OxyFuel Combustion Technologies

Prof. Greg Jackson
Dept. of Mechanical Engineering
Colorado School of Mines
Golden, CO 80401

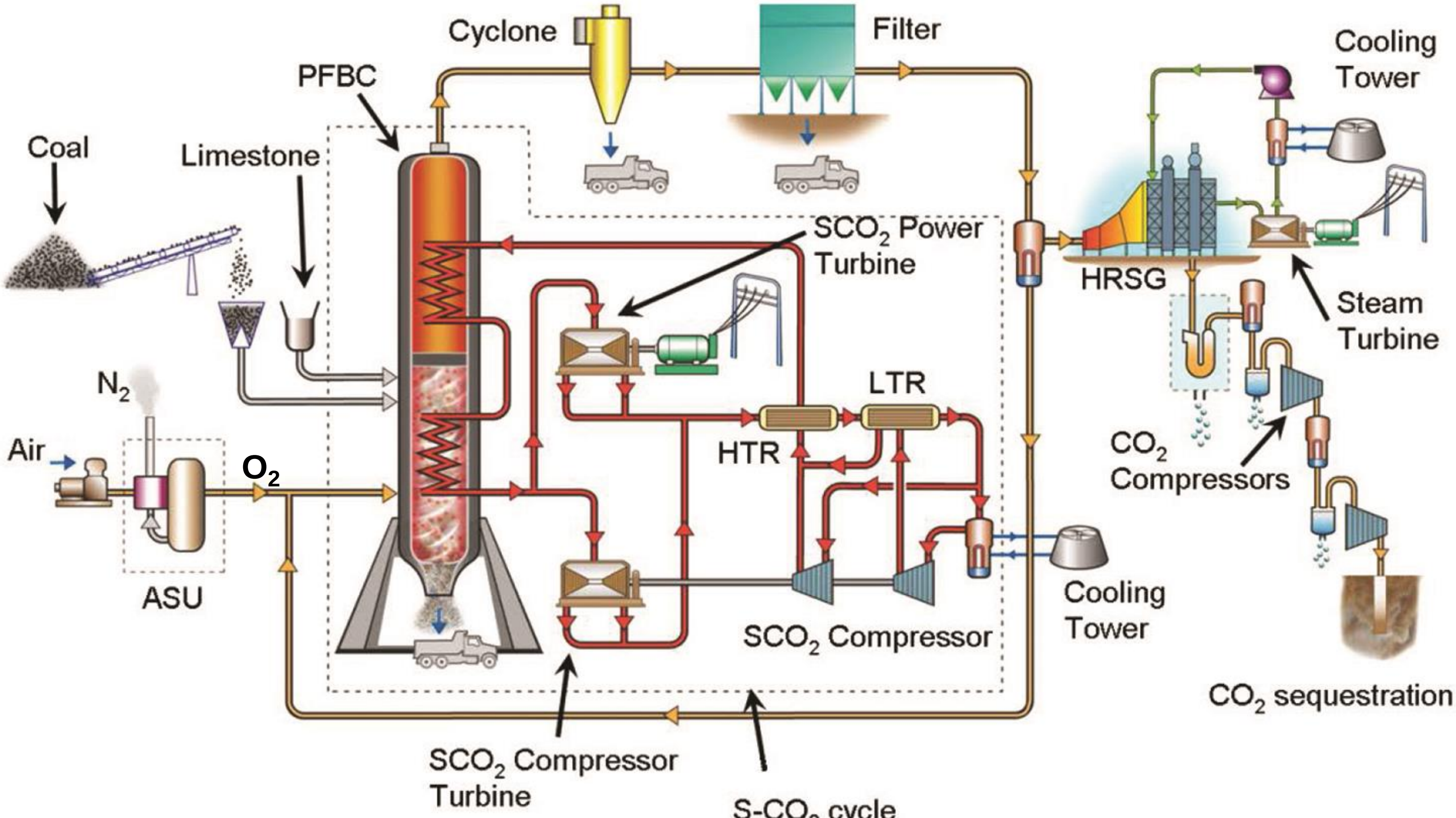
CCUS Student Week
October 17, 2018

Outline of presentation

- **Current Oxyfuel Combustion**
- Oxygen-ion Transport Membranes for Air Separation
- High-Temperature Fuel Cells
- Chemical looping Combustion

Oxyfuel combustion of coal with closed Brayton supercritical-CO_2 power cycles and CO_2 capture

- U.S. DOE NETL funded efforts to design oxyfuel combustion with high efficiency s-CO_2 cycles and bottoming steam cycle and CO_2 capture



From Vega, Sonwane, & Eastland (Rocketdyne) 2014

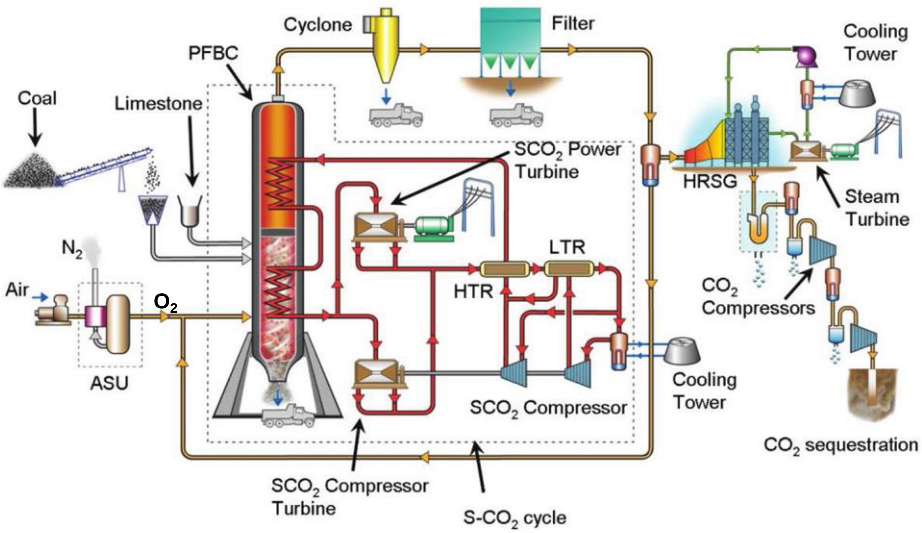
Penalty of conventional oxyfuel combustion

- Comparison of plant generating efficiency and capital expenditure of CO_2 capture technologies from Chen, Yong, & Ghoneim (2012).

PC: Conventional pulverized coal with supercritical steam cycle without CO_2 capture
Post: PC with post CO_2 capture,
A-Oxyf: Atmospheric oxy-coal with flue gas recycle and CO_2 capture
P-oxyf: Pressurized oxy-fuel combustor with flue gas recycle and CO_2 capture,

Oxyfuel combustion of coal with closed Brayton supercritical-CO_2 power cycles and CO_2 capture

- Advantages of oxyfuel combustion
  - Technology largely available
    - Air separation unit
    - Pulverized fluidized bed combustor
    - CO_2/H_2O flue gas separation
  - Combustor coupling to a variety of higl efficiency power plants
    - Supercritical steam
    - Developing supercritical CO_2
  - Minimal emissions
    - Almost no NO_x emissions
    - Ease of flue-gas processing
  - Not sensitive to high-purity O_2

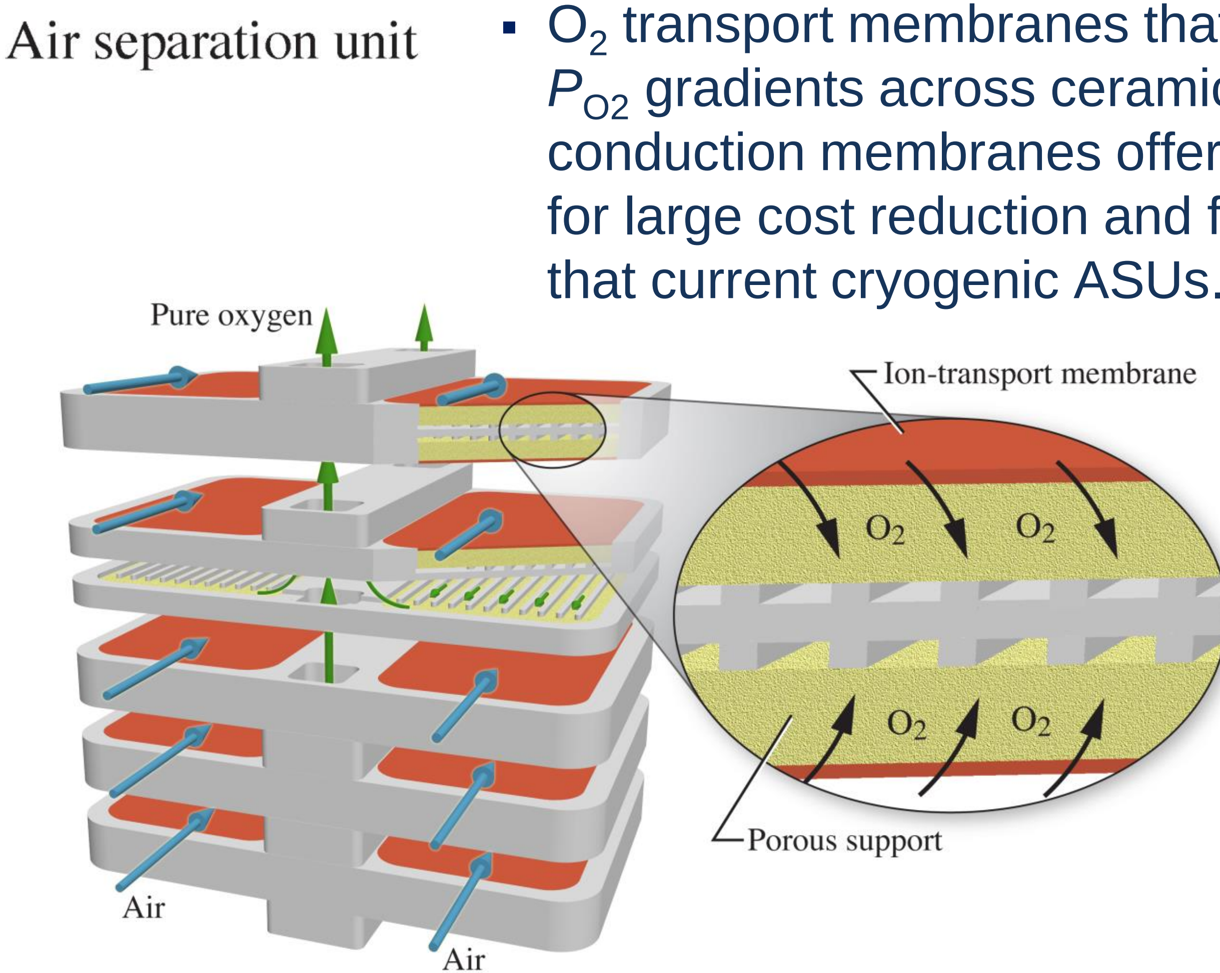


- Disadvantages
  - LCOE costs high (≥ 10¢/kWh)
  - Temperature distributions in the boiler

Outline of presentation

- Oxyfuel Combustion
- **Oxygen-ion Transport Membranes for Air Separation**
- High-Temperature Fuel Cells
- Chemical looping Combustion

Oxygen-transport membranes (OTMs) as efficient air separation units to replace cryogenic units



- O_2 transport membranes that rely on P_{O2} gradients across ceramic ion-conduction membranes offer potential for large cost reduction and faster times that current cryogenic ASUs.

- Large gas companies have invested in this technology but challenges remain.

Scaled-up OTMs for air-separation with failures in commercial service environments

LCF-based
air-separation system

AIR PRODUCTS

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Anderson, Armstrong, Broekhuis, Carolan, Chen, Hutcheon, Lewinsohn, Miller, Repasky, Taylor, Woods, "Advances in ion transport membrane technology for oxygen and syngas production," *Solid State Ionics*, 288:331-337 (2016)

Chemo-mechanical coupling significant local stresses leading to failures in OTMs

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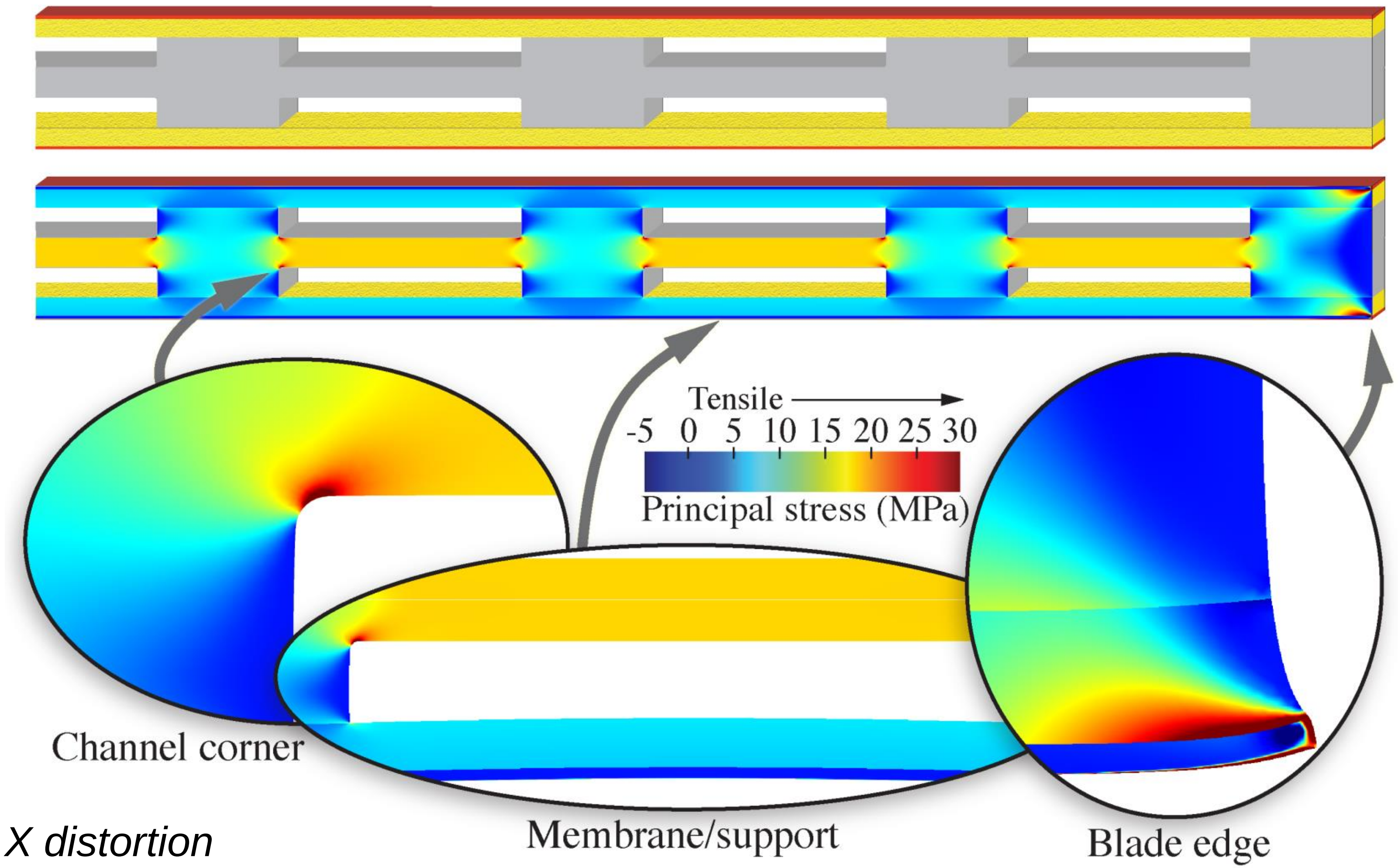
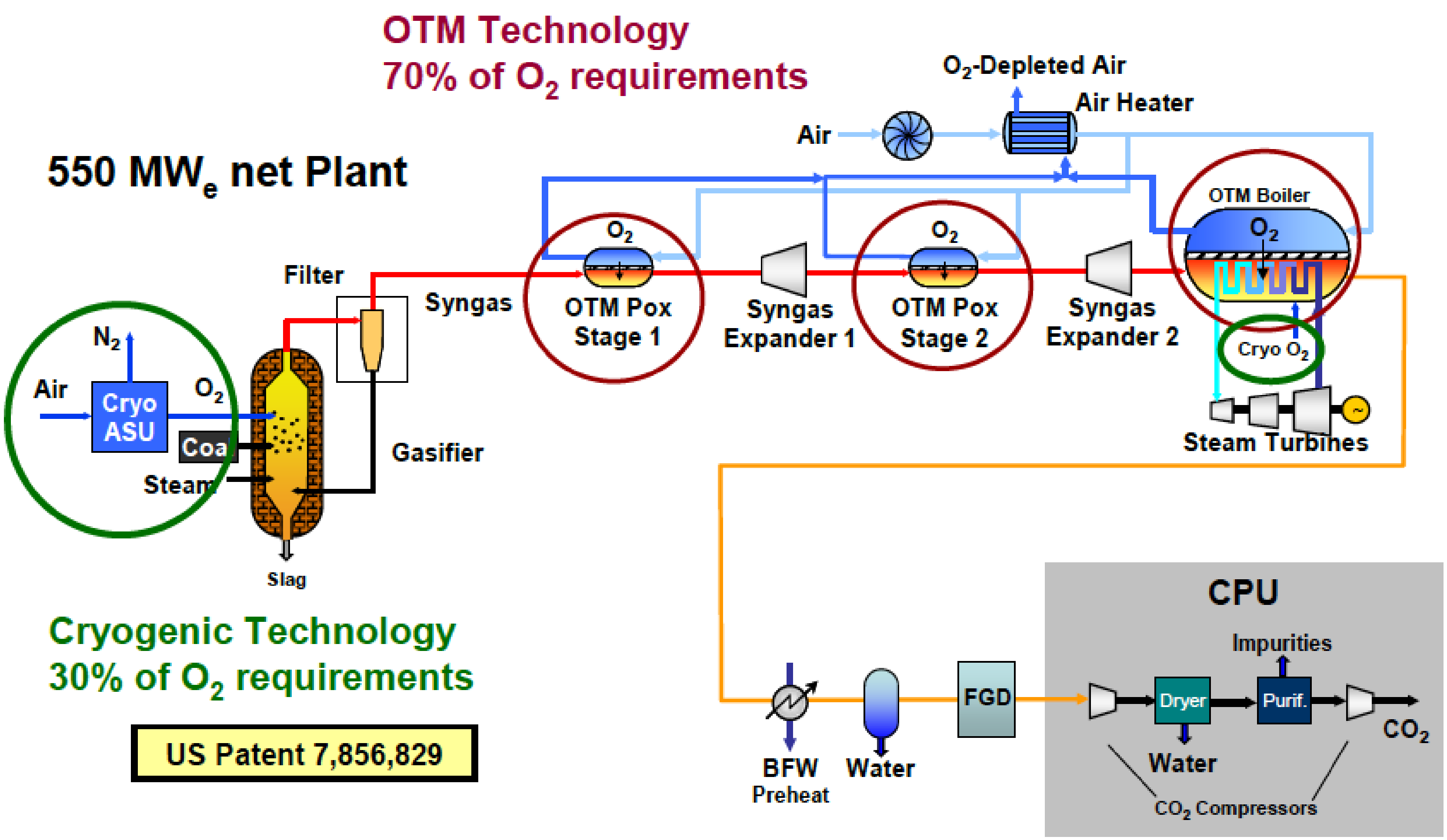


250 X distortion

From Euser, Zhu Berger, Zhu, Lewinsohn & Kee (Mines) 2017

OTMs have been proposed for many aspects of a zero emission combustion plant



From Shah, Jamal, Drenvich et al (Praxair) 2010

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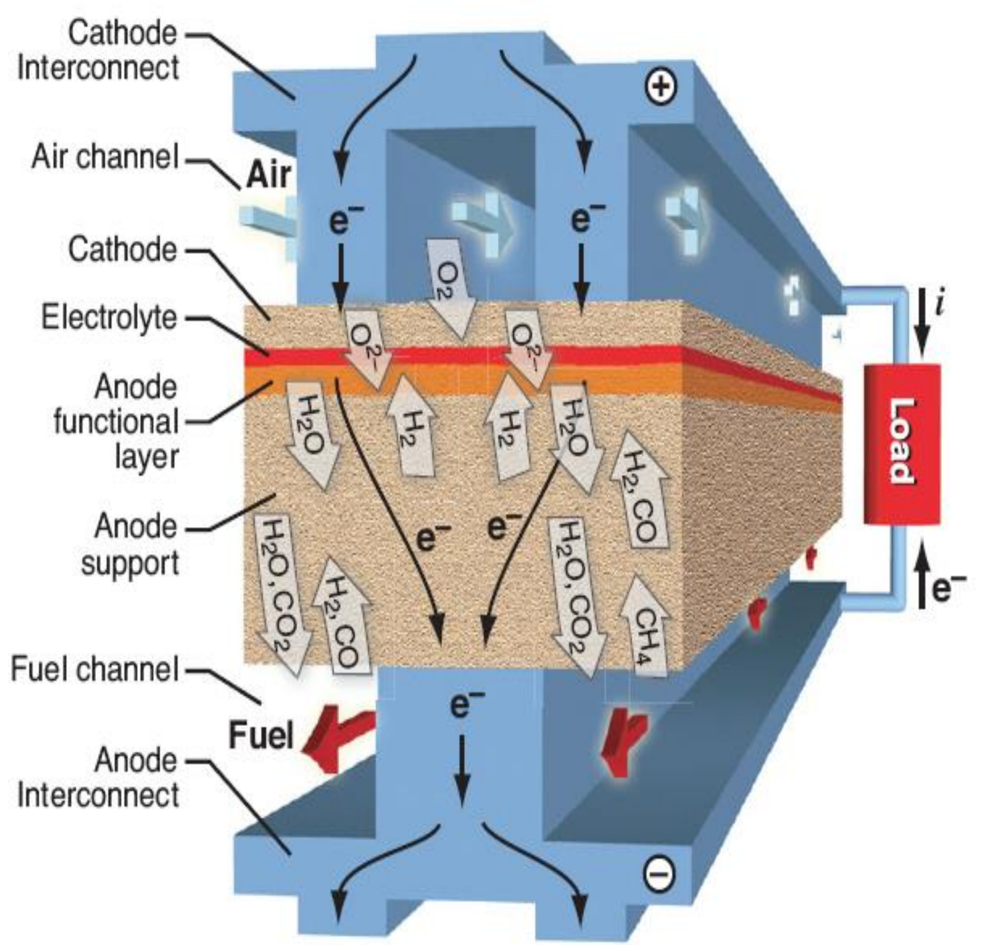
Solid oxide fuel cells (SOFCs) as an oxy-fuel combustion with direct electrochemical conversion

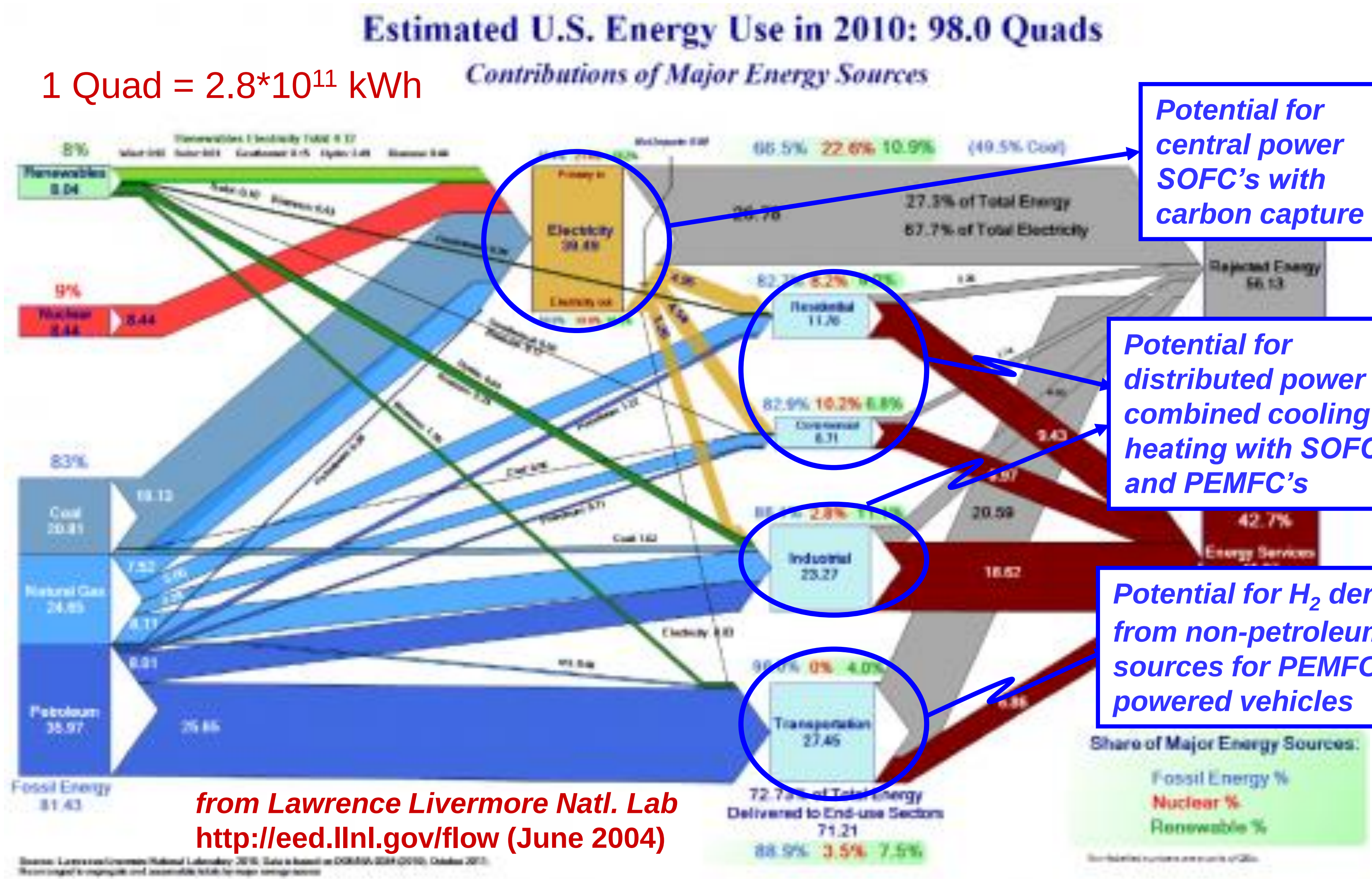
- **Solid oxide fuel cells (SOFCs) provide a lot of benefits for fossil fuel conversion.**
- **High potential for CO_2 capture**
- Thin (10-20 µm) O^{2-} conducting electrolytes provide oxidizer from air-fed cathode to fuel-fed anode
- To date, distributed power SOFCs have costs >>$2000 kW_{elec} due in part to low production volumes but also to high energy ceramic processing.



from Kee, Zhu, Sukeshini, and Jackson, Combust. Sci. Tech. 2008

Fuel cells as a potential energy conversion technology to assist in carbon capture

1 Quad = 2.8×10^{11} kWh



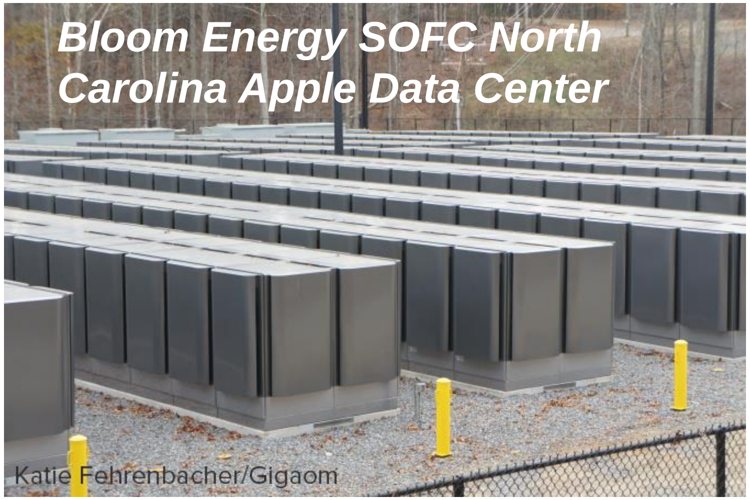
Potential for central power SOFC's with carbon capture

Potential for distributed power with combined cooling and heating with SOFC's and PEMFC's

Potential for H_2 derived from non-petroleum sources for PEMFC powered vehicles

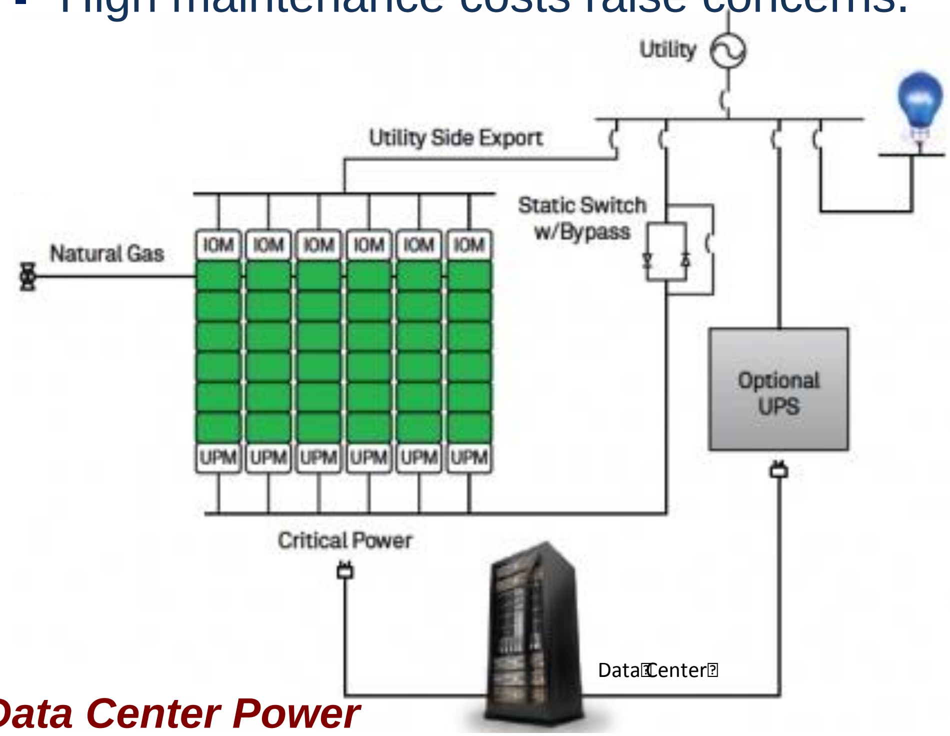
from Lawrence Livermore Natl. Lab
http://eed.llnl.gov/flow (June 2004)

SOFCs for distributed power applications



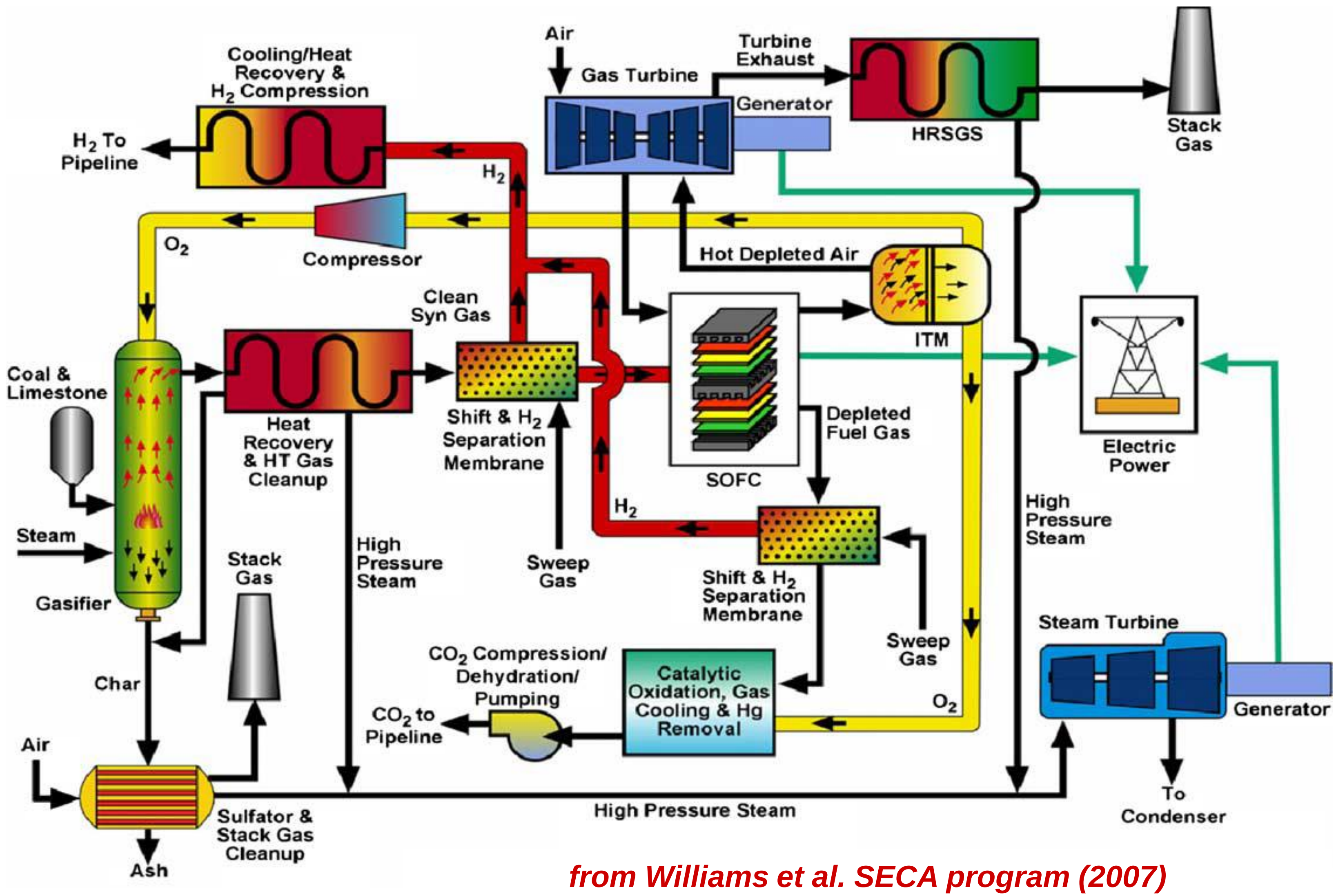
- Bloom Energy supplies 125 & 250 kW_{elec} natural-gas fueled SOFC systems that run at 50 – 60% efficiency but at costs of >$7000 kW_{elec} (in comparison to $1000 kW_{elec} for diesel with 40-50% efficiency).
- High maintenance costs raise concerns.

- If NG costs ~$0.035/$kW_{th}$ and electricity costs ~$0.10/$kW_{elec}$, a payback period of 20 years would exist for a 55% efficient SOFC at $8000 kW_{elec}.
- Economics are highly sensitive to gas and electricity costs and make value proposition region specific.



Data Center Power from Bloom Energy

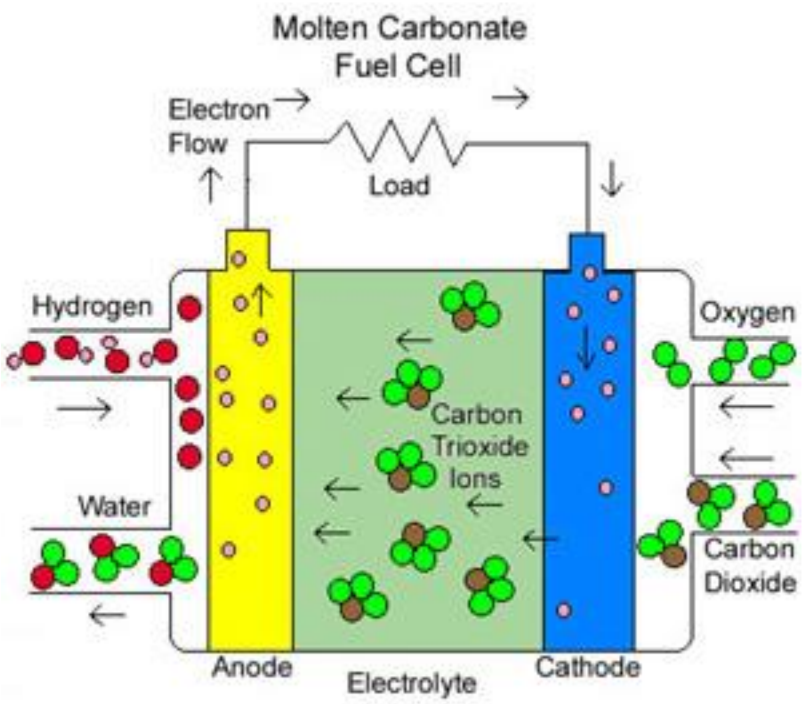
Early proposals for SOFCs on central coal power with gas-turbine pressurization and bottoming cycle



from Williams et al. SECA program (2007)

Molten carbonate fuel cells as a means of carbon capture

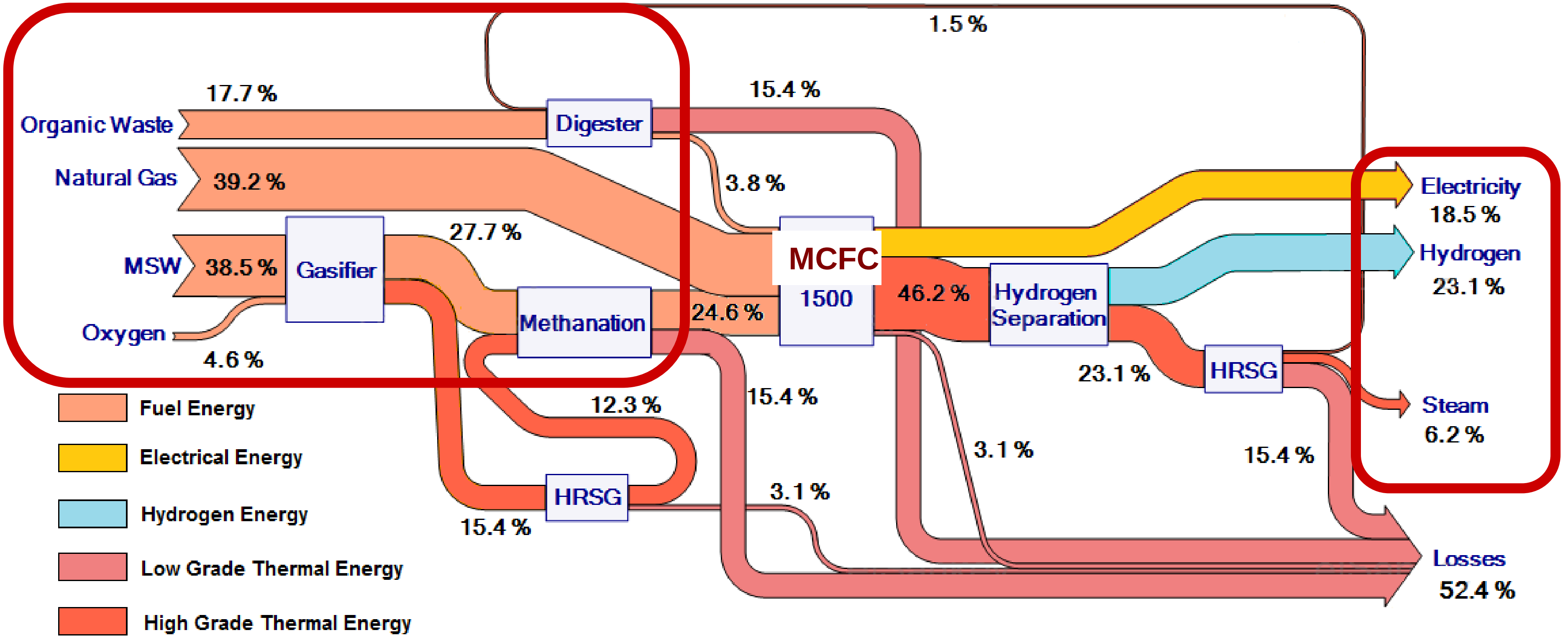
- High-temperature fuel cells such as molten carbonate fuel cells (MCFC) require large capital investments for both development and plant assembly.
- Thus, systems are relatively large for fuel cells (> 300 kW) and typically not cheap (~$1400 kW$_{elec}$).
- World leaders Fuel Cell Energy are showing, high-T fuel cells like MCFC can be more than power generation.
- Opportunities for combined heat, power, and hydrogen show the value in fuel cells converting low-cost gas into value-added products.



from NPTEL Fuel Cell Course http://nptel.ac.in/courses/103102015/3

Molten carbonate fuel cell opportunities for multi-functional distributed power plants

- MCFC can add much more value such as conversion of waste to relatively clean energy , heat and H_2 (CHHP).



from Spencer, Moton, Gibbons, et. al 2013

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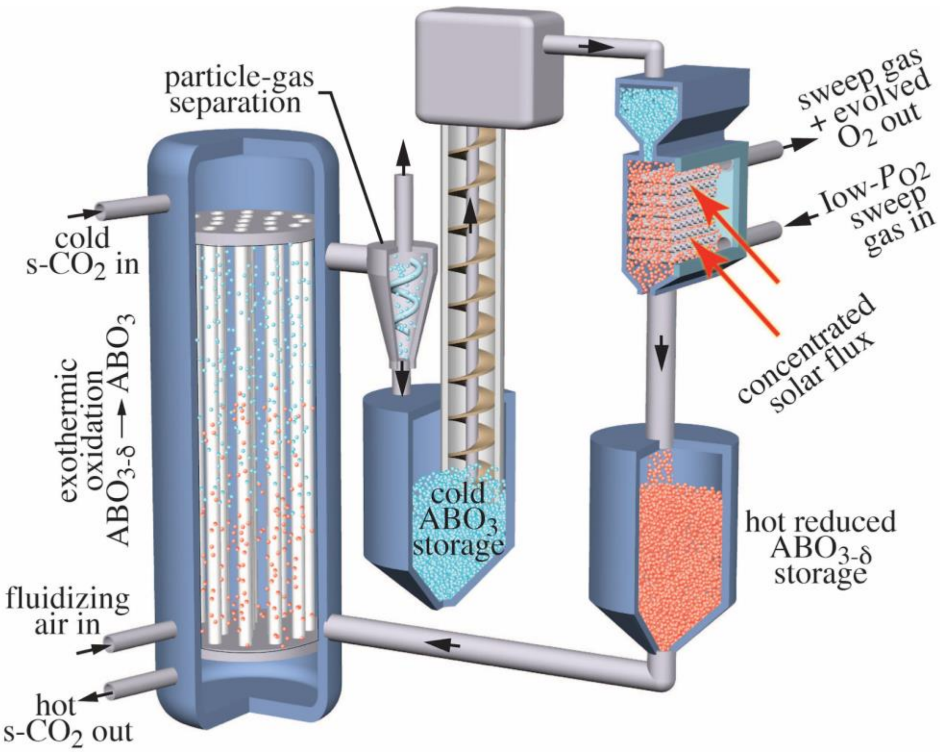
- **High-Temperature Fuel Cells**
- **Chemical looping Combustion**

Chemical looping can be coupled to thermochemical energy storage

- Reducible perovskite oxides such as $CaMnO_3$ can provide thermo-chemical energy storage (TCES) and controlled heat release at temperatures T above 800˚C.
- High chemical reduction occurs at O_2 partial pressures, $P_{O2} \geq 10^{-4}$ bar.
- Re-oxidation and cooling can be sustained at T relevant for driving supercritical CO_2 power cycles.
- The challenge is how to accelerate kinetics for high specific TCES.



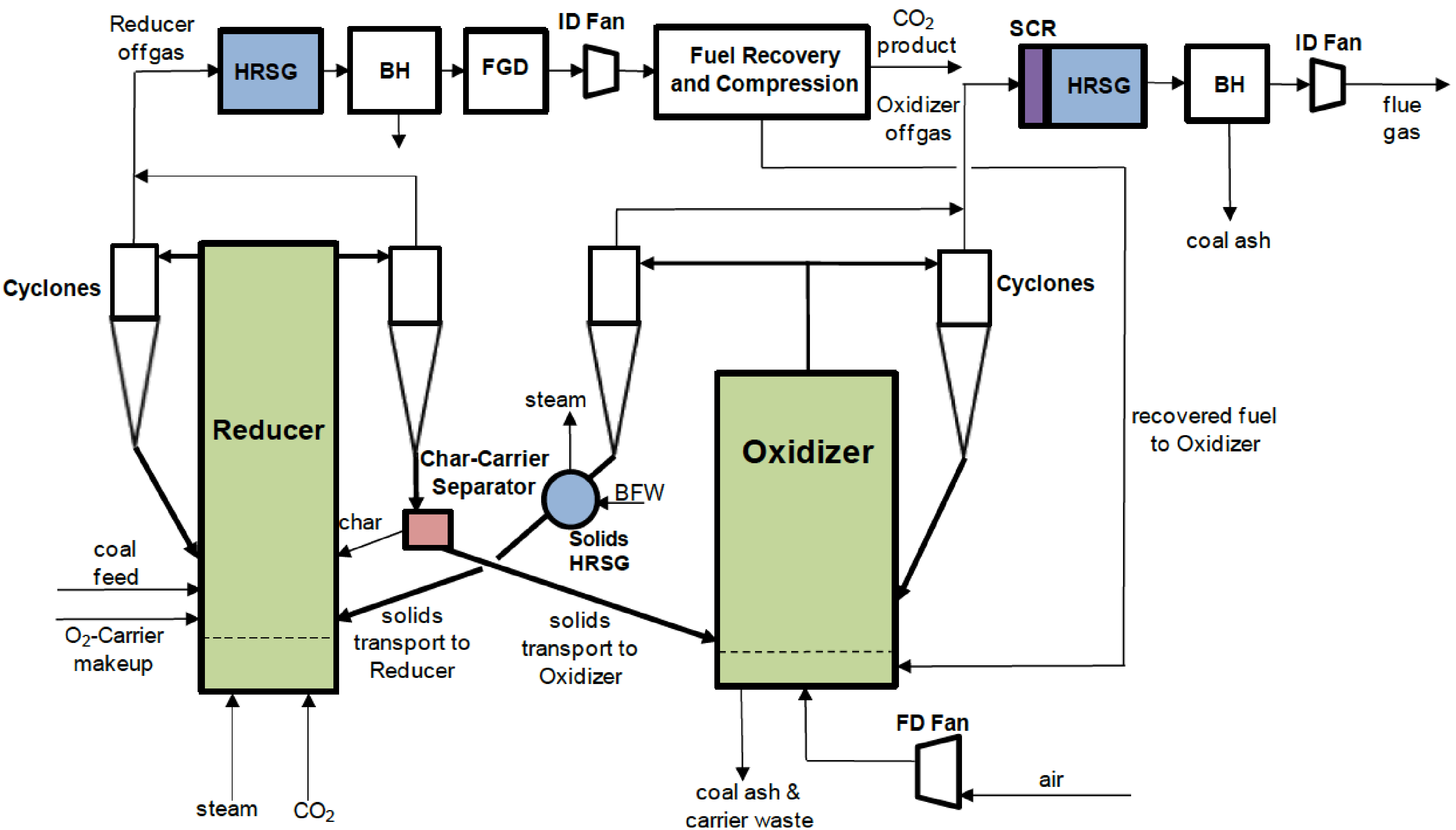
from Imponenti et al. 2017, Albrecht et al.2018

$CaMnO_3$ (@ $T_C \leq 500$˚C & $P_{O2} \approx 0.2$ bar) + heat

⇕

$CaMnO_{3-\Delta\delta}$ (@ $T_H \geq 900$˚C & $P_{O2} \approx 10^{-4}$ bar) + $\Delta\delta/2 \cdot O_2$

Chemical looping combustion integrated with gas processing for CO_2 sequestration



from NETL 2014

Chemical looping combustion materials and potential costs

- NETL-funded studies on two common chemical looping materials have shown cost performance superior to conventional pulverized bubbling bed reactor with oxyfuel combustion

Oxygen Carrier Type	Fe_2O_3	$CaSO_4$	Conventional PC BBR Case 12
Plant Net Capacity (MW)	550	550	550
Plant Efficiency (%, HHV)	35.1	32.6	28.4
Carbon Capture Efficiency (%)	95.8	91.4	90
CO_2 Product Purity (mole% CO_2)	98.9	99.7	100
Total Plant Cost ($/kW; $2011)	2,379	2,597	3,563
Cost of Electricity ($/MWh; 1^{st}-year w/o T&S)	115.2	104.7	137.3
Reduction in COE (%) [Reference IGCC w CCS @ 133 $/MWh]	13.4	21.3	-3.2
Cost of Captured CO_2 ($/tonne) [Reference SC PC plant @ 81.0 $/MWh]	40.1	26.8	56.5

Particle materials for chemical looping

- Multivalent cations such as Fe^{x+} and Mn^{x+} provide promising potential for chemical looping with CO_2/H_2O effluent for ease of carbon capture.

Material	ρ [kg/m³]	$C_{p,avg}$ [kJ/kg-K]	$\Delta h_{500\text{-}800}$ [kJ/kg]	$\Delta h_{500\text{-}900}$ [kJ/kg]	Cost [$/kg]	Cost[b] [$/kWh]
Co_3O_4	6110	0.96	**1125**[b]	**1226**	≈ 27.0	≈ 86
$Mn_{1.8}Fe_{0.2}O_3$	4630	0.88	219	620	< 1.5	< 12
$Ca_{0.9}Sr_{0.1}MnO_{3-\delta}$	4530	0.86	524[b]	706[a]	<2.0	<21

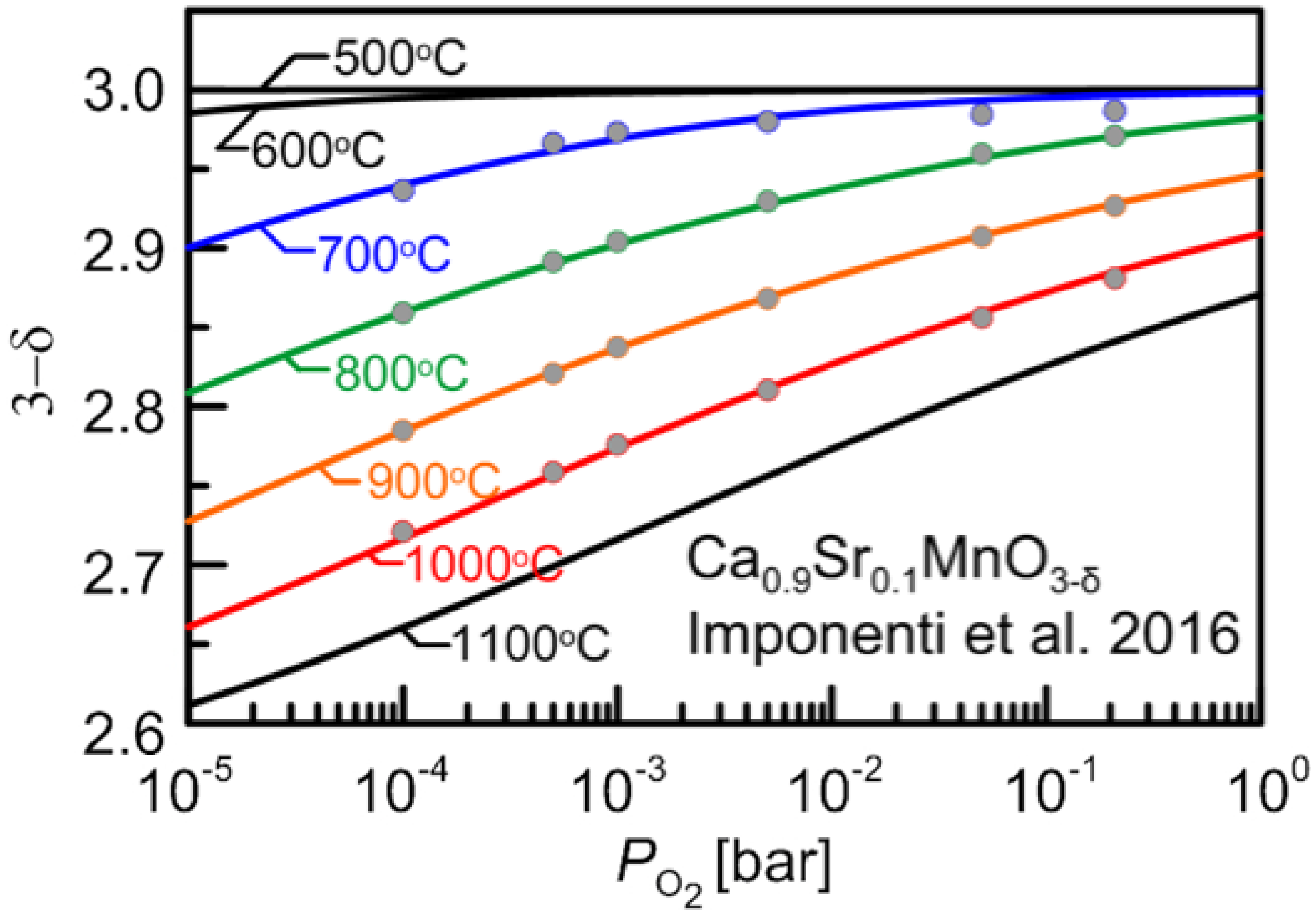
a) equilibrated at P_{O2} = 0.0001 bar
b) Based on thermal energy stored from 500 to 750˚C

- European researchers have identified doped $CaMnO_{3-\delta}$ as a promising chemical looping oxygen carrier.

Compositions	kg oxide / kg fuel]	T_H [˚C]	P_{O2} [bar]	Δh_{R2} [kJ/kg]
$Ca_{0.90}Sr_{0.10}MnO_{3-\delta}$ + C_nH_{2n} fuel	52.2	920	5e-6	835
	63.2	830	3e-6	690
	79.0	750	706	552

Cost-effective doped $CaMnO_{3-\delta}$ for reversible release and uptake oxygen in chemical looping systems

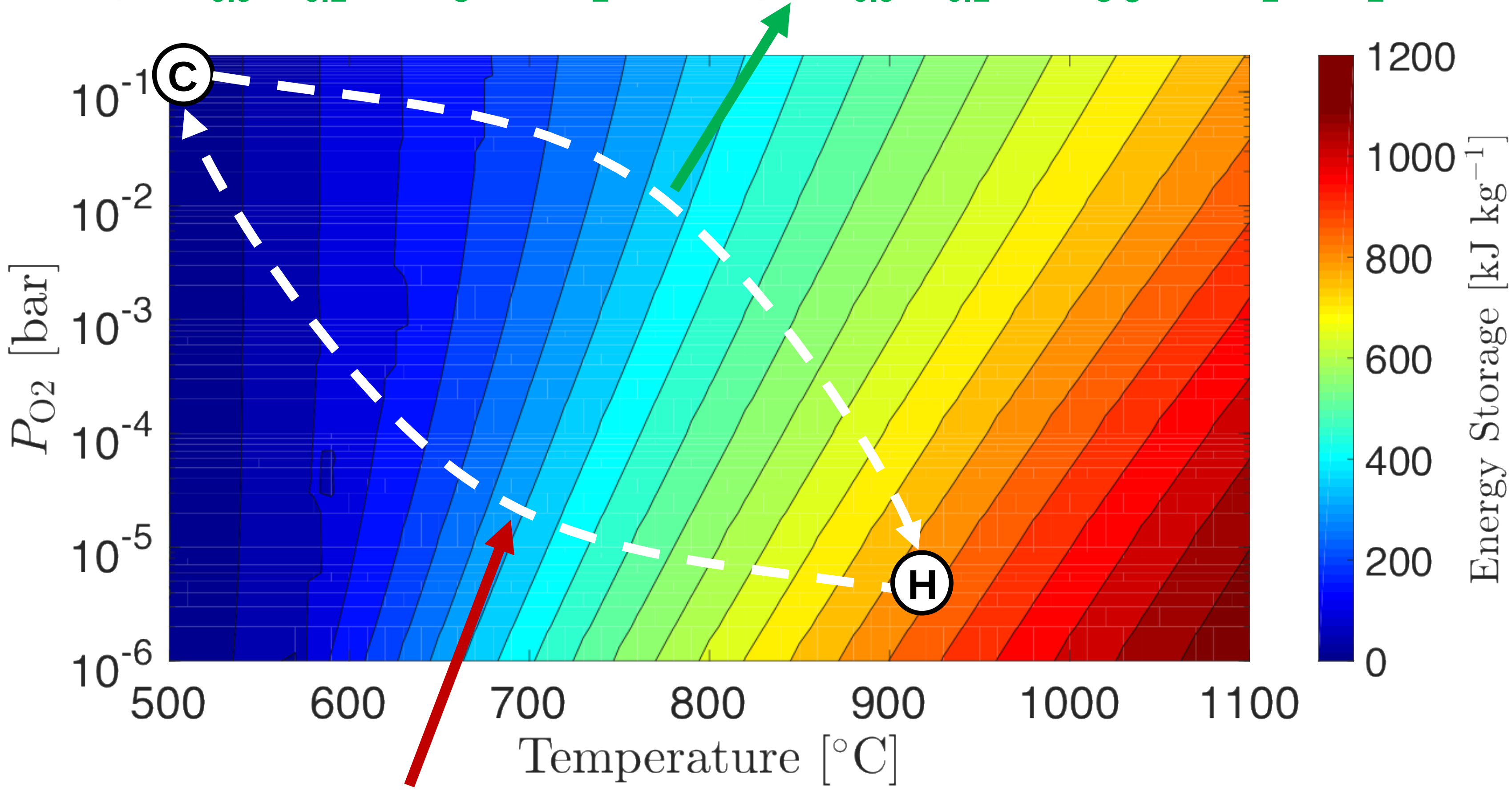
- Thermochemistry modeled by two-step point-defect reaction mechanism:



Thermodynamics of chemical looping combustion with Sr-doped $CaMnO_{3-\delta}$

- Specific energy stored during reduction and heating from T_C = 500˚C in air

$(3/\delta)\cdot Ca_{0.9}Sr_{0.1}MnO_3 + CH_2 \Rightarrow (3/\delta)\cdot Ca_{0.9}Sr_{0.1}MnO_{3-\delta} + CO_2 + H_2O$



$(3/\delta)\cdot Ca_{0.9}Sr_{0.1}MnO_{3-\delta} + O_2 + 3.76N_2 \Rightarrow (3/\delta)\cdot Ca_{0.9}Sr_{0.1}MnO_3 + 3.76N_2 + \Delta h_{R2}$

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Compositions	kg oxide / kg fuel]	T_H [˚C]	P_{O2} [bar]	Δh_{R2} [kJ/kg]
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	63.2	830	3e-6	690
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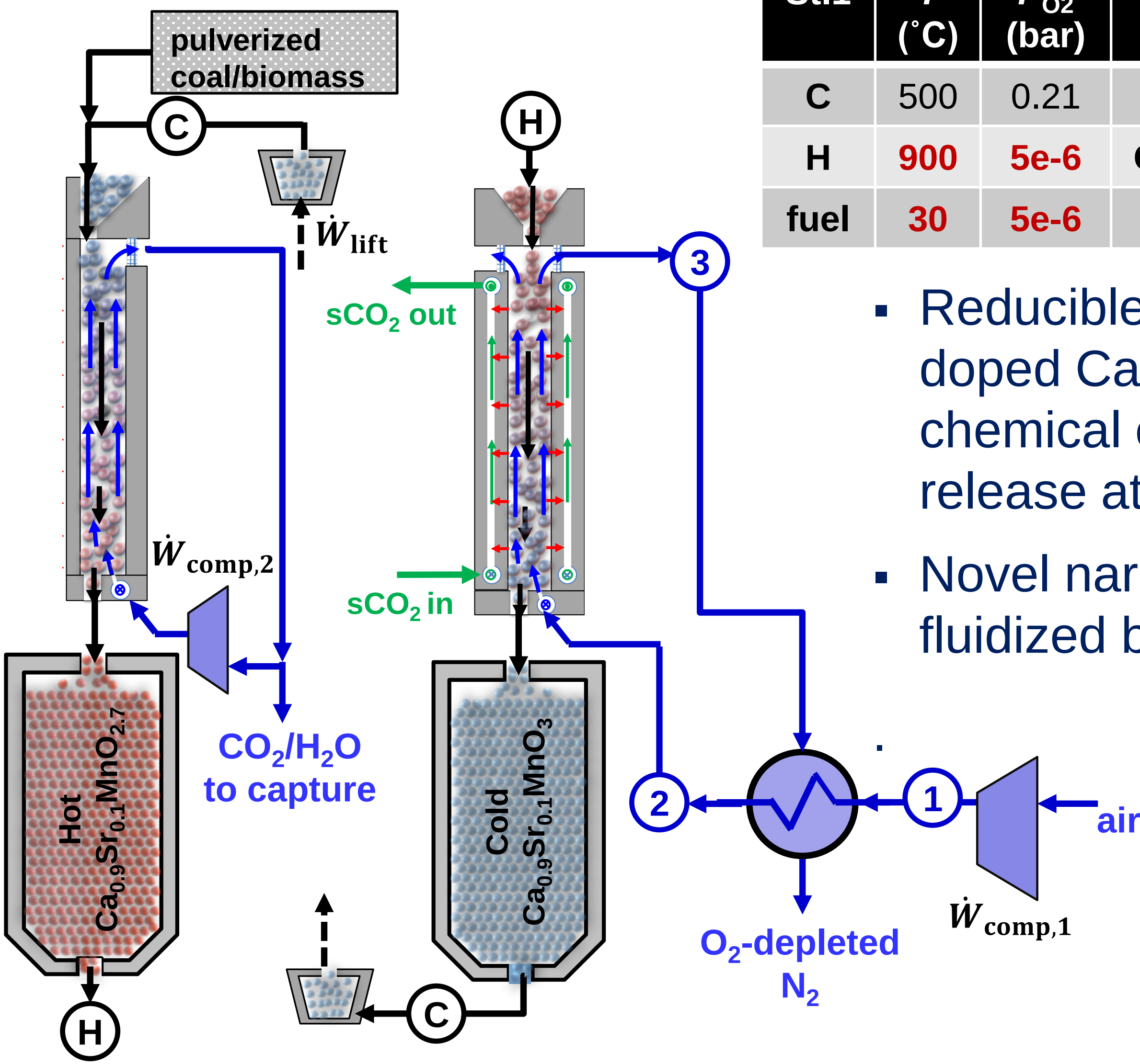
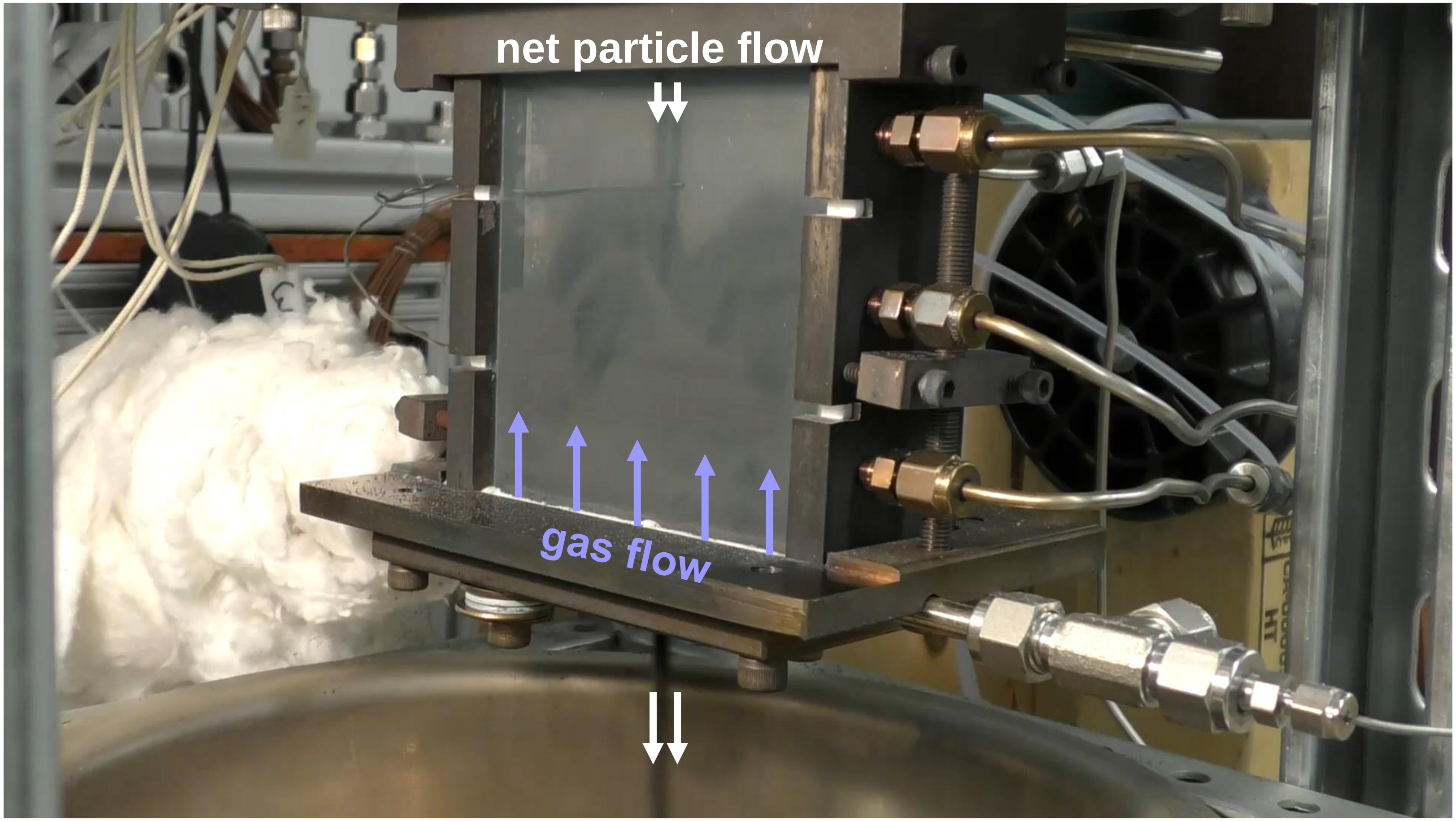
Proposed Perovskite Chemical Looping Combustion Subsystem for 100 MW_{elec} plant



St.1	T (˚C)	P_{O2} (bar)	Stoich.	Δh_{tot} kJ/kg	Flow (kg/s)
C	500	0.21	$Ca_{0.9}Sr_{0.1}MnO_3$	0.0	239.5
H	900	5e-6	$Ca_{0.9}Sr_{0.1}MnO_{2.7}$	835	232.1
fuel	30	5e-6	C_nH_{2n}		4.6

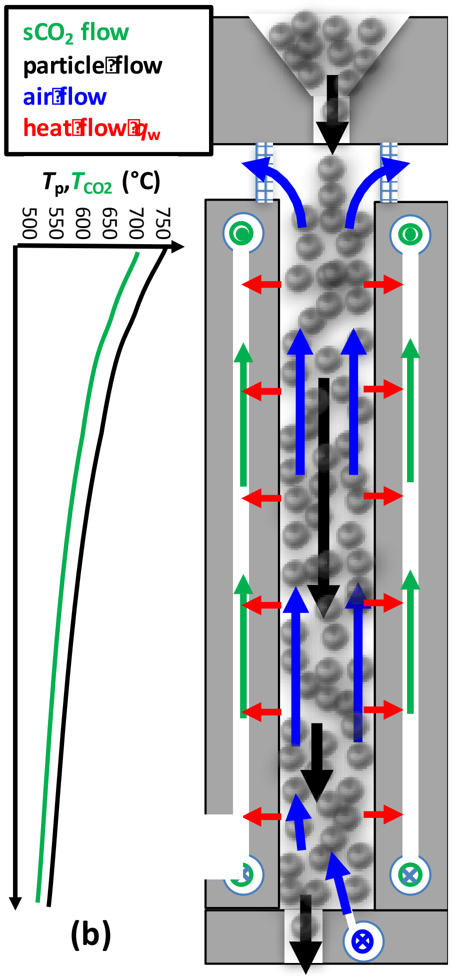
- Reducible perovskite oxides such as doped $CaMnO_3$ can provide thermo-chemical energy storage for heat release at off peak hours.
- Novel narrow-channel, counterflow fluidized beds offer modular system.

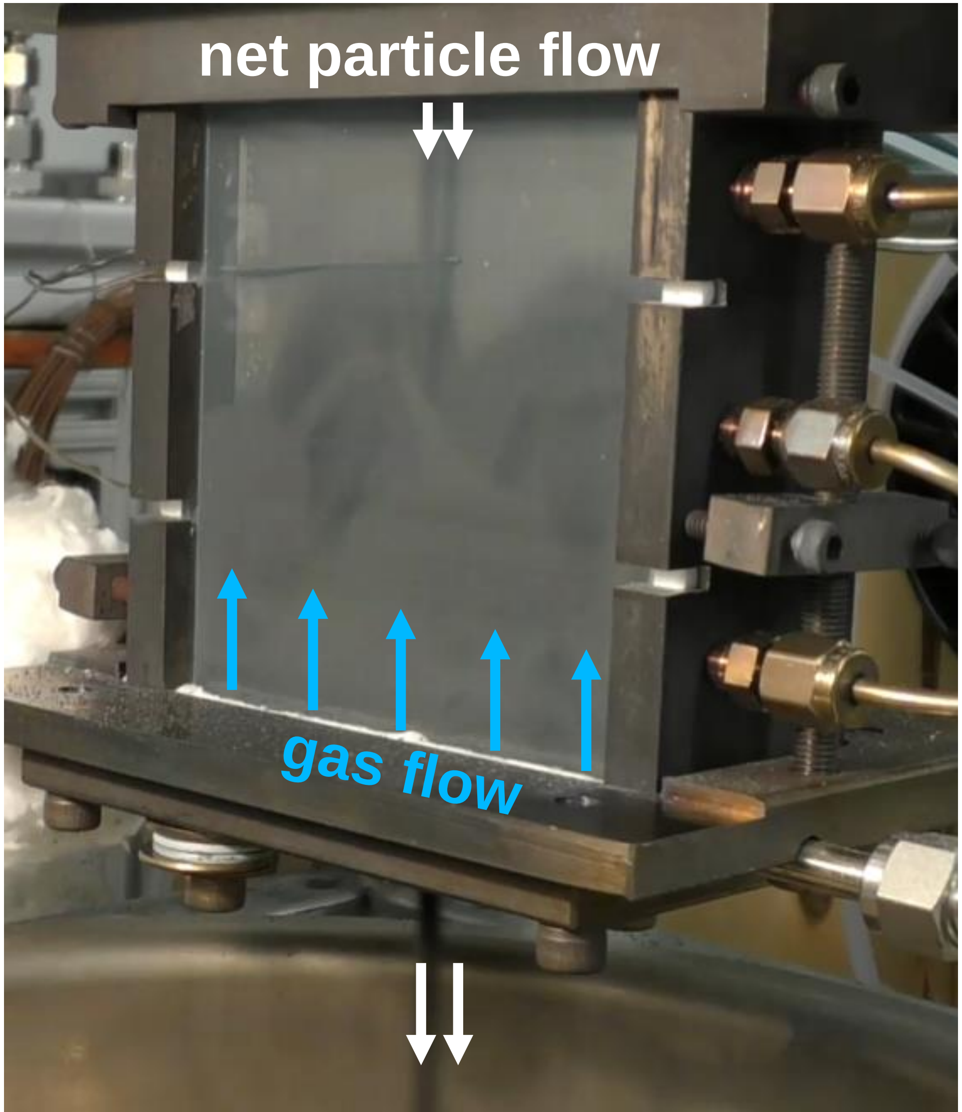
Visualization of narrow-channel, counterflow fluidized bed



from Miller, Pfutzner, & Jackson 2018

Novel modular heat recovery devices to make coal, waste and biomass combustion more modular





Thoughts for further exploration

- Current oxyfuel combustion technologies with traditional air-separation units and steam power plants do not make a compelling technical or economic cases.
  - Game changers include supercritical-CO_2 power cycles and oxygen transport membranes for lower cost and more flexible O_2 separation.
- Solid oxide fuel cells provide an novel approach to achieving very high efficiencies with carbon capture, but their costs do not scale and applications seem currently limited to distributed power applications.
- Chemical looping seems like a promising approach to combust pulverized coal, biomass, and waste.
  - High mass of reduced oxide can serve as thermochemical energy storage
  - Novel fluidized bed designs for energy transfer to the power cycle and fluidized combustor here may enable modular designs.

Acknowledgements

- Solid oxide fuel cell work and oxygen transport membrane work was supported by Prof. Robert Kee, Prof. John Berger Dr. Huayang Zhu, and former student Bryan Euser.

- Perovskite redox cycles based on particle fluidized beds ha been supported by students Luca Imponenti , Dan Miller, and Rounak Kharait, and formerstudent Dr. Kevin Albrecht, and Profs. Rob Braun and Ryan O'Hayre.

- Collaborations with National Renewable Lab (Dr. Zhiwen Ma, Dr. Janna Martinek, and Judy Netter) have been helpful in modeling and demonstrating a test receiver design.

- Our team acknowledges the support of the Department of Energy through the SunShot Initiative under the CSP:ELEMENTS program.

- Thanks to Brent Kinson, Devin Clay, Steven Landin, and Frank Anderson at CoorsTek for the engineering efforts and time dedicated to perovskite synthesis for this project.

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