

Department of Energy
Fuel Cell Manufacturing
R&D Workshop

High Temperature BOP
and Fuel Processing

August 11-12, 2011

Agenda

- Acumentrics Overview & Approach
- Fuel Preparation
- Reforming
- Heat Recovery
- Gas Utilities
- Power Conversion & Controls
- Conclusion

Acumentrics Corporation

Strategic Partners



U.S. Department of Energy
Energy Efficiency and Renewable Energy



- ~ 95 Employees
- Manufacturing since 1994
- Based in Westwood, Mass.
- ~40,000 sq. ft facility
- *Critical disciplines in-house*
 - Electrical Engineering
 - Mechanical Engineering
 - Chemical Engineering
 - Thermal Modeling
 - Ceramics Processing
 - Manufacturing
 - Sales & Marketing
 - Automation
 - Finance

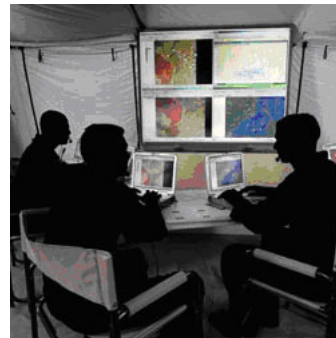
Acumentrics *Battery-based* UPS

Uninterruptible Power Supplies for Harsh Environments



Features:

- Sealed electronics
- Able to withstand vibration
- Unity power factor input
- Wide input 80VAC - 265VAC
- Isolated 120 / 240VAC output
- Hot swap battery case
- Parallelable to 20 kWatts



Acumentrics Approach

Target Markets (250 watts to 10 kW – AC or DC):

- **Remote Power:** Offgrid AC or DC
- **Military:** Tactical Quiet Generator; Battery Charger
- **MicroCHP:** 1-2.5 kWe residential

Perfect the individual System pieces followed by optimizing their integration:

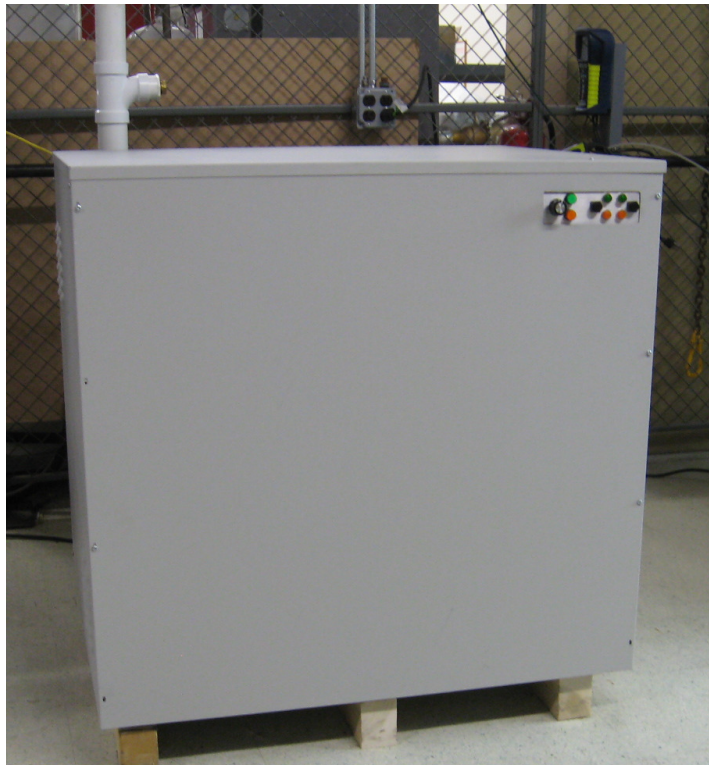
- **Cell Technology:** Improve power & stability of the cell building block
- **Cell Manufacturing:** Improve processing yield & productivity while decreasing material consumption
- **Stack Technology:** Refine stack assembly and improve heat removal and integrity while cost reducing components
- **System Performance:** Develop simplified controls and BOP to allow for a reliable, highly efficient unit.

Wall Mounted mCHP

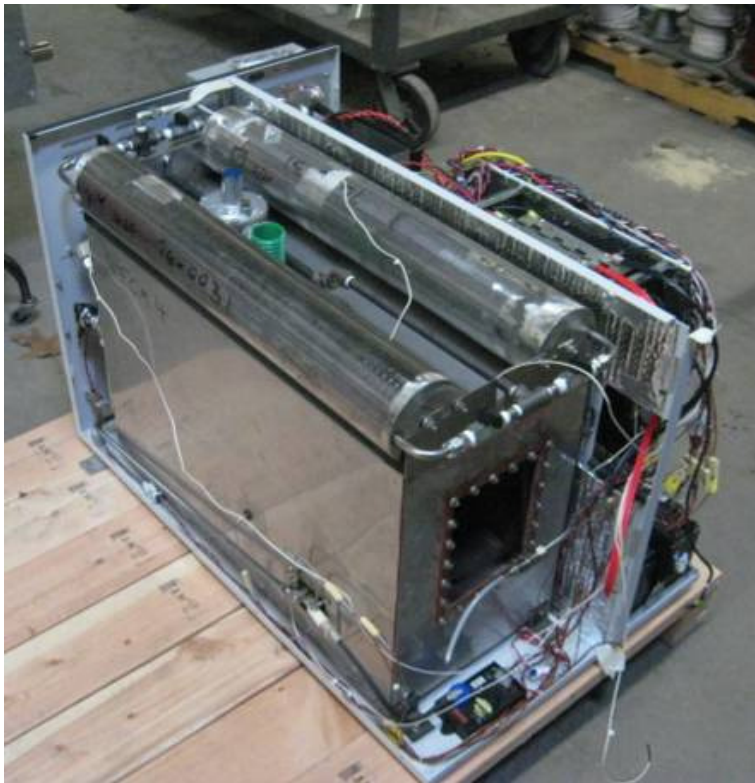
- One kilowatt unit with 20 kW thermal boiler
- 80-90% total efficiency, 33"x22"x18"
- 180lb total, 100lb FC sys



Floor Mount MicroCHP



Remote Power Unit

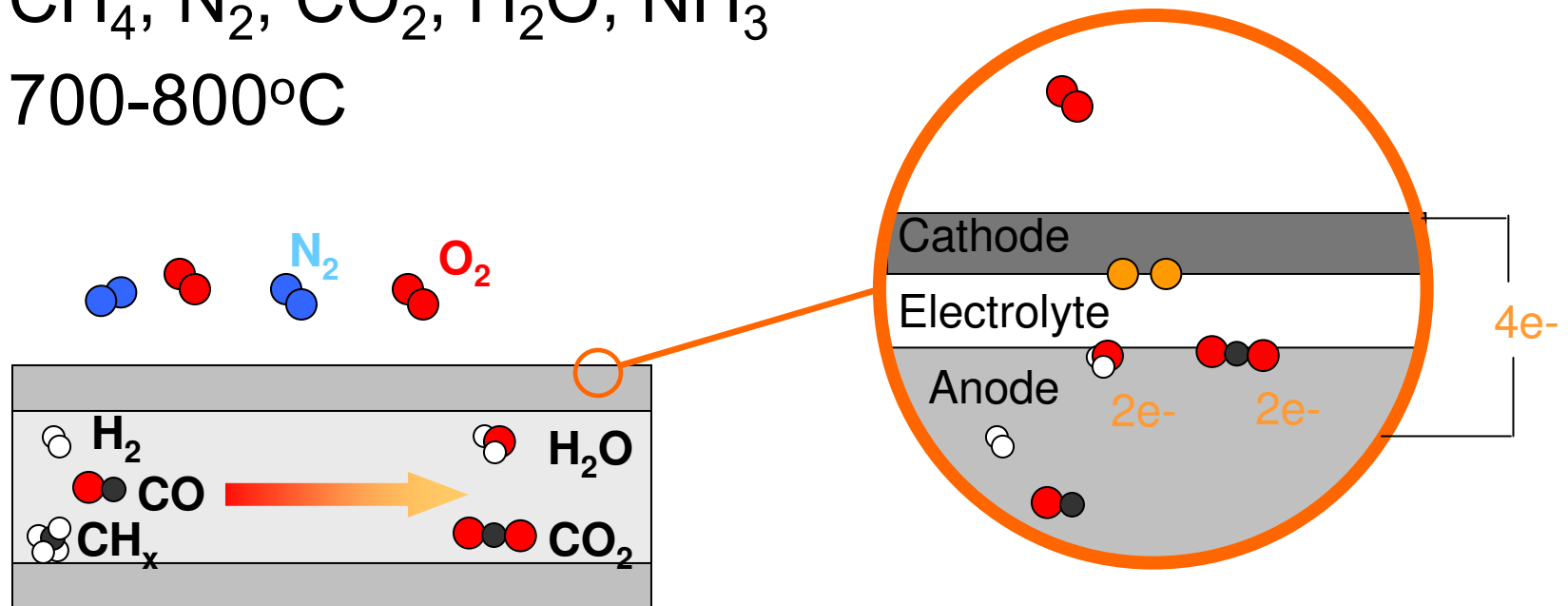


Liquid Fuel Tactical Generator



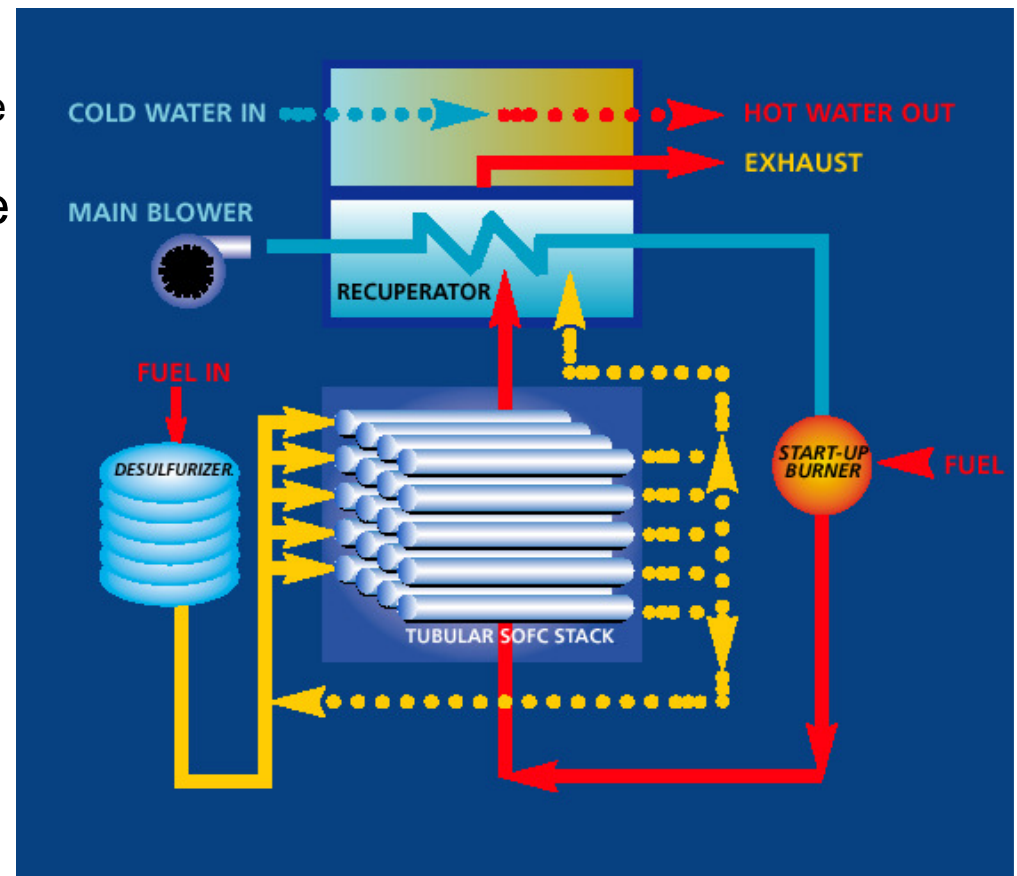
Acumentrics Tubular SOFC

- Standard Ni anode based SOFC can operate stably on fuel streams containing H_2 , CO , CH_4 , N_2 , CO_2 , H_2O , NH_3
- 700-800°C

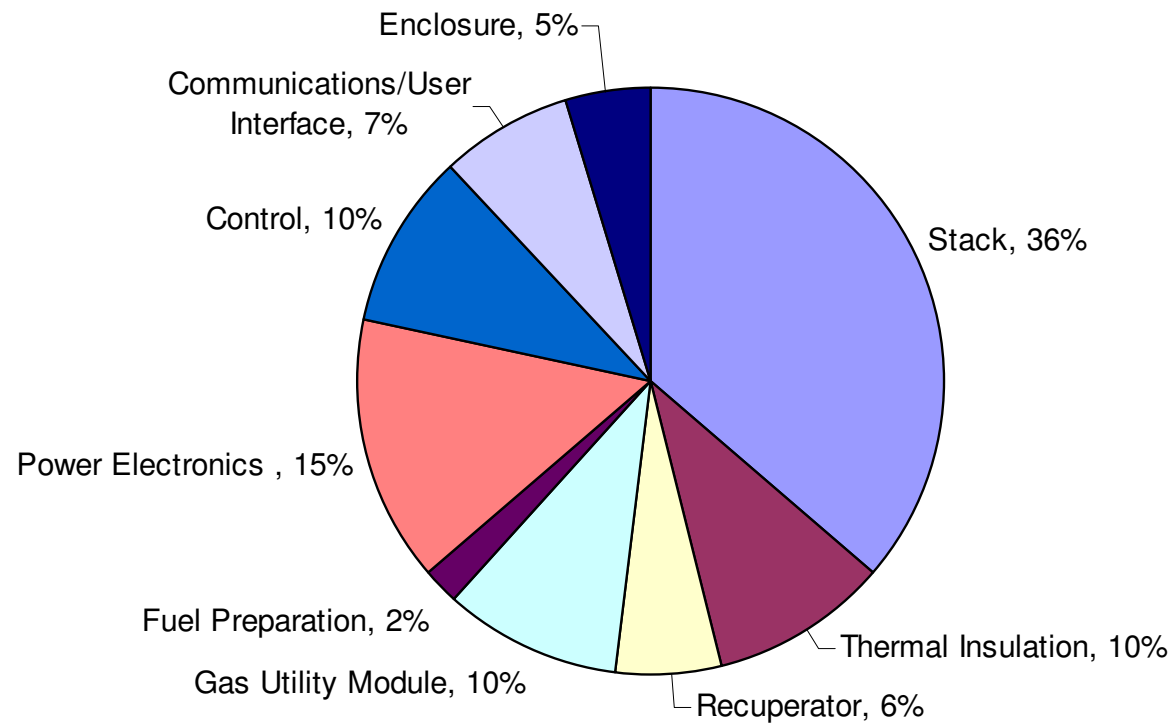


System Configuration

- Tubular Cells
 - Inherent strength and tolerance to rapid temperature change
- High Operating Temperature (700-800 C)
 - Internal fuel reforming and cogeneration opportunity
- Standard Manufacturing Process
 - Low Capital Expenditure
- Standard Components
 - Standard HVAC balance-of-plant components
 - Leverage 12 years DC/AC conversion experience



Relative Costs



SOFC Fuel Processing Challenge

■ Natural gas

- Residential, 85-95% methane, composition well regulated
- Sulfur odorant varies geographically

■ LPG

- Mostly propane in US
- Propane and Butane in other parts of the world.
- Less well regulated
- Feed from bottle changes as tank empties
- Sulfur composition changes as tank empties

■ Bio-fuels

- Newly regulated
- Biogas
 - ▶ From anaerobic digestors, ~40-60% methane in CO₂ with contaminants
 - ▶ Thermal gasification of bio feedstocks, e.g. woodchips, to wet syn-gas with contaminants
- Bioethanol with minor sulfur contaminant
- Biodiesel, Fatty Acid Methyl Ester (FAME) blend with minor sulfur contaminants.
 - ▶ Other challenges – 100% biodiesel is not compatible with many metals and polymers. Can be quite corrosive Biogas

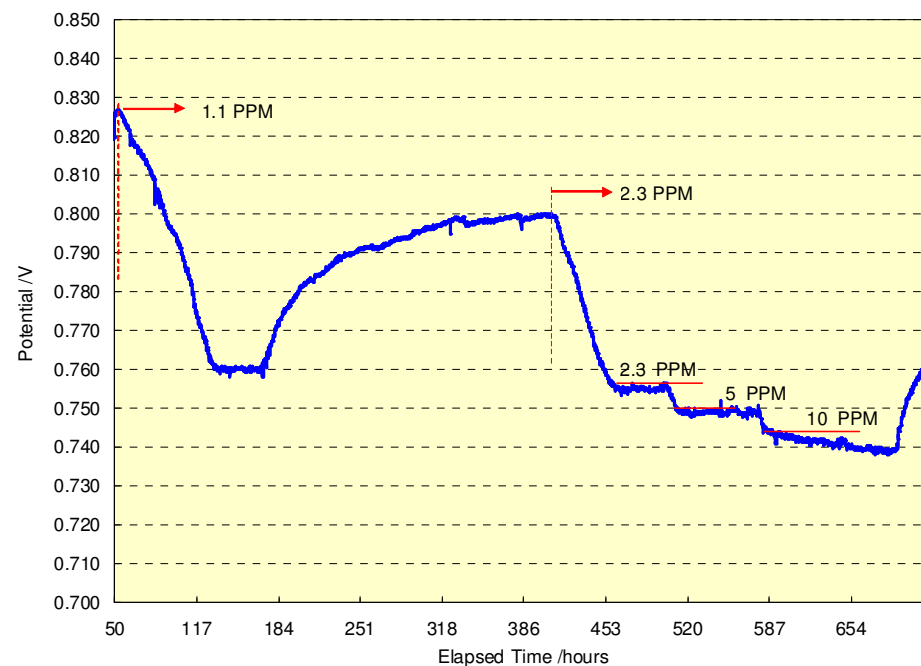
Contaminants

- Natural gas – typically odorants in residential gas
 - ▶ Usually well defined odorant composition based on commercial mixes
 - ▶ Difficult species dimethyl sulphide, isopropyl mercaptan
- LPG
 - ▶ Odorant is typically ethyl mercaptan ~10ppm, but sulfur can exist in other forms depending on source.
 - ▶ COS not usually present but has been seen up to 200ppm
 - ▶ Batch fractionation – composition is time dependent. Instantaneous composition also has strong temperature dependence
- Biogas
 - ▶ Sulfur and trace contaminants
 - Sulfur 100-10000ppm H₂S
 - Siloxanes
 - Arsenic, Phosphorous

Fuel Contaminants (Ni anodes)

Gas Species	Specification
Sulfur	Total <0.1ppmV

- 1) Depreciation in cell performance H_2S in H_2 at $800^\circ C$
- 2) Verified for NG CPOX in residential systems. Sulfur breakthrough can be tolerated and performance recovered



Fuel Contaminants (Ni anodes)

Gas Species	Specification
Sulfur	Total <0.1ppmV
Sb, As, P, Zn and metals	Total <0.1ppmV ?

Contaminants possible in landfill gas from anaerobic digestors
Little data on heavy metals but the species listed above have vapor species known to react with Ni.
There is some fuel cell data to show degradation at even 1 ppm level.

Fuel Contaminants (Ni anodes)

Gas Species	Specification
Sulfur	Total <0.1ppmV
Sb, As, P, Zn and metals	Total <0.1ppmV ?
Water vapor	<1% ?

Tolerance has improved but water vapor (and condensables in general) can interfere with sorbent function. Water concentrations depend on gas source and/or purification techniques

Fuel Contaminants (Ni anodes)

Gas Species	Specification
Sulfur	Total <0.1ppmV
Sb, As, P, Zn and metals	Total <0.1ppmV ?
Water vapor	<1% ?
Silicon species	<0.01% ?
<p>Silicon species will decompose to form a hard silica scale on high temperature surfaces such as reformer and catalyst, leading to fouling and catalyst deactivation</p>	

Fuel Contaminants (Ni anodes)

Gas Species	Specification
Sulfur	Total <0.1ppmV
Sb, As, P, Zn and metals	Total <0.1ppmV ?
Water vapor	<1% ?
Silicon species	<0.01% ?
Chloride species	<10 ppm
<p>Chlorides are poisonous with depreciated performance at 10ppmV Effects are reversible even at concentration ~100ppm.</p>	

Fuel Contaminants (Ni anodes)

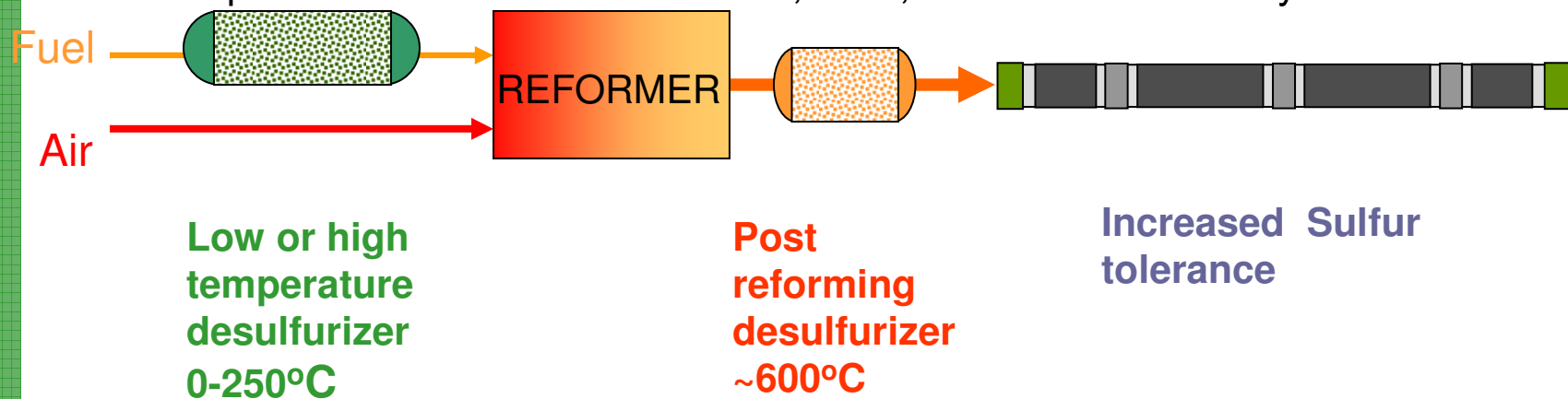
Gas Species	Specification
Sulfur	Total <0.1ppmV
Sb, As, P, Zn and metals	Total <0.1ppmV ?
Water vapor	<1% ?
Silicon species	<0.01% ?
Chloride species	<10 ppm
Particulates	<0.5mm, <1mg/Nm³

Purification

Gas Species	Volume % (or ppm as stated)
Sulfur	Species dependent
Sb, As, P, Zn and metals	Activated carbon
Water vapor	Coalescing filters
Silicon containing species	Activated carbon
Halogen species	Activated carbon
Particulates	HEPA filters, ceramic filter media

Sulfur Poisoning

- Sulfur present in varying quantities in all of the fuels
- Common Ni anode susceptible to sulfur poisoning. Need <5ppm and ideally less than 0.1ppm
- Solutions:
 - Desulfurization of fuel (pre reforming), activated carbon, mixed metal oxides
 - Desulfurization of reformat (post reforming), carbonates
 - Improved sulfur tolerance of anode, ceria, tolerant functional layers



Desulfurizer Beds

- For general LPG and NG applications –
 - Field replaceable bed
 - Low temperature (0-100°C)
 - Multi sorbent bed
 - ▶ COS conversion catalysts (converts COS to H₂S)
 - ▶ High capacity reagent for H₂S and mercaptans - mixed metal oxides, Activated carbon
 - ▶ Zeolite based adsorbents - higher capacity for THT and DMS
 - Caveats
 - ▶ High water concentrations can reduce capacity of sorbents for sulfur because of competitive adsorption. Most catalyst companies have improved sorbents
 - ▶ Over many sorbents/catalysts mercaptan species are not chemically stable – molecular rearrangements can occur over mixed metal oxides. disulfides form. Care needs to be taken when doing bed experiments

Desulfurization Beds

- Sulfur contaminant varies with application and geographic location.
 - US – Tetrahydrothiophene (THT), isopropyl mercaptan (IPM), tert-butyl mercaptan (TBM)
 - Europe - THT, diethyl sulfide (DES), methyl ethyl sulfide (MES)
 - Japan - dimethyl sulfide (DMS), TBM
- Most Fuel Cell catalyst companies (Norit, Sud Chemie, TDA, BASF) have sorbent solutions although effectiveness varies

Gas Species	Sorbent	Capacity
H₂S	AC, Cu/Zn oxides	20-40 wt%
COS	Hydrolysis catalysts	-
mercaptans	AC, Cu/Zn oxides	~3-6 wt%
disulphides	AC, Cu/Zn oxides	-
THT	zeolites	1-2 wt%
DMS	zeolites	0.1-1 wt%

Desulfurizer Beds

- For residential natural gas
 - ~5-10ppm, typically diluted to <1 ppm in reformat
 - SOFC will operate at depreciated performance at breakthrough
 - Adsorbent cost ~\$50 /kW /year

- Other NG, biogas and LPG applications, cost is far less certain
 - Uncertainty in odorant type and concentrations.
 - Beds typically sized for worst case and changed at end of specified life or when dramatic deviations in stack performance occur
 - Leads to inefficiency

- *Low cost*, high or low temperature sulfur sensor can reduce service visits and sorbent costs.

Carbon Deposition

- Nickel is a very good catalyst for carbon deposition!

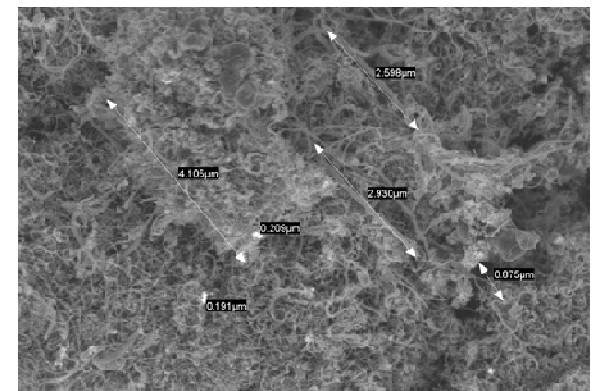
Carbon deposition on anode cermet from methane/air (O/C=0.3) at 800°C



- From thermodynamics, carbon activity < 1 to avoid carbon deposition, usually requires oxygen and water and high temperatures
 - Adding air to fuel stream reduces system efficiency and dilutes fuel (~50% CPOX reformat is N_2)
 - Adding water increases system complexity – vaporizers, condensers, purifiers

Carbon Fouling

- Carbon fouling of pipes is frustrating!
 - Carbon must be avoided over ~40,000hrs!
 - Very sensitive to gas composition, temperature, metal surface structure and composition
- Metal dusting phenomena
 - Carbon forms on surface , $\text{CO} + \text{H}_2 \rightarrow \text{C(s)} + \text{H}_2\text{O}$
 - Carbon dissolves into Ni and Fe metal lattice and crystallizes breaking off metal tip
 - Carbon continues to grow from catalyst tip creating carbon nanotubes



Reforming

■ Reforming Modes

● Steam reforming (H_2O , CH_x)

- ▶ High efficiencies,
- ▶ Can use less expensive base metal catalysts but carbon activity must be controlled, typically use $S/C > 2$
- ▶ requires significant water ($S/C > 2$), 1 kW electricity from NG requires ~0.4 LPH
- ▶ Heat transfer limitations, larger reactors because of poor kinetics.

● Partial oxidation (O_2 , CH_x)

- ▶ Less efficient, but small reactors and fast dynamics
- ▶ Easy, feasible over precious metal catalysts
- ▶ NG, LPG, ethanol, probably FAME but mixture preparation important

NG easy ←..LPG,ethanol....→ Bio diesel most difficult

● Autothermal reforming (O_2 , H_2O , CH_x)

- ▶ Best (and worst) of both worlds?
- ▶ Still need precious metal catalyst, water
- ▶ Heat transfer less important, high efficiencies still possible while mitigating carbon

Water for Steam Reforming and ATR

■ Utility water

- Quality varies but generally will have high mineral content
- Total Dissolved Solids >300ppm
- Vaporization of untreated water leads to scaling

■ Utility water must be purified

- Reverse Osmosis
- High Water Usage
- Expensive

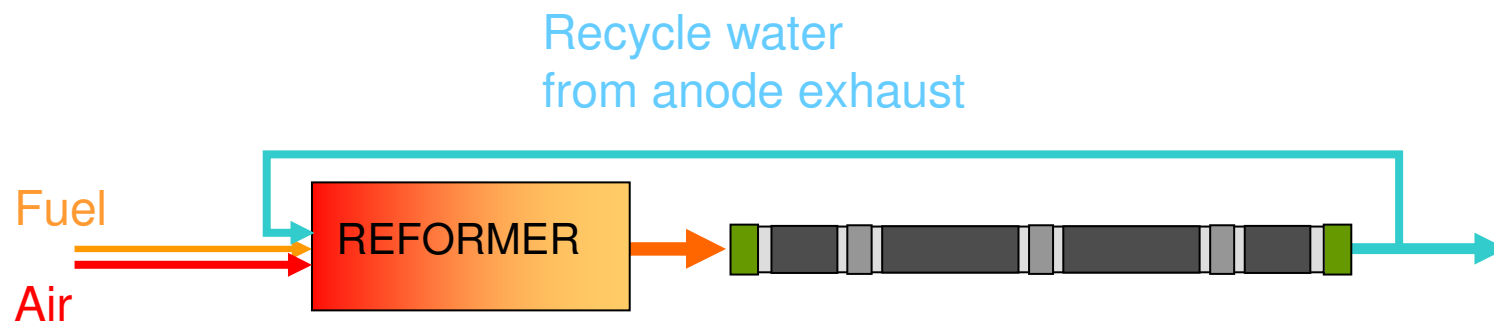
■ Technology Need

- low cost water flow meter and metering device



Water for Steam Reforming and ATR

- Fuel cells produce pure water
 - Water condensation or hot anode gas recycle
 - Increased system complexity but higher efficiency is possible



Water Recovery

■ Offgas Recirculation

- Fan Based
 - ▶ Expensive
 - ▶ Metering Difficult
 - ▶ Reliability ??
- Ejector Based
 - ▶ High Pressure Gas Required
 - ▶ Gas Boosters Expensive

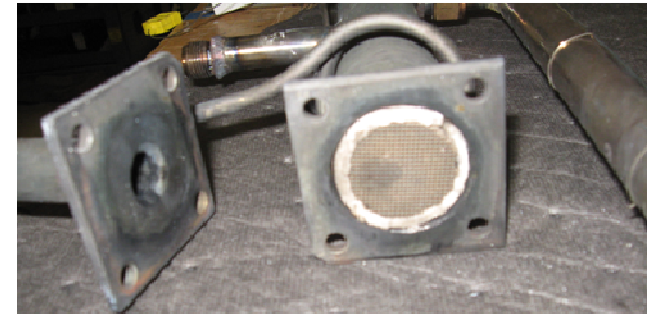
■ Offgas Condensation

- Requires condenser, water storage and delivery system
- Offgas handling/sealing issues
- Technology Need – low cost pump, metering device, flow meter

External, Integral and Internal Reforming

■ External reformers

- CPOX and ATR
- Monolith reforming elements
- Commercial catalyst companies e.g. Sud Chemie, BASF offer good solutions



■ Integral reformers

- For SR and ATR
- Proprietary reactor designs would depend on hot box design
 - ▶ needs good heat transfer and typically low aspect ratio designs

■ Internal reforming

- For SR, companies have proprietary catalyst formulations and grading for optimal cell temperature distribution

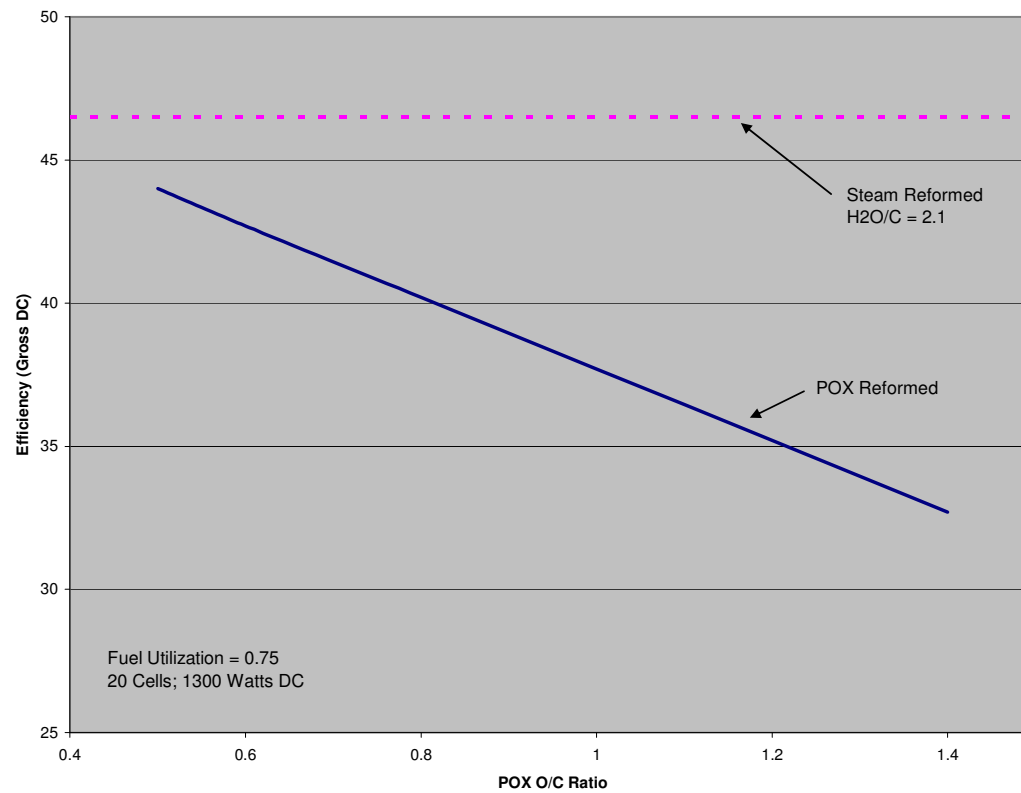
SOFC and Reforming Synergy

- Heat must be removed to avoid high stack temperatures
 - Steam reforming is ideal for efficiency
 - convert heat to chemical fuel using steam reforming reactions
- $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ $\Delta H = +226 \text{kJ/mol}$ at 800°C**
-while removing heat from cells
- Drives integral reformer and internal reforming designs

High Efficiency POX Advantages

- Acumentrics tubular cell geometry allows for proprietary method for internal recirculation permitting low o/c operation
- Eliminates the need for:
 - Offgas Condenser or Water Filtration System
 - Steam Generator
 - Water Metering Pump or Flowmeter/Modulating Valve

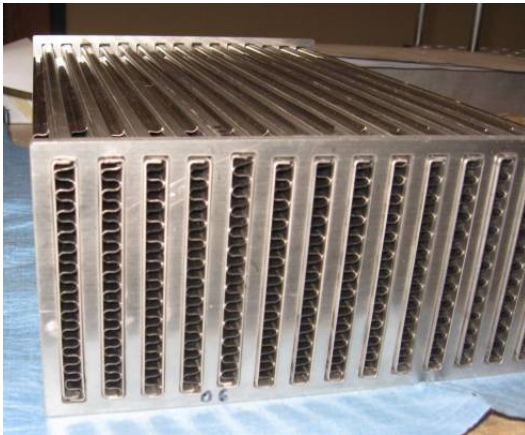
Steam vs POX Stack Efficiency



Recuperator Summary

- High Effectiveness, >80%
- High Preheat Temperature, 600-750 C
- Staged Configurations to Reduce High Alloy Materials
- Several suppliers offering solutions: Catacel, Niagara Thermal, Thermotec, Trad
- Close integration with stack allows for reduction in ducting and insulation

In-House Brazed Recuperator Manufacture



Shell and Tube

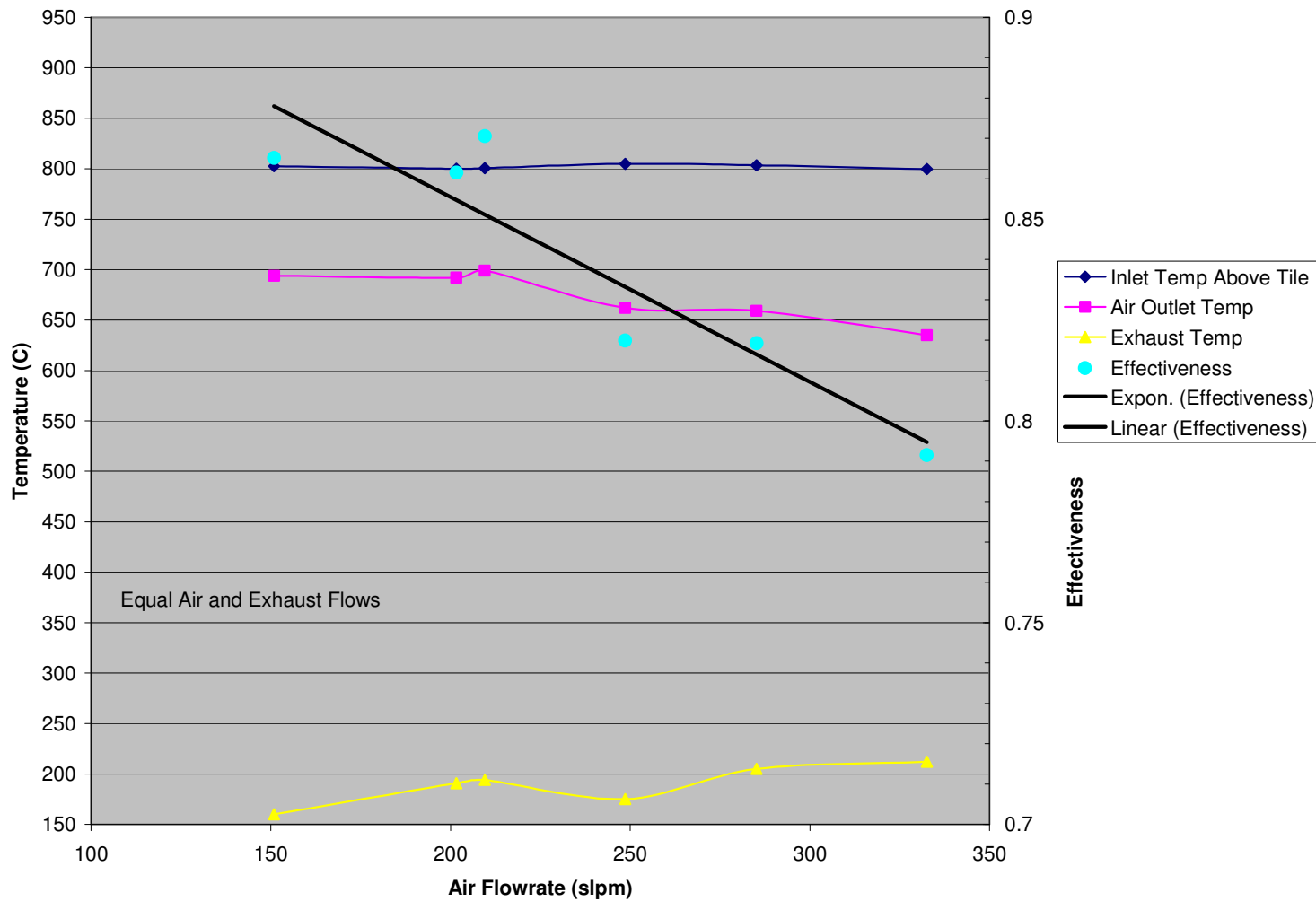


Flat Tube Radiator Style



Single Panel

Acumentrics Radiator Style Recuperator

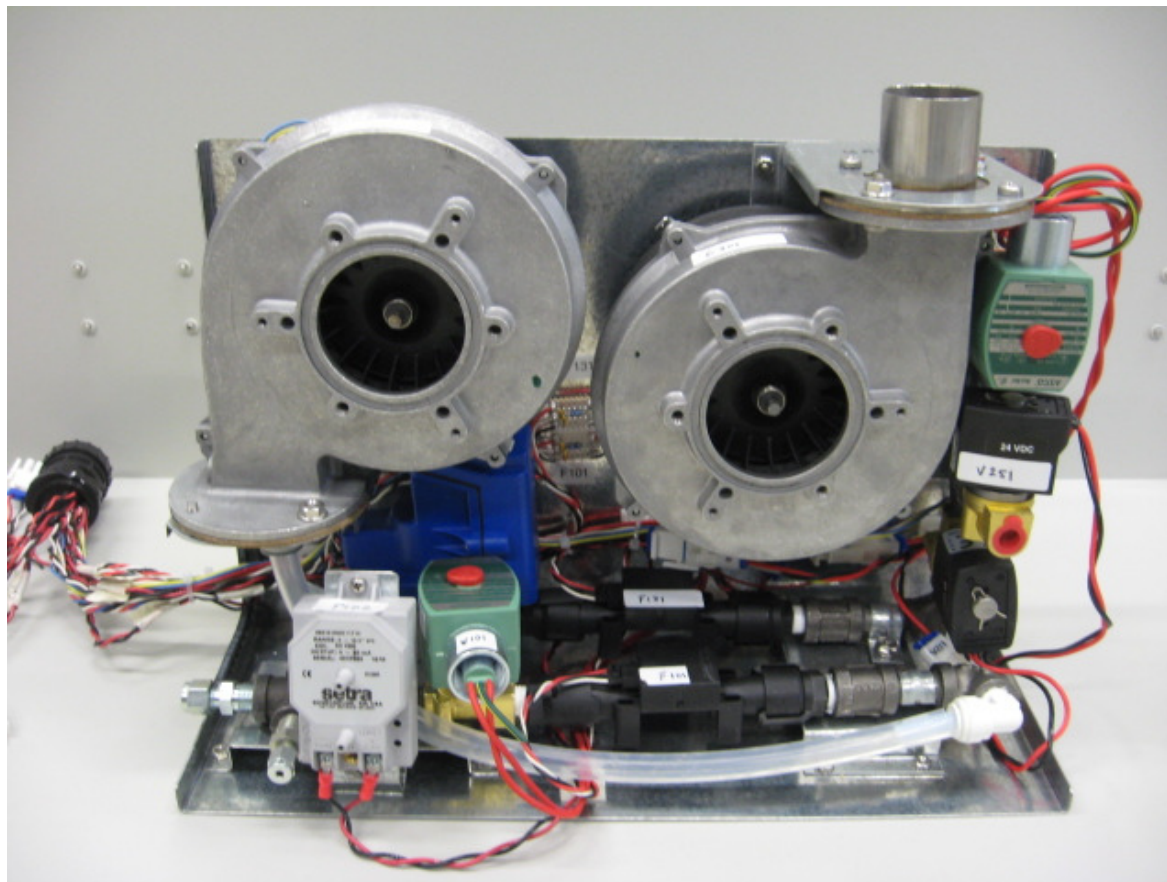


Waste Heat Recovery

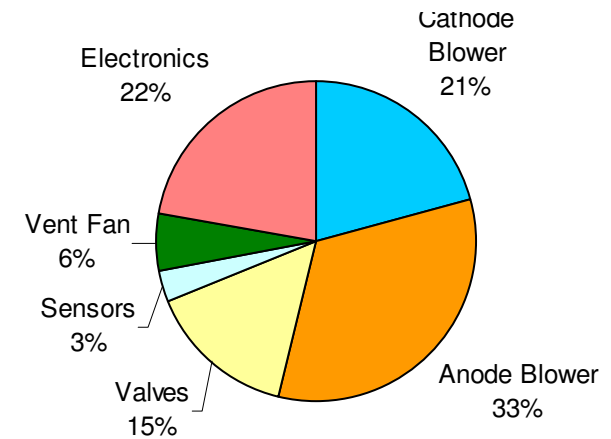
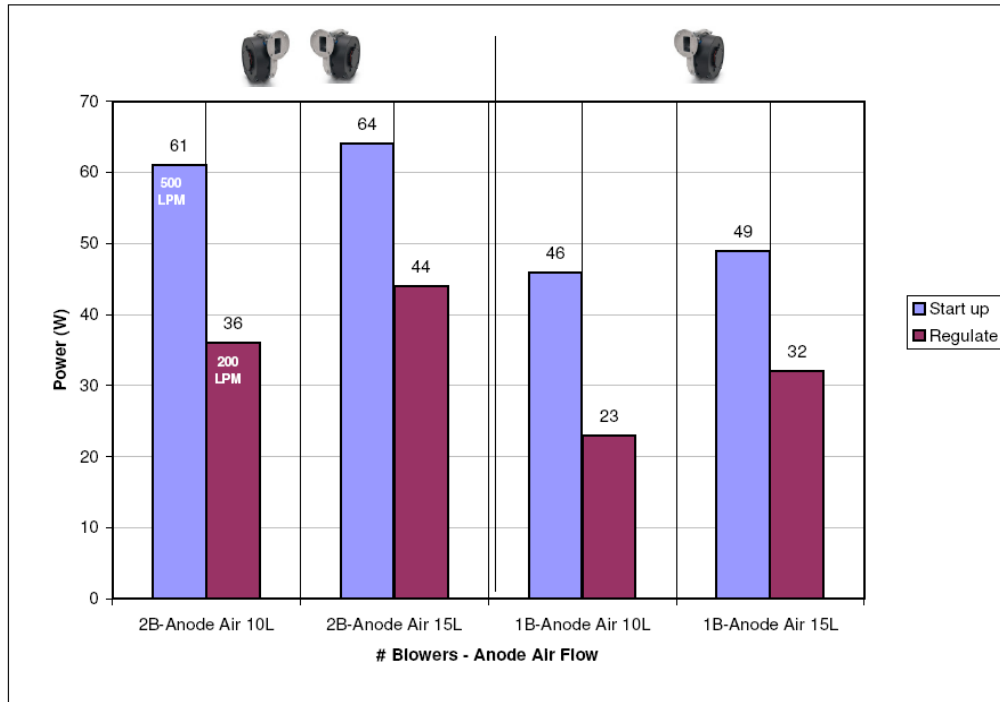
- Integration with or use of atmospheric or condensing boiler heat exchanger cores easily achieved
- Low cost due to volume production



POX Gas Utility Module



Parasitic Power



	Power (W)
Cathode Blower	17
Anode Blower	27
Valves	12
Sensors	3
Vent Fan	5
Electronics	18
Total	81

Gas Utility Module Summary

- HVAC blower and valves available at volume production costs
- Low cost air and fuel flow meters needed
- Metering pumps for liquid fuel operations extremely expensive and unproven life.
- The average 20yr home furnace only runs 20,000 hrs – 24/7 operation of HVAC components needs to be demonstrated

Power Electronic Development Needs

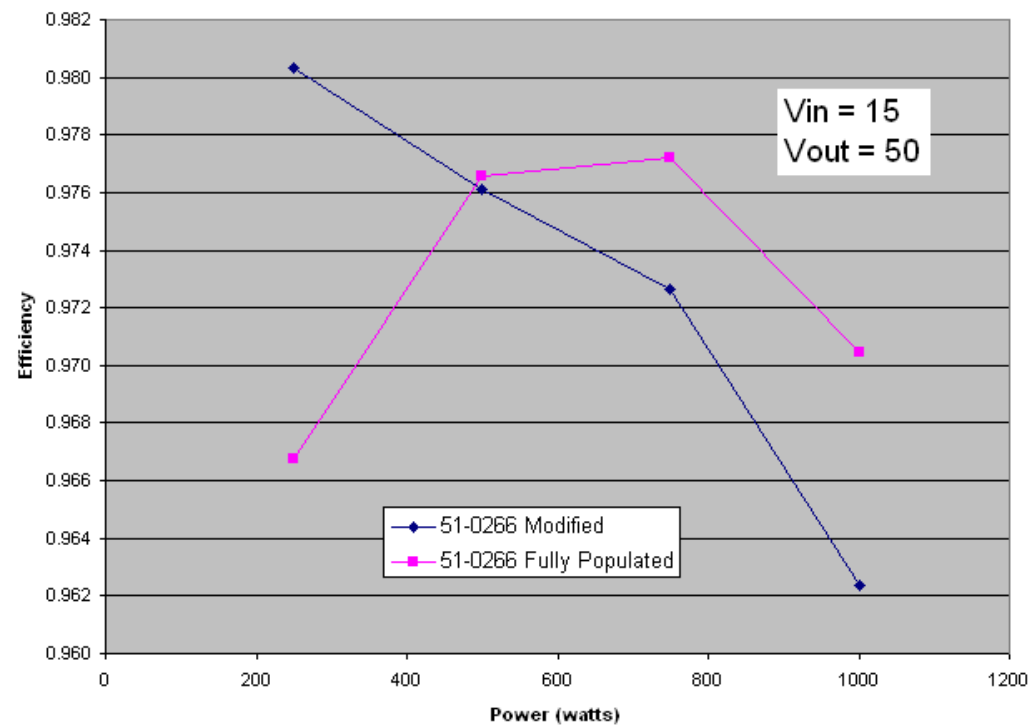
- High Efficiency, >95% Needed
- For \$500-\$750/kW factory cost, inverters can not cost more than \$100/kW
- Solar inverters in 2-3kW range are presently \$600-\$900/kW
- The battle of high efficiency and low cost requires integrated design and key trade-offs.
- Fuel cell inverters not only provide DC/AC conversion but also a DC bus for parasitics

Power and Control



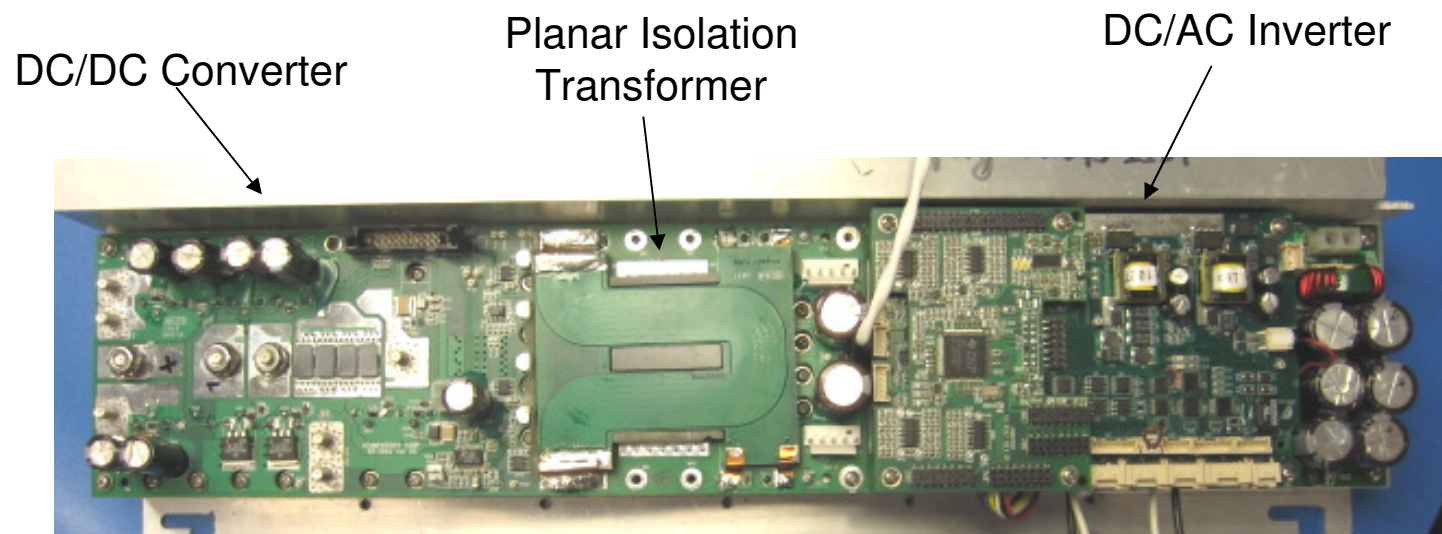
DC Regulator Re-Powering

- Baseline design de-populated to reduce cost
- Inductors reduced from 8 to 4
- Mosfets reduced from 32 to 16



Low Cost Inverter Design

- Acumentrics utilizes state of the art conversion technologies in military RUPS products
- Stand alone and Grid Connect Residential Units under development



Conclusions

- For 250 watt to 10 kW sized units, HVAC components available for the majority of process control components
 - Exceptions: sulfur sensor, air/gas flow meters, offgas recirculator
- Close integration of reformer and heat recovery equipment is necessary leading to custom, fuel cell manufacturer specific, designs
 - Elimination of components is biggest cost saving e.g. high temperature ducting, external reformer
- Subsidized, multi-unit demonstrations in niche markets needed to advance system integration and gain operating hours