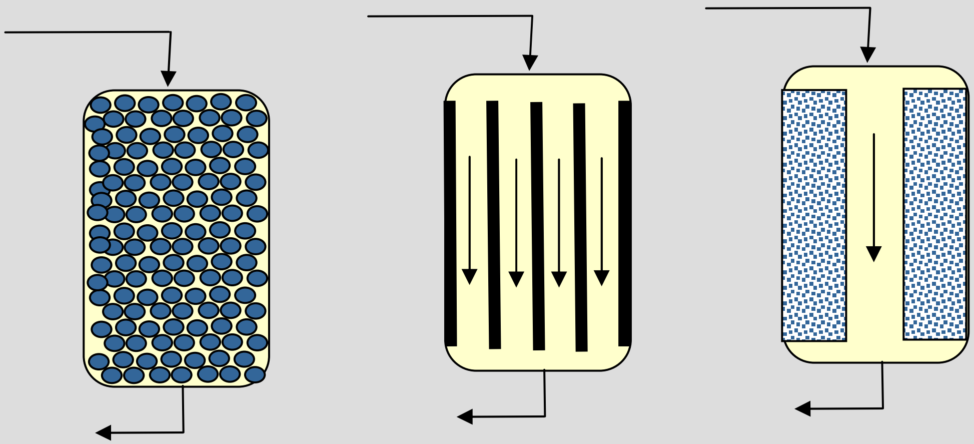
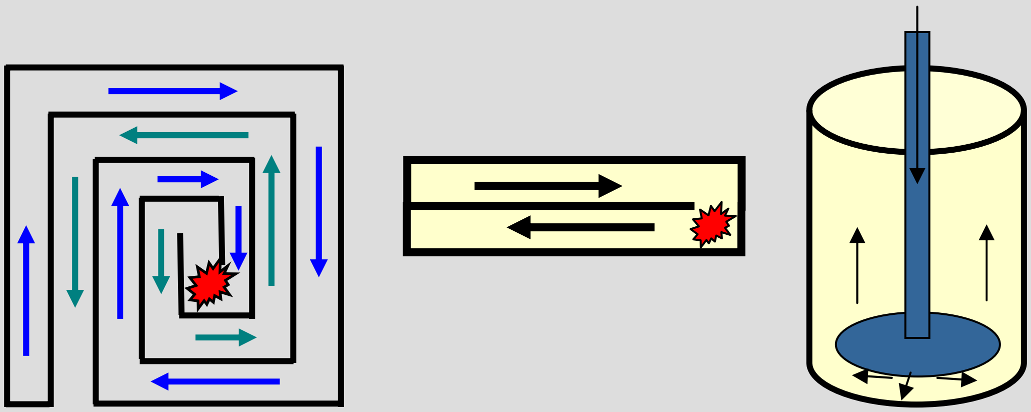
Design Options

- Reactor
  - Packed Bed
  - Coated walls
  - Engineered



- System
  - Spiral – Swiss roll
  - Counter-flow
  - Radial



Material Selection

Material	Benefits	Challenges
Low Temp. Ceramic Casting	- Flexible fabrication - Refractory and durable - Low costs - No clean room required	- Non-standard fabrication - Low thermal conductivity - Sealing - Fragile
Silicon	- Well characterized Si fab. techniques - High precision - Low to modest costs	- Modest thermal conductivity - Fragile - Requires clean room
Metal	- Conventional fabrication techniques - Durable - Low costs - No clean room required	- High thermal conductivity - Poor compatibility with ceramics and glass

Adapted from Thompson, L. T. Microreaction Technology and Process Intensification Symposium at the 226th American Chemical Society National Meeting, New York, NY, 2003; p abstract 35.

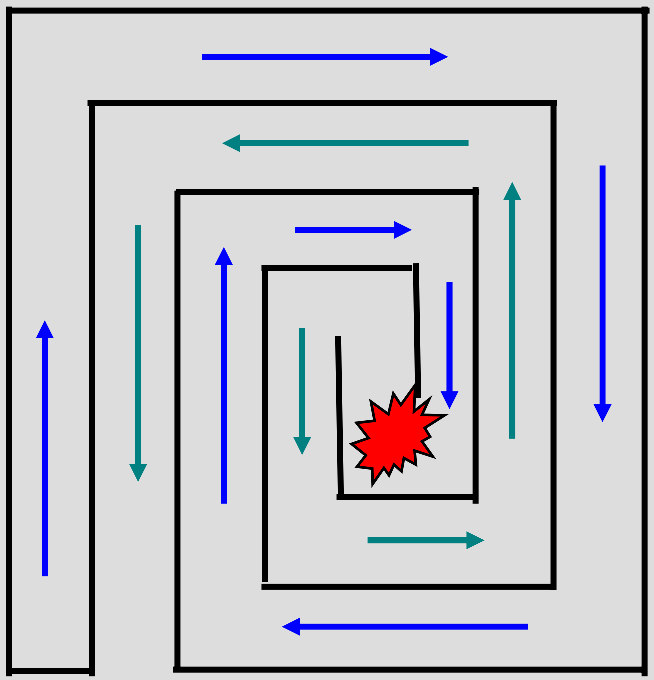
Material Properties

- If thickness of SS is << zirconia, then the thermal conductivity can be less!

Material	Thermal Conductivity (W/m*K at 600K)	CTE (1/C) RT	Ductility
Silicon	62	$2.6*10^{-6}$	Brittle
SiO_x	5	$5*10^{-7}$	Brittle
Silicon nitride	11	$3.6*10^{-6}$	Brittle
Alumina	16	$8.8*10^{-6}$	Brittle
Zirconia	~3	10^{-6}	Brittle
316 SS	18	$16*10^{-6}$	Ductile

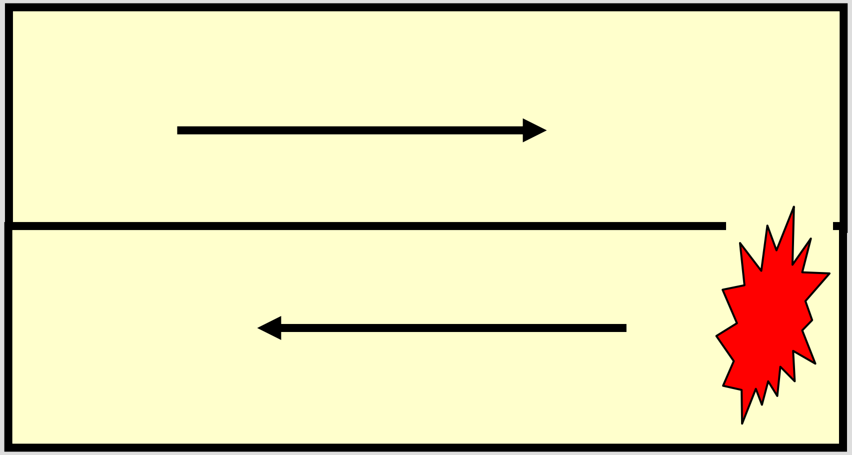
Design 1: Swiss Roll

- Reactor: Engineered Catalyst
- Materials: LTCC – low thermal conductivity
- Results: Never built
  - Device would be large
  - Complex
  - Thick walls required for strength
  - Sealing issues



Design 2: Counter-Flow

- Reactor: Engineered Catalyst
- Materials: LTCC – low thermal conductivity
- Results: Built
  - Small device
  - Simple to build
  - Fragile – kept breaking
  - Sealing issues

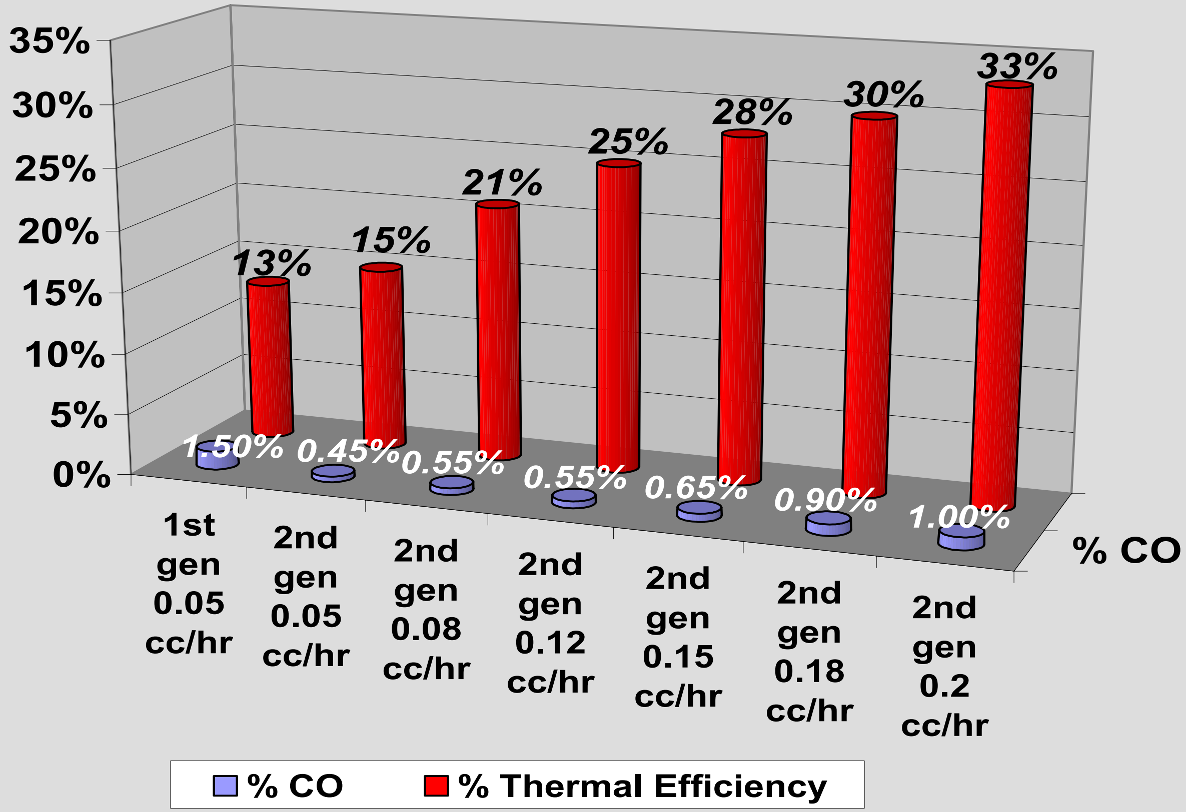


Design 3: Radial

- Reactor: Engineered Catalyst
- Materials: Stainless Steel – higher thermal conductivity but thinner walls
- Results: Built and tested
  - Surprisingly efficient, 9%
  - Small
  - Simple
  - Strong
  - No sealing issues
- Gas composition:
  - H_2 = 72-74%
  - CO_2 = 24-26%
  - CO = 0.9-1.9%

Design 4: Radial

- Reactor: Mixed Engineered + Packed Bed
- Results: Improved efficiency with reduced CO^-



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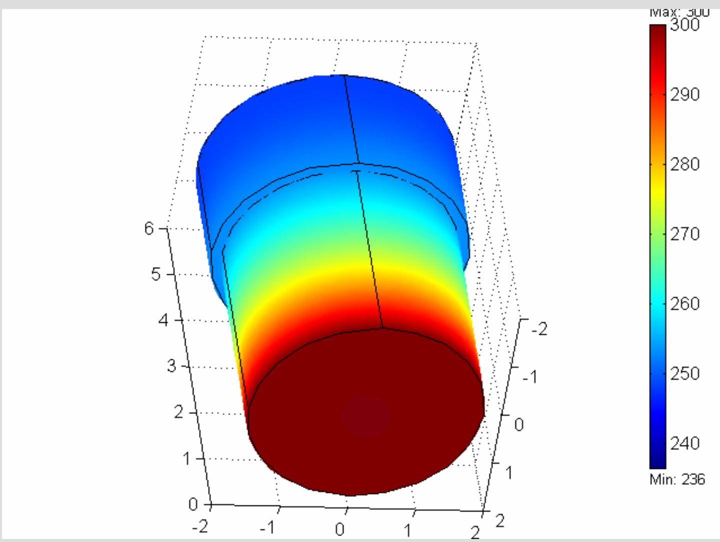
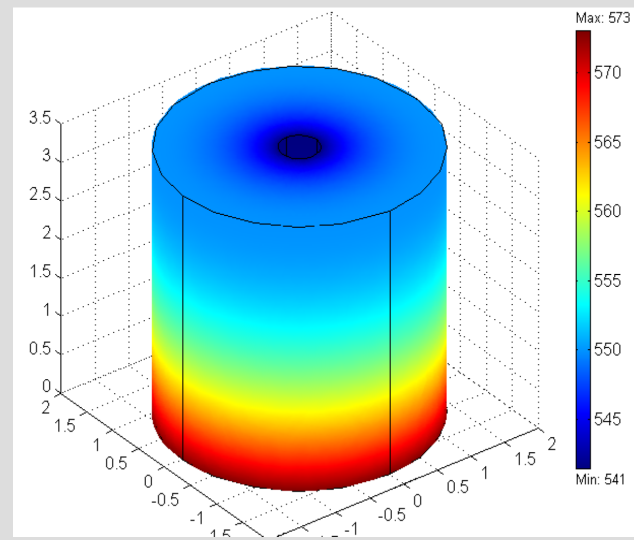
Design 4: Radial – Model

- Heat loss: conduction > radiation + convection
- Methanation reactor integration feasible
  - T = 230-270°C

Surface temperature profile (C) (with methanation reactor)

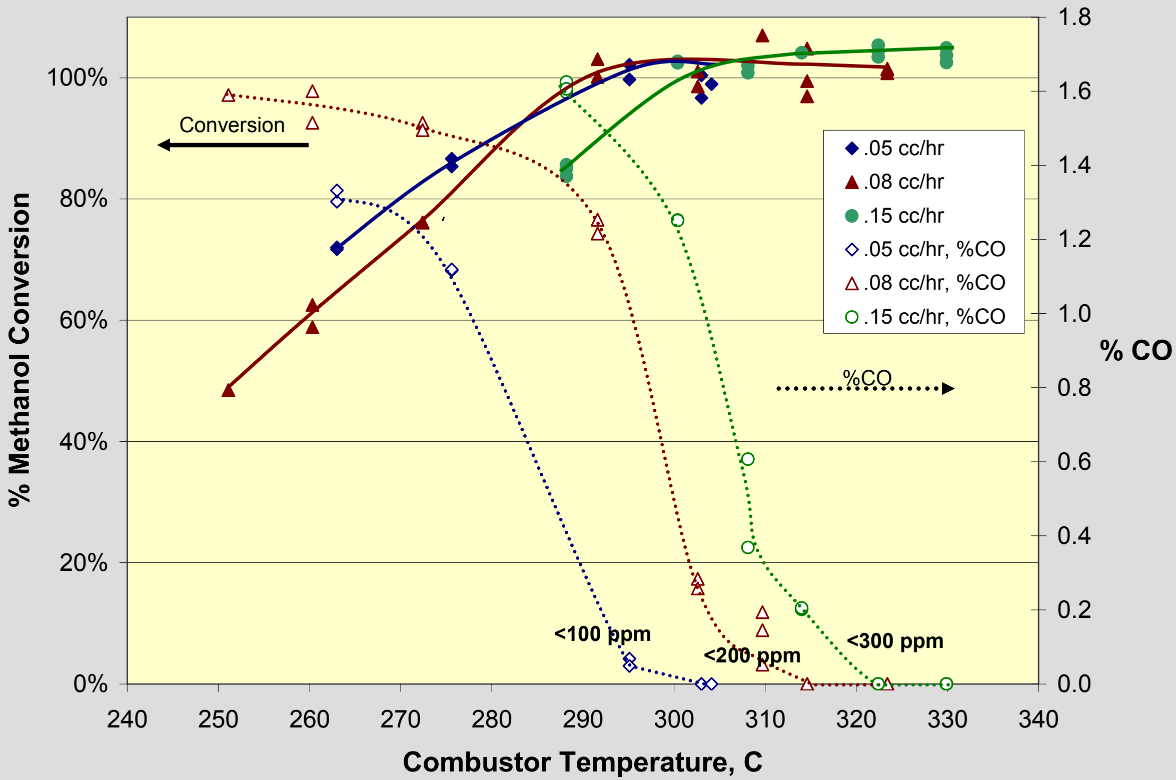


Surface temperature profile (K)



Design 5: Radial

- Reactor: Mixed Engineered + Packed Bed
- Results: Improved efficiency with lower CO concentration



Radial Design Summary

Feed Flow, cc/hr	T, °C	Gas Flow, sccm	H_2, %	CO_2, %	CH_4, %	CO, ppm	Approx. Thermal Eff., %
0.05	304	1.0	69-70	25	5.0-5.5	<100	9
0.08	323	1.65	69-70	25	6.0-6.2	<200	14
0.1	330	2.1	69-70	25	6.0-6.2	<200	17
0.15	345	3.2	68-69	25-26	5.3-6.0	<300	19