Updates on the Operation of NETL's 50-kW Chemical Looping Combustion Test Facility

Sam Bayham, Justin Weber, Doug Straub

Thermal Science Team, Research & Innovation Center

Solutions for Today | Options for Tomorrow

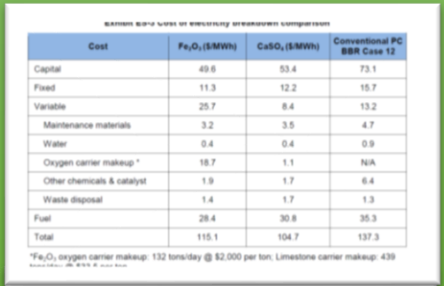
Chemical Looping at NETL

Component Development

- Experimental (cold models)
- Simulations (MFIX, Barracuda)

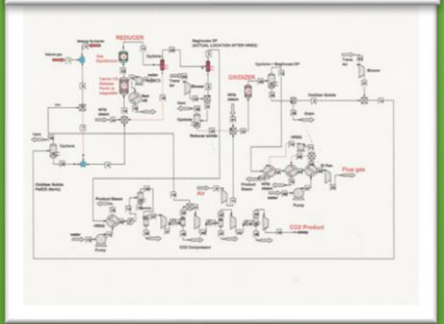
Chemical Looping Reactor

System Studies



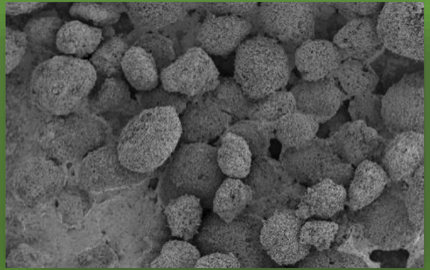
Cost	Fe_2O_3 ($/MWh)	$CaSO_4$ ($/MWh)	Conventional PC BBR Case 12
Capital	49.6	53.4	73.1
Fixed	11.3	12.2	15.7
Variable	25.7	8.4	13.2
Maintenance materials	3.2	3.5	4.7
Water	0.4	0.4	0.9
Oxygen carrier makeup *	18.7	1.1	N/A
Other chemicals & catalyst	1.9	1.7	6.4
Waste disposal	1.4	1.7	1.3
Fuel	28.4	30.8	35.3
Total	115.1	104.7	137.3

*Fe_2O_3 oxygen carrier makeup: 132 tons/day @ $2,000 per ton; Limestone carrier makeup: 439

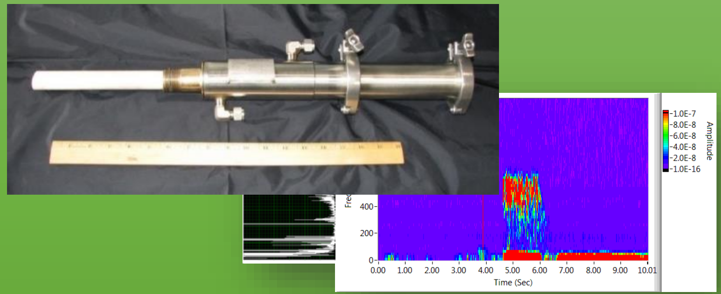


Oxygen Carrier Performance and Durability

- Reactivity
- Strength/Attr.
- Characterization



Sensor Development

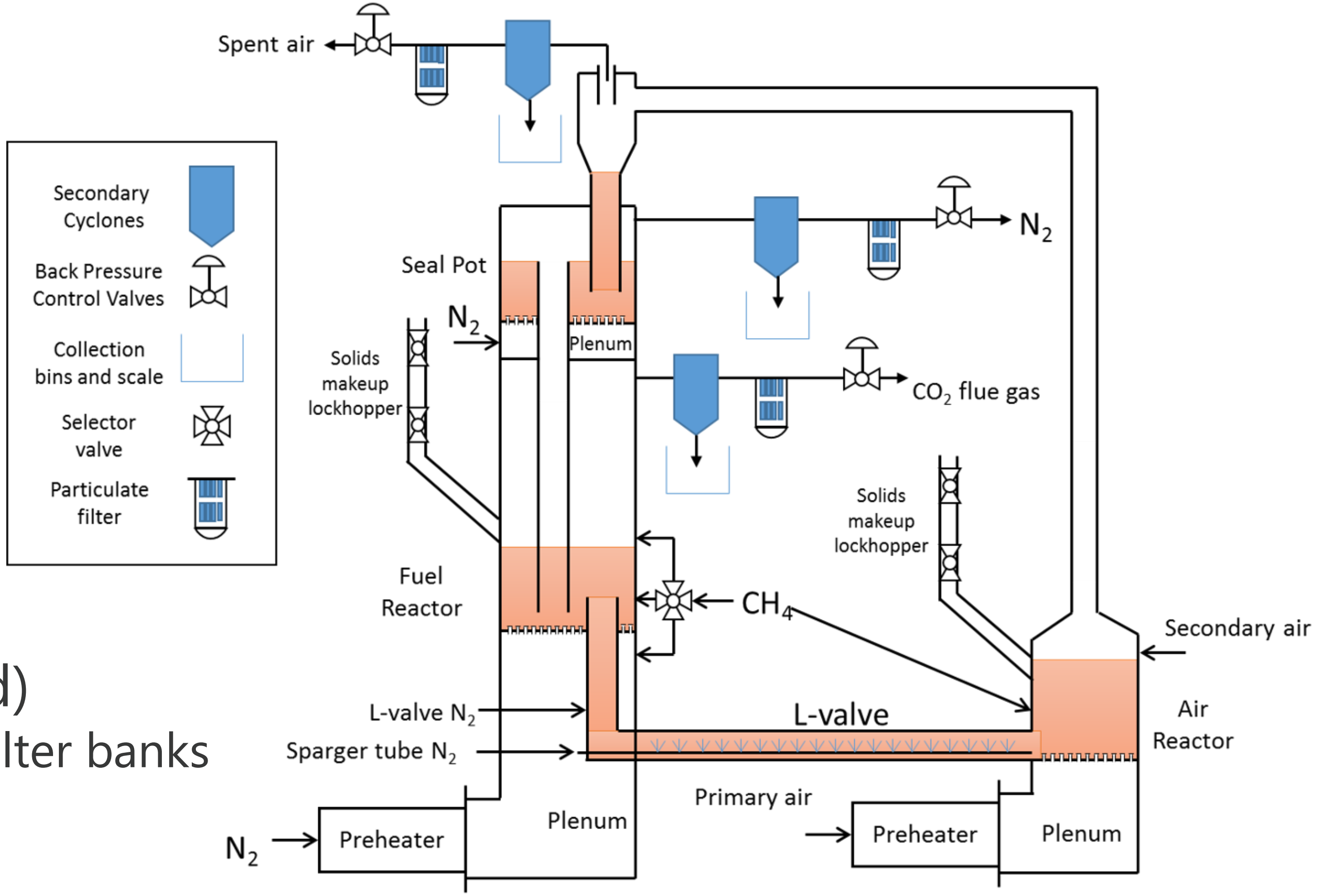


- Gas composition
- Solids flowrate

Experimental testing and operations

NETL 50 kW_{th} Natural Gas Circulating CLC Testing

- Carbon steel shell/refractory lined
- Fuel Reactor
  - Bubbling bed (8″ dia)
  - Natural gas (1 of 3 locations)
- Air Reactor
  - Turbulent fluidized bed (6″ dia)
  - Natural gas for startup
- Gas Seal/Seal Pot
  - Bubbling bed (8″ dia)
- Vent lines (3 individually controlled)
  - Cyclones remove hot solids prior to filter banks
  - Back-pressure control valves

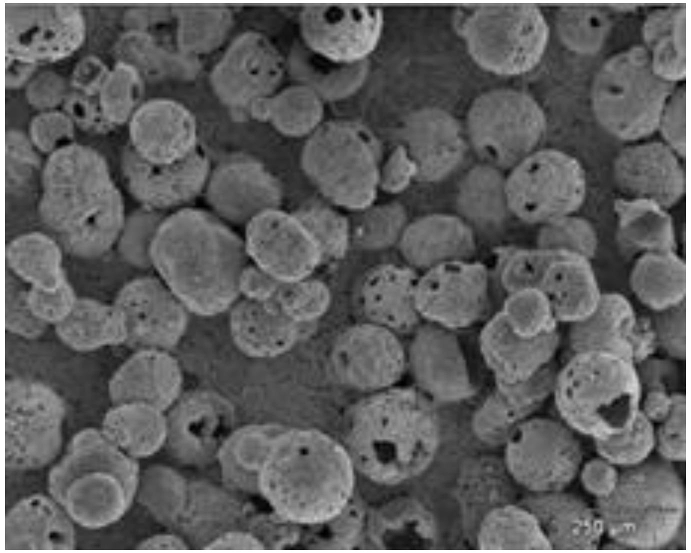


Ref: Bayham, S., Straub, D., and Weber, J., (2017), "Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material," https://www.osti.gov/scitech/biblio/1347568-operation-netl-chemical-looping-reactor-natural-gas-novel-copper-iron-material

Carriers tested in the CLR

	Hematite	Promoted Hematite	Synthetic Carrier	
Particle density	4.9	4.9	2.9	g/cm3
Sauter Mean Diam.	210	210	343	µm
D50	238	238	397	µm
Sphericity	0.876	0.876	0.91	--
Umf (at 298 K)	8.55	8.55	14	cm/s
Fe_2O_3	86.6%		31%	
CuO			37%	
“Inert”	13.4%		31%	

- Bi-metallic carrier (CuO and Fe_2O_3) with alumina
- High reactivity (compared to raw hematite)
- Reduction of material with CH_4 is slightly exothermic.
- Scaled up to ~400 kg batch by Nextech



Ref: Bayham, S., Straub, D., and Weber, J., (2017), “Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material,” https://www.osti.gov/scitech/biblio/1347568-operation-netl-chemical-looping-reactor-natural-gas-novel-copper-iron-material

Original Test Plan

Main Goals:

- Long autothermal trials reusing ejected solids for makeup
- Increase FR CH4 until heaters/AR CH4 can be turned off

Test Condition		Natural Gas Only				
		TC-03	TC-04	TC-05	TC-06	TC-07
Pressure	psig	8	8	8	8	8
Heating Value	kWth	10	20	30	40	50
Fuel Reactor Temperature*	°F	1550	1550	1550	1550	1550
Flows into FR						
Nat. gas FR (FIC-325)	scfh	32	68	102	136	171
Nitrogen FR (FIC-525)	scfh	397	361	327	293	259
Steam FR (FIC-407)	lb/hr	0	0	0	0	0
Flows into AR						
Primary Air (FIC-165)	scfh	500	500	500	500	500
Secondary Air (FIC-125)	scfh	1400	1400	1400	1400	1400

*Difficult to control and will depend on extent of reduction reaction

Conditions:

- Constant FR gas velocity (0.276 m/s) with changes in methane concentration
- Solids Inventory: 100 lb (kept constant through run)

Performance Parameters Measured

NATIONAL ENERGY TECHNOLOGY LABORATORY

1. Carbon Balance

$$C_{\text{bal}} = \frac{\dot{N}_{\text{CH}_4,\text{out}} + \dot{N}_{\text{CO}_2,\text{out}} + \dot{N}_{\text{CO,out}}}{\dot{N}_{\text{CH}_4,\text{in}}}$$

"Sanity check", and to determine if major fuel reactor gas leakage

2. Methane Conversion

Measured two ways:

$$X_{\text{CH}_4} = \frac{\dot{N}_{\text{CH}_4,\text{in}} - \dot{N}_{\text{CH}_4,\text{out}}}{\dot{N}_{\text{CH}_4,\text{in}}}$$

Overall conversion

$$X_{\text{CH}_4 \rightarrow \text{CO}_2} = \frac{\dot{N}_{\text{CO}_2,\text{out}}}{\dot{N}_{\text{CH}_4,\text{in}}}$$

Conversion to CO_2

If a significant fraction of fuel is converted to CO or carbon, instead of CO_2, then the first approach would bias the calculated conversion toward higher values than the second approach.

3. Oxygen Carrier Conversion

$$X_{OC} = \frac{\dot{N}_{\text{O,out}}}{\dot{N}_{\text{O,total}}}$$

$$\dot{N}_{\text{O,out}} = \dot{N}_{\text{H}_2\text{O,out}} + 2\dot{N}_{\text{CO}_2,\text{out}} + \dot{N}_{\text{CO,out}}$$

$$\dot{N}_{\text{O,total}} = \dot{m}_{\text{OC}} \left(\frac{3 f_{\text{Fe}_2\text{O}_3}}{MW_{\text{Fe}_2\text{O}_3}} + \frac{f_{\text{CuO}}}{MW_{\text{CuO}}} \right)$$

Determines how many moles of oxygen are being extracted over the theoretical maximum

4. Gas and Solid Residence Times

$$\tau_{\text{g,FR}} = \frac{h_{\text{bed,FR}}}{U_{\text{g,LM}}}$$

Determined from log-mean flowrate

$$Q_{\text{LM}} = \frac{Q_{\text{T,wet}} - Q_{\text{in}}}{\ln\left(\frac{Q_{\text{T,wet}}}{Q_{\text{in}}}\right)}$$

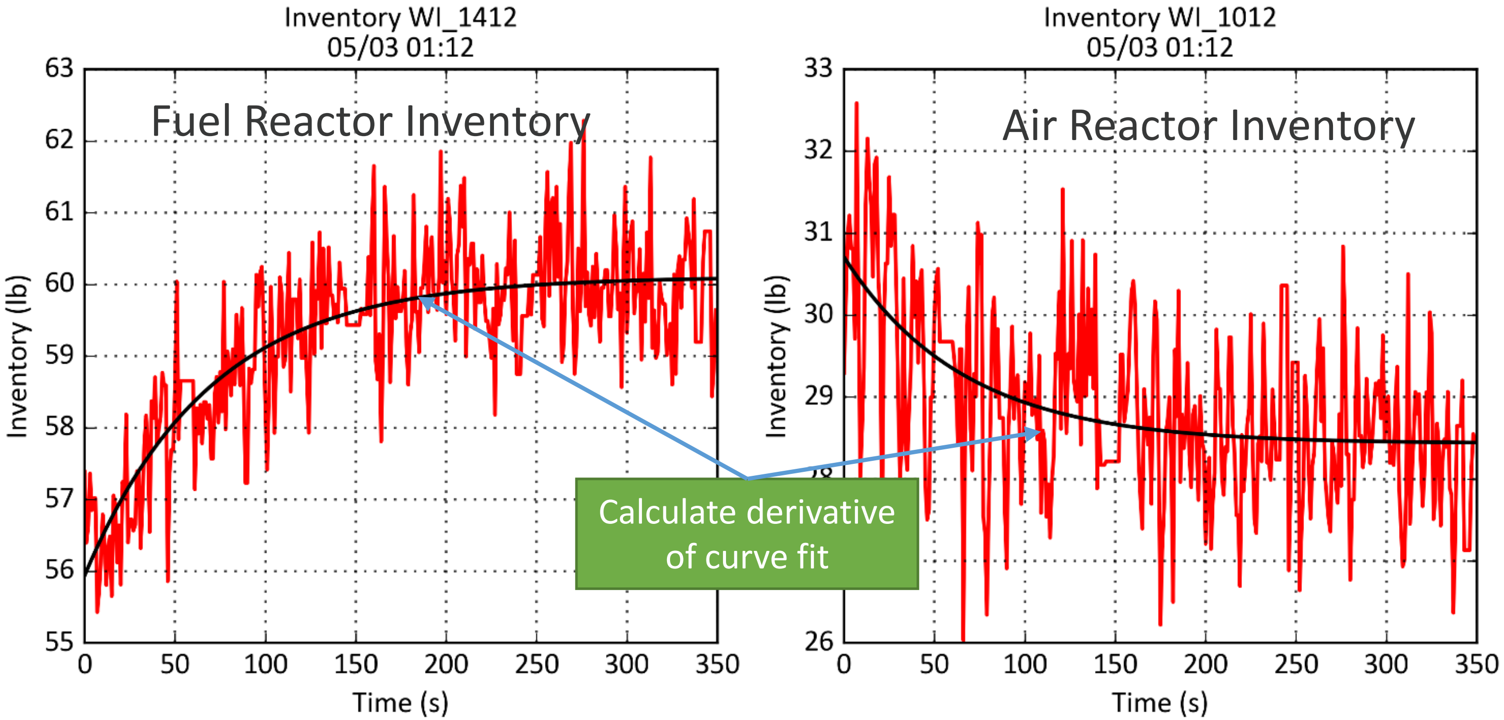
$$\tau_{\text{OC,FR}} = \frac{m_{\text{bed,FR}}}{\dot{m}_{\text{OC}}}$$

**Important parameters for how long it takes fuel to react with oxygen carrier.

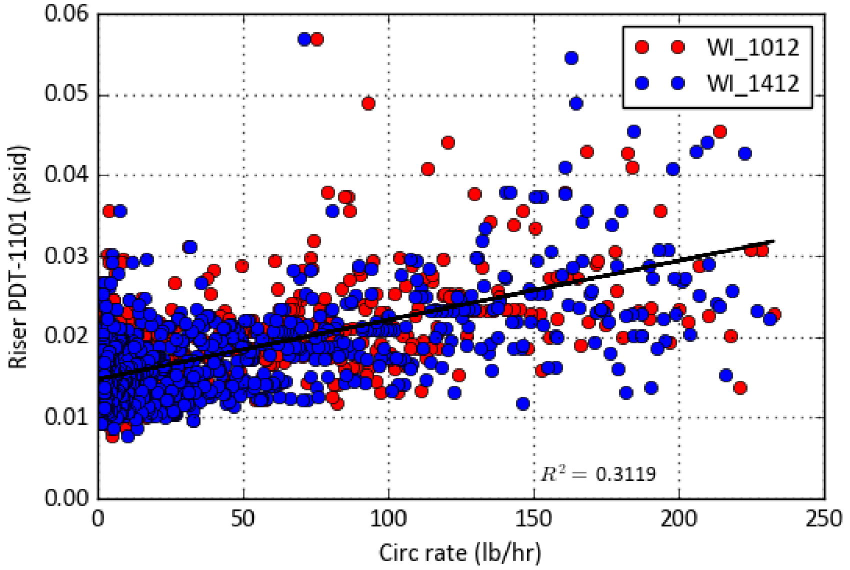
U.S. DEPARTMENT OF ENERGY

Solid Circ Rate with L-Valve Cutoff Tests

- Shut off L-valve and solids flow to observe change in inventory in air and fuel reactors
- Fit riser pressure drop data to derivative of exponential inventory curves
- FR Backpressure controller was set to zero during cutoff test
  - This allowed for solids to stop circulating, since we were running it higher than usual



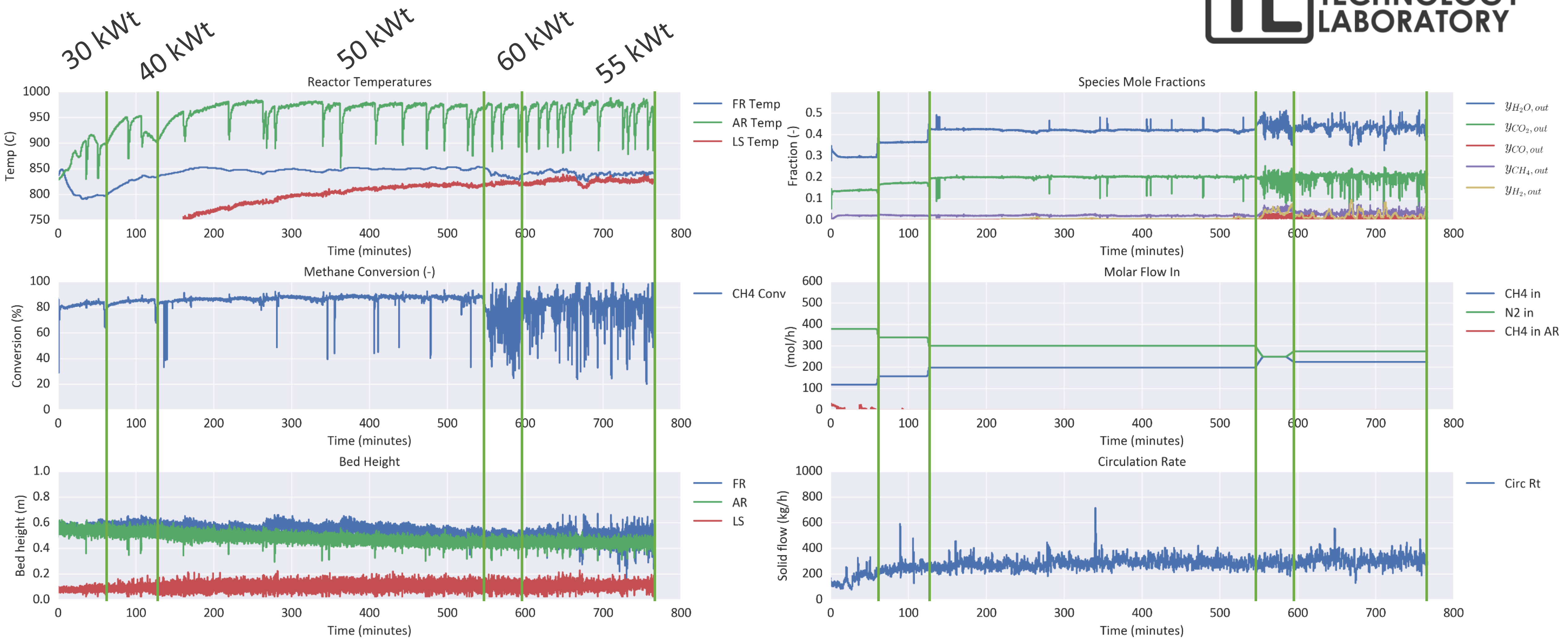
Riser DP Correlation



Riser pressure as a function of riser DP

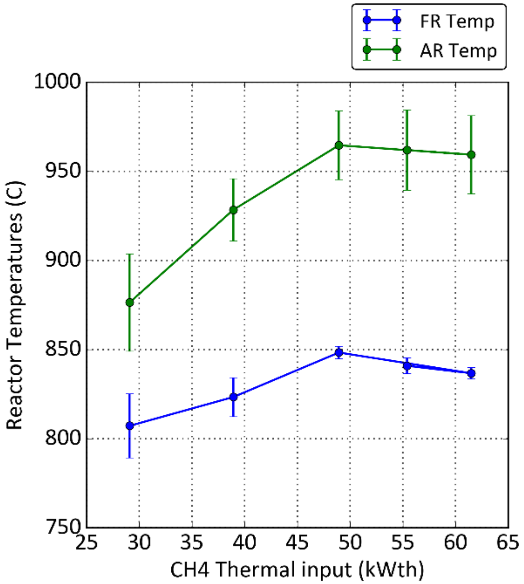
$$\dot{m}\left[\frac{\text{kg}}{\text{h}}\right] = 6187 \cdot \Delta P_{\text{riser}}[\text{psid}] - 91.19$$

Autothermal trials

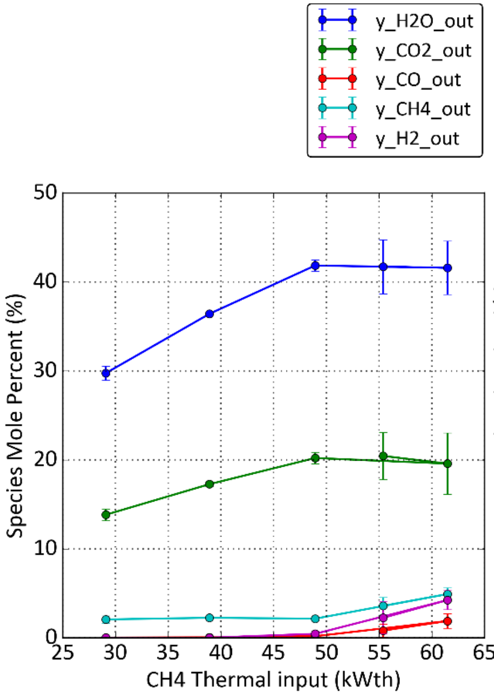


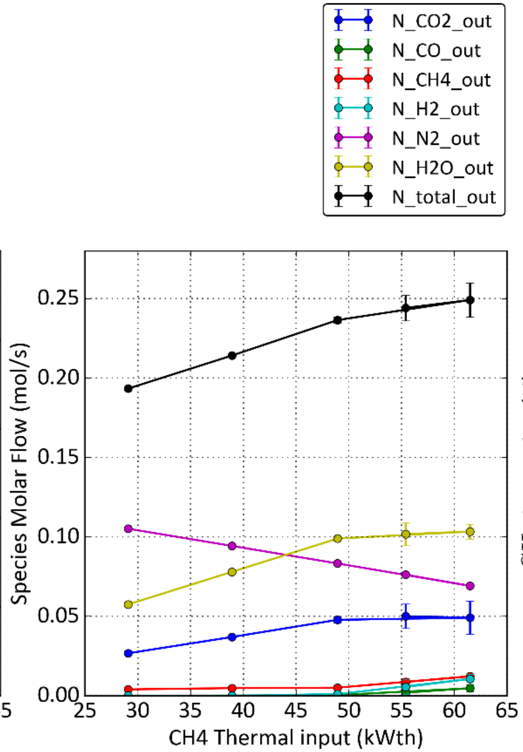
Autothermal trials

Plotted as a function of FR natural gas input

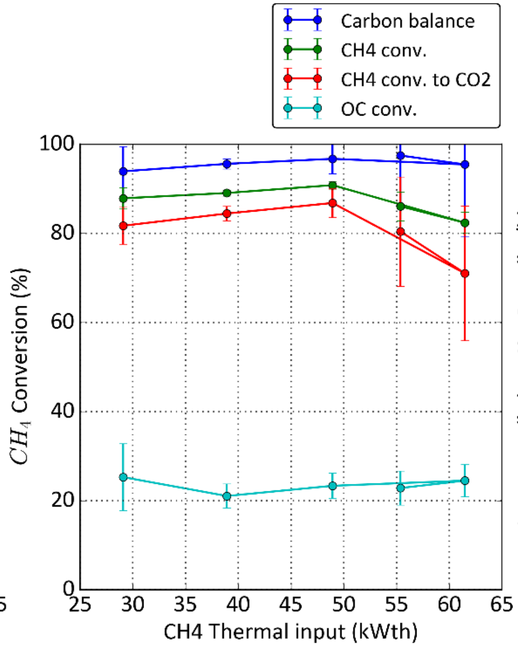


Temperature increased as more natural gas was fed into the FR

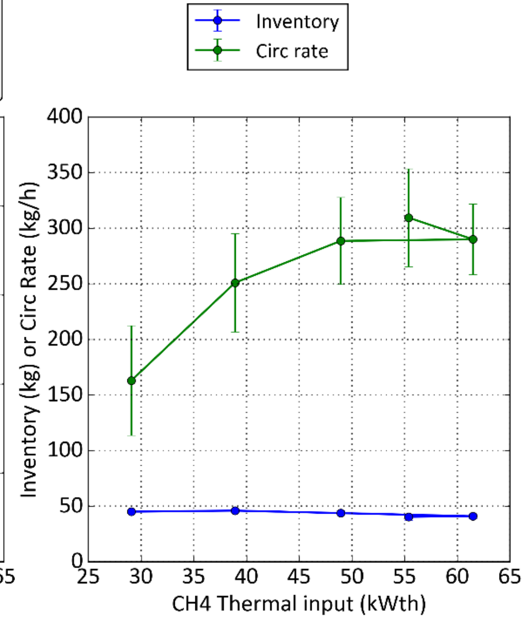




It seems CO/H2 breakthrough occurred around 50 kWth, but it's hard to say if inventory or recycled solids breakdown had an effect.



CH4 conversion performance increased as temperature increased but dropped above 50 kWth



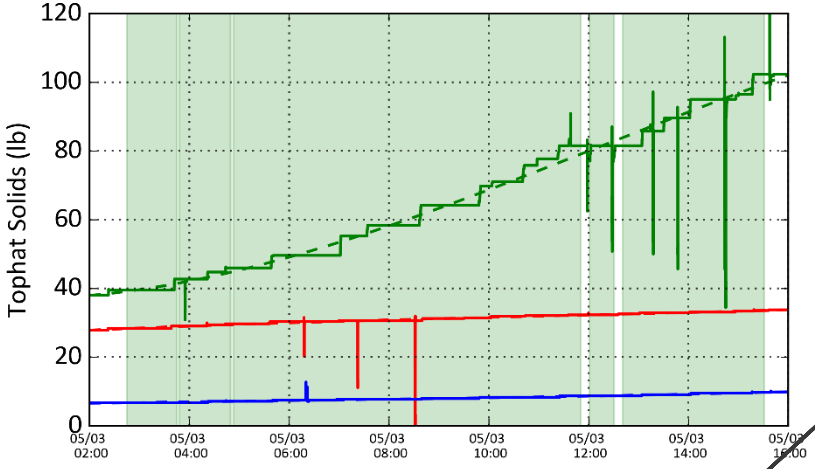
Circulation rate increased with higher natural gas concentration

- CH4 → 3 moles of gas products!

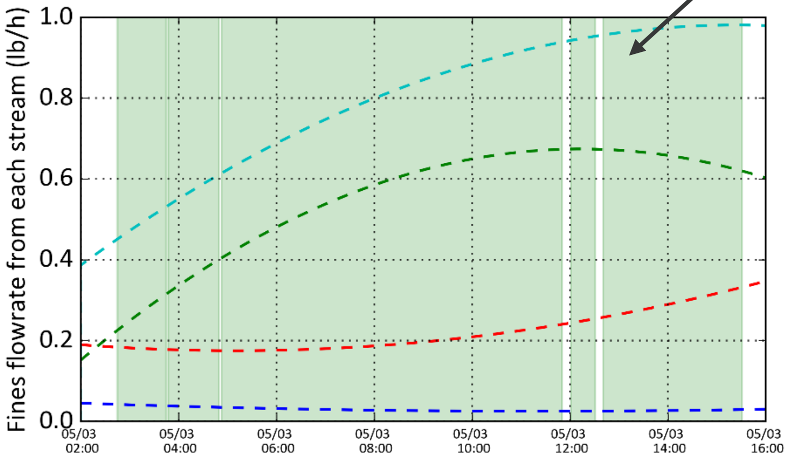
Determination of Attrition Rate

Calculated during Autothermal Trials

Collected solids from secondary cyclones



Derivative of curve fit of collected solids



Datafit of solids collection from secondary cyclones to a polynomial

$$\dot{m}_{attr} = \dot{m}_{FR} f^{m}_{FR,fines} + \dot{m}_{AR} f^{m}_{AR,fines} + \dot{m}_{LS} f^{m}_{LS,fines}$$

$\dot{m}_i$ = Rate of solids collected from secondary cyclones

$f^{m}_{i,fines}$ = Assumed mass fraction of fines in tophat

Fuel Reactor	92.4%
Loop Seal	11.8%
Cyclone	7.1%

Fines defined as particles less than 150 micron

Limitations to analysis:

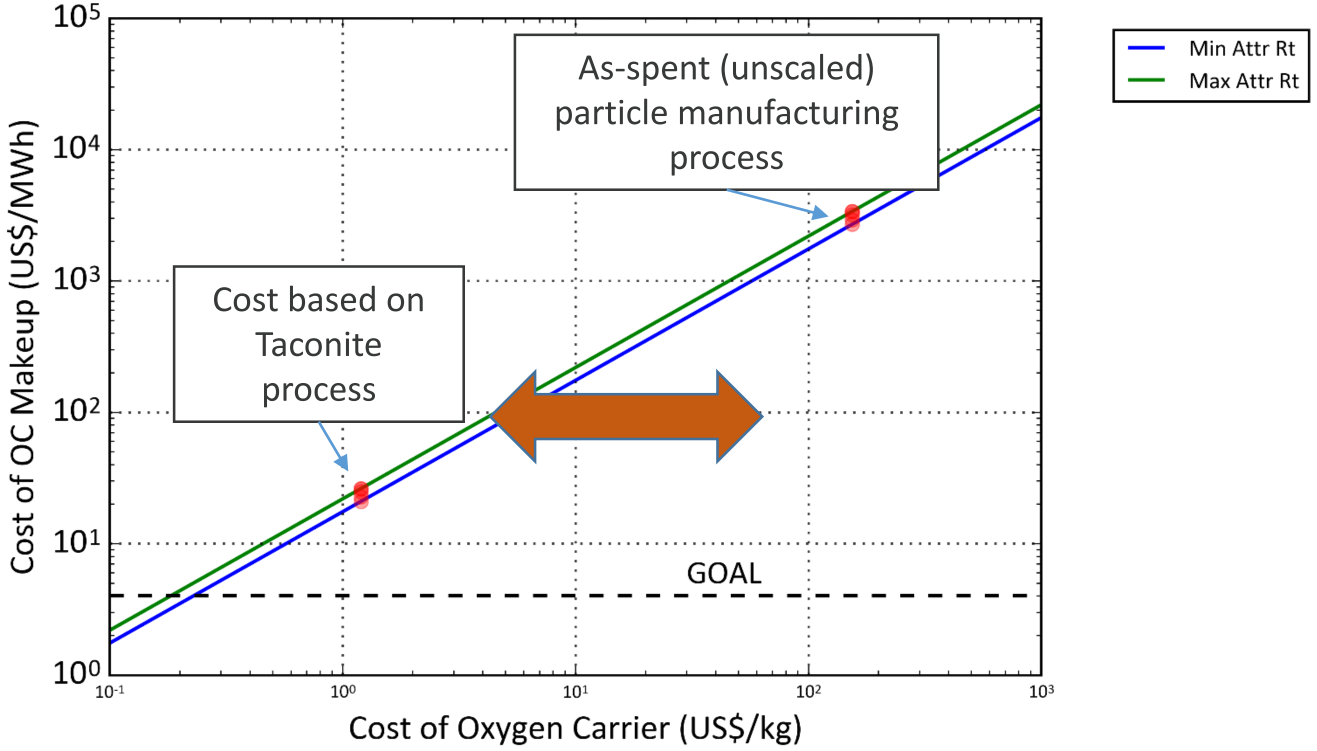
- Mass fraction of fines in each stream is assumed constant (“bulk value” measured at end of run)
- Does not take into account mass of fines collected in filter
- Derivative of polynomial fit is quite crude and does not capture subtlety of mass flows

NETL 50 kW$_{th}$ Circulating CLC Testing

NATIONAL ENERGY TECHNOLOGY LABORATORY

Demonstrate oxygen carrier make-up costs $5/MW$_{th}$-hr in a circulating CLC test facility

- O_2 carrier make-up costs
  - Baseline for 50kW$_{th}$ test unit estimated
  - Key issue for CLC technology maturation
- Gaps to address . . .
  - Lower-cost O_2 carriers
  - Fundamental effects of redox cycling on attrition
  - Need longer duration tests under redox and circulating conditions
- More studies are needed!



$$\text{Makeup Cost}\left(\frac{\$}{\text{MW}_{\text{th}}-\text{hr}}\right) = \frac{W_{\text{OC}}\dot{m}_{\text{loss}}(1-\alpha)}{\dot{N}_{\text{CH}_4,\text{in}}X_{\text{CH}_4\rightarrow\text{CO}_2}HHV_{\text{CH}_4}} \times \left(3.6\times10^{6}\,\frac{\text{kJ}}{\text{MWh}}\right)$$

Conclusions and Future Run Objectives

- 11 hours of autothermal with CuFe material performed with recycled solids
  - Methane conversion to CO_2 ranged from 70-90%
  - Carrier underwent 75 oxidation-reduction cycles during autothermal trials (most of it at least)
  - Methane conversion increased up to a certain point (48 kWth), then decreased
- Oxygen carrier cost still too high
  - Lower attrition rate and/or manufacturing cost

Next:

- Continue to do **longer** autothermal trial(s)
  - Less focus on complex test plan/matrix
  - More focus on solids sampling

Acknowledgements

NATIONAL ENERGY TECHNOLOGY LABORATORY

- The authors would like to acknowledge the financial and technical support of US DOE's Advanced Combustion Program
  - Rich Dennis, Dan Driscoll, John Rockey, Steve Markovich, Briggs White, Geo Richards
- Operating and support staff :
  - Dave Reese, Jeffrey Riley, Mark Tucker, Richard Eddy, and Stephen Carpenter
- Without the contributions of these people, this work would not be possible!

U.S. DEPARTMENT OF ENERGY

Disclaimer

NATIONAL ENERGY TECHNOLOGY LABORATORY