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Integrated Oxygen Production and CO_2 Separation through Chemical Looping Combustion with Oxygen Uncoupling

Project DE-FE0025076

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The University of Utah

2018 NETL CO_2 Capture Technology Project Review Meeting
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Project Overview

Participants: THE UNIVERSITY OF UTAH; Amaron Energy

Funding:

Source	University of Utah	Amaron Energy	TOTAL
DOE	$ 1,597,665	$ 282,655	$ 1,880,320
Cost share	$ 399,416	$ 70,664	$ 470,080
TOTAL	$ 1,997,081	$ 353,319	$ 2,350,400

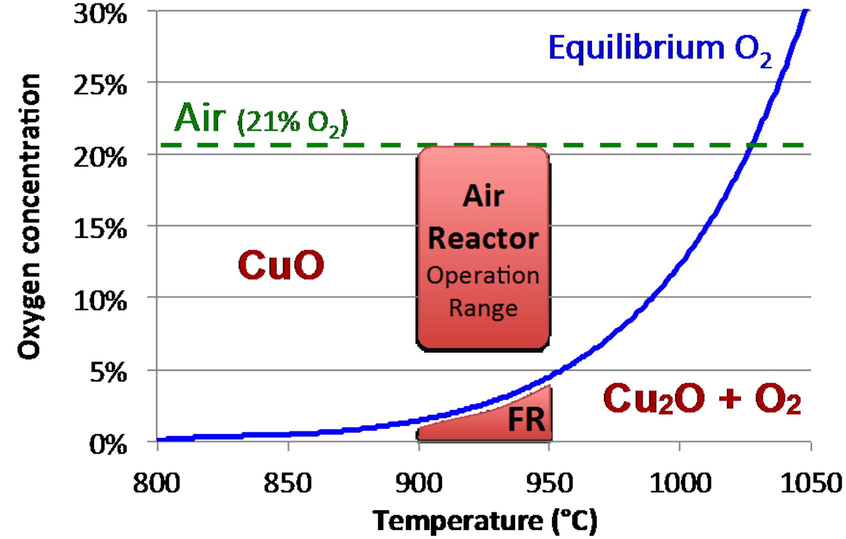
Project Dates: September 1, 2015 – March 31, 2019

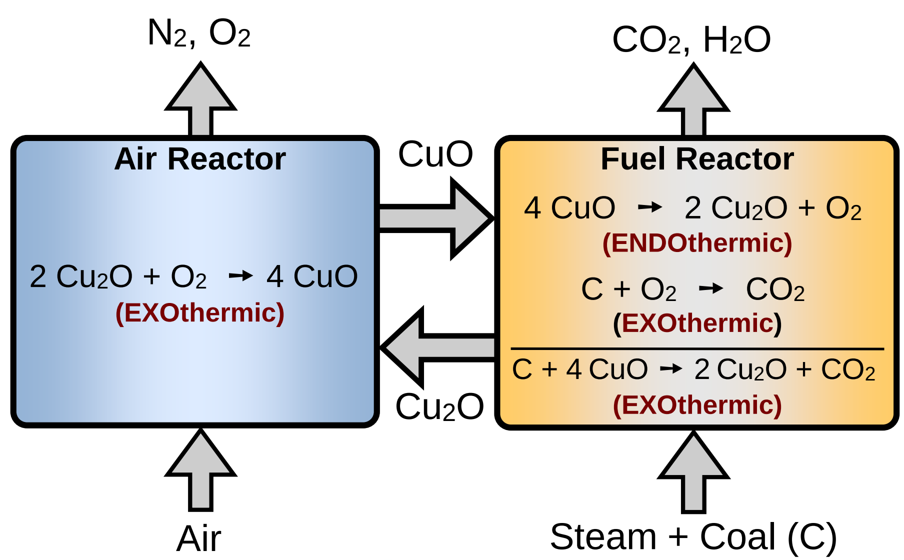
Objectives: Advance chemical looping combustion with oxygen uncoupling (CLOU) technology to pilot scale (NETL TRL 5) through system scale-up, operation of a 200 kW process development unit, process modeling and reactor simulation

Technology Background: Fundamental Science Chemical Looping with Oxygen Uncoupling (CLOU)

$Cu_2O(s) + \frac{1}{2} O_2(g) \rightleftarrows 2\ CuO(s)$

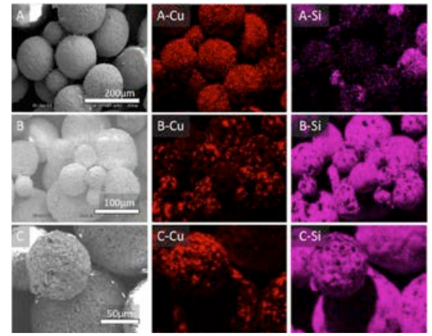
- Copper is one of few metals for which oxidation equilibrium (Cu_2O/CuO) lies within CLC operating temperatures.
- Cu_2O is oxidized in air reactor
- CuO spontaneously releases O_2 in fuel reactor due to low O_2 partial pressure
- Released O_2 reacts with solid coal char, converting more than 50x faster than with non-CLOU oxygen carriers

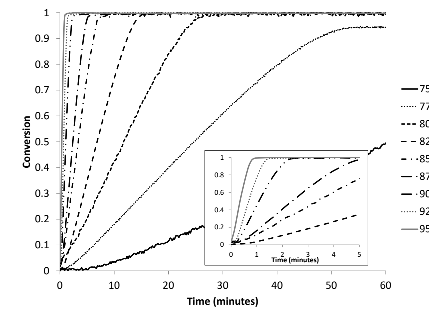


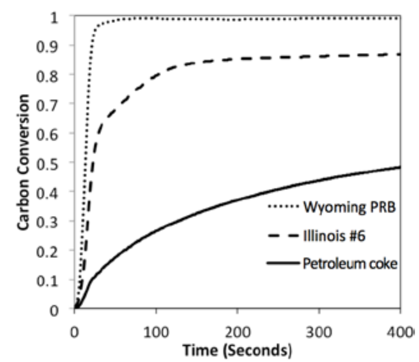


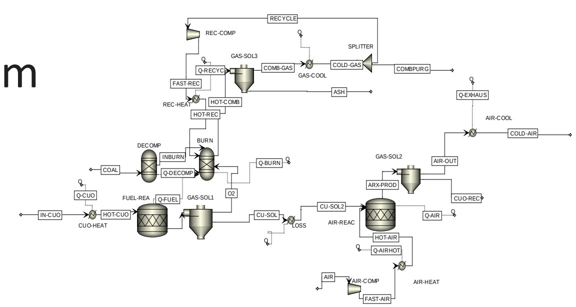
Technology Background: Previous R&D at University of Utah

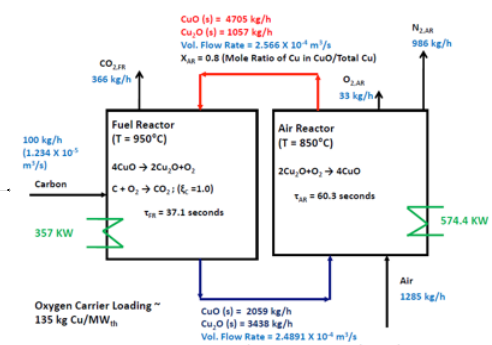
- **Oxygen carrier development**
  - Focus on inexpensive copper-based carriers with scalable production
  - Dozens of alternatives tested
- **Reactor and process development**
  - Fundamental studies of CLOU reaction kinetics
  - Lab-scale experiments of coal conversion
  - Design/preparation of 200 kW PDU
- **Process modeling and reactor simulation**
  - Aspen Plus modeling of CLC system
  - Barracuda VR® modeling of integrated fluidized bed system











Technology Background: Advantages and Challenges of CLOU

Advantages

- CLOU can convert coal char up to 50 times faster than conventional CLC
  - Carbon conversion > 99.9% has been achieved in bench-scale tests
  - CO_2 capture > 99% has been achieved in bench-scale tests
  - High conversion in fuel reactor eliminates need for carbon stripper
- Fast reactions reduce reactor size and oxygen carrier inventory
- High conversion and CO_2 capture improves economics

Challenges

- Operation of dual fluidized bed
  - Circulation, temperature control, particle retention
- Oxygen carrier production
  - Balance copper availability, reactivity, physical strength
- CLOU carriers are comparatively expensive
  - Physical robustness and retaining activity are especially important

Technical Approach

- **Three major research areas**
  1. Scale up of CLOU oxygen carrier production
  2. CLOU Experiments
     - 200 kW PDU
     - 10 kW bench-scale
  3. System modeling and reactor simulation

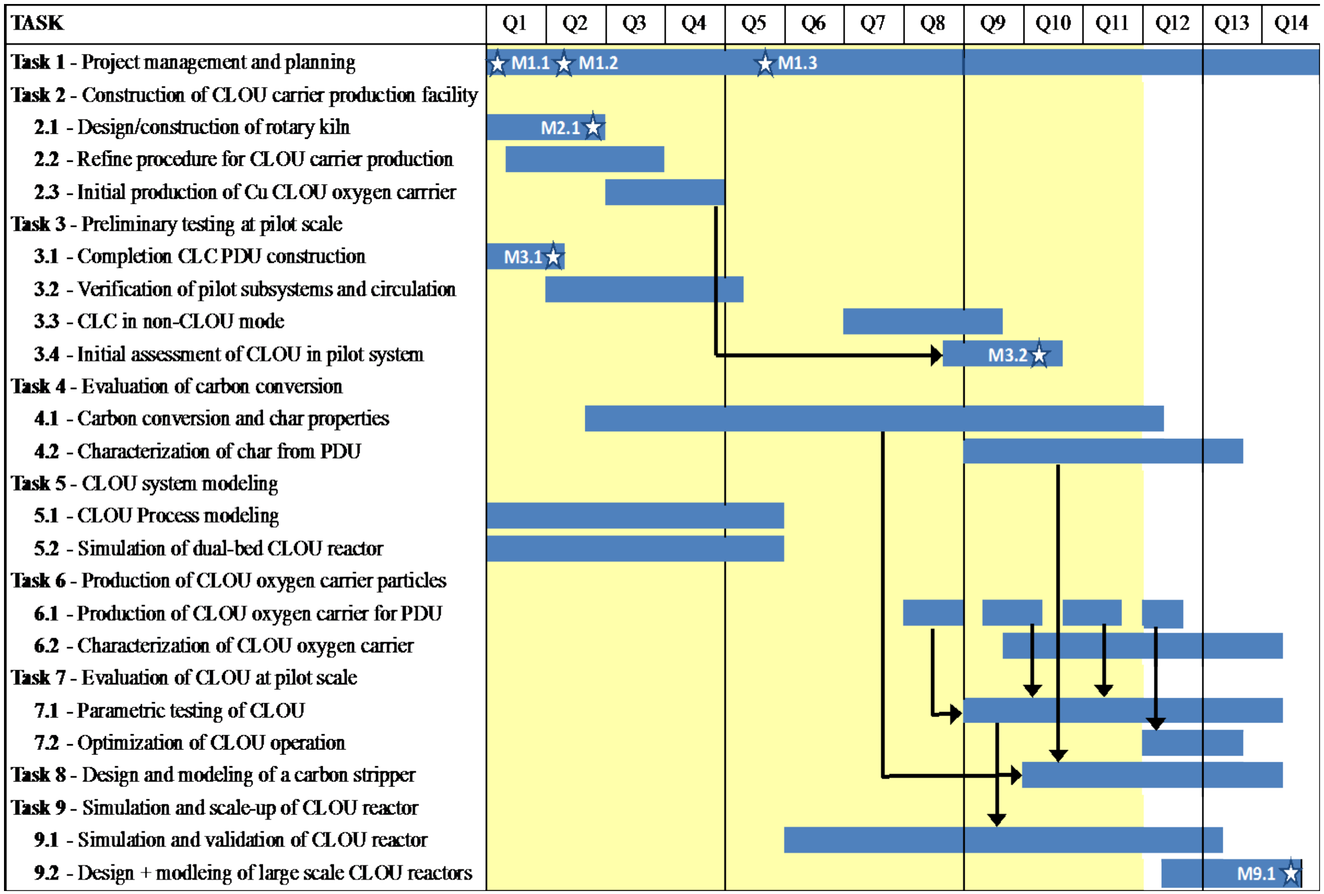
- **Performance targets**
  - CO_2 capture (target min. 90%)
  - CO_2 purity (target min. 95%)
  - Coal conversion (target min. 99%)

Work plan / Tasks

1. Project management
2. Construction of pilot-scale rotary kiln for oxygen carrier production ✓
3. Complete construction/initial testing of pilot-scale CLC system ✓
4. Evaluation of carbon conversion in CLOU environment
5. CLOU system modeling ✓
6. Production and characterization of CLOU carrier particles
7. Evaluation of CLOU performance and CO_2 capture at pilot scale
8. Carbon stripper design and modeling
9. Design of pilot/demo scale CLOU reactors

Project Scope:
Schedule, Milestones, Success Criteria, Risks

- **Technical milestones**
  - 2.1 Complete pilot rotary kiln
  - 3.1 Complete CLC PDU
  - 3.2 Start CLOU testing
  - 9.1 Large CLC system design
- **Success criteria** focus on PDU
  - Key operation steps (*) require that specific performance can be achieved
- **Technical risks**
  - CLOU carrier unsuitable
    - Target lower Cu loading
  - Inadequate pilot performance
    - Component redesign
  - Excessive carrier attrition/loss
    - Reduce velocity, produce more carrier, find alternates
  - Bed agglomeration
    - Reduce Cu content, ease into CLOU testing



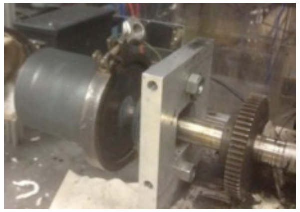
Progress and Current Status

- Oxygen carrier production scale-up
- Evaluation of carbon conversion
- Pilot system operation
- Reactor simulation

Progress and Current Status:
Scale-up of CLOU Oxygen Carrier Production

- **Equipment**
  - 0.1 kg lab scale rotovap
  - 1 kg lab scale
  - 10 kg bench scale
  - 100 kg pilot built (Amaron)
- **Manufacture**
  - Wet or dry impregnation
  - Support material is key
    - strong
    - inert
    - reasonable surface area
  - Complexes and stabilizers
  - Calcining
    - nitrate decomposition

System	Type	Capacity	Heating	Max T	Length	Diam
RV-1	Rotary evap	1 kg	Water bath	95°C	n/a	0.15 m
RK-1	Rotary kiln	1 kg	Elec Inductive	800°C	0.15 m	0.1 m
RK-10	Rotary kiln	10 kg	Elec radiative	350°C	0.8 m	0.2 m
RK-100	Rotary kiln	100 kg	Natural gas	600°C	1.4 m	0.4 m

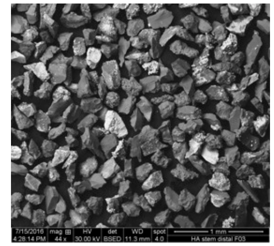
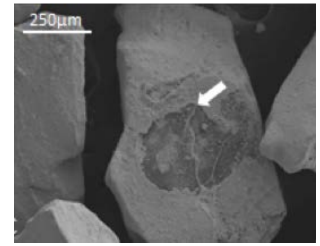

RK-1 lab-scale induction kiln

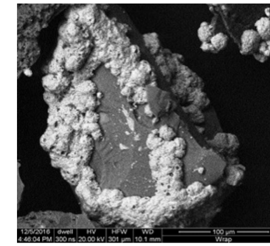

RK-10 bench-scale rotary kiln

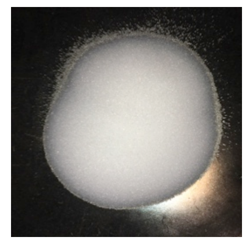

RK-100 oxygen carrier production kiln

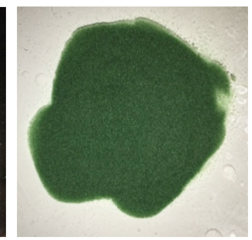
Progress and Current Status:
Improvement of CLOU Oxygen Carriers

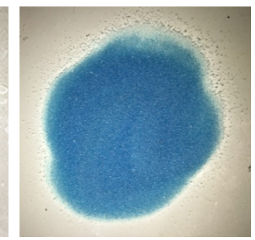
- **Status**
  - Over 65 carriers tested
  - Baseline support: SiC
    - cheap but poor Cu distribution
  - New supports: SiO_2, $MgAl_2O_4$
    - also with stabilizers
  - Test batches of 50 kg produced
  - Good cyclability in small fluid bed
- **Characterization**
  - TGA: oxygen loading/rates
  - BET: surface area
  - SEM: morphology, Cu distribution
  - Crush strength
  - Lab-scale fluidized bed for long-term performance in a cycling fluidized bed reactor




Silica support


1 addition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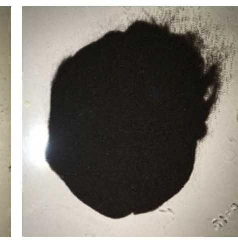
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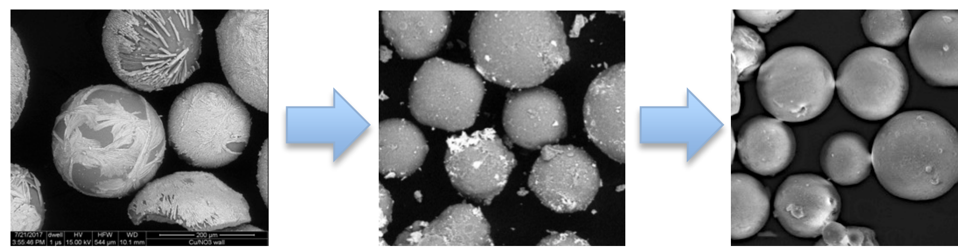
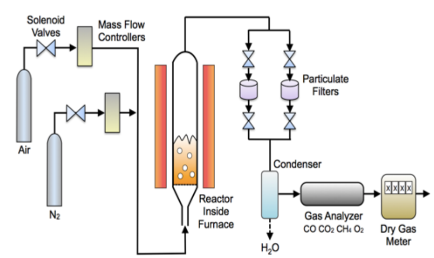
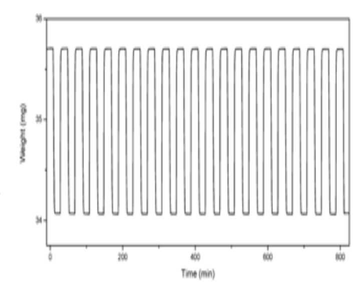


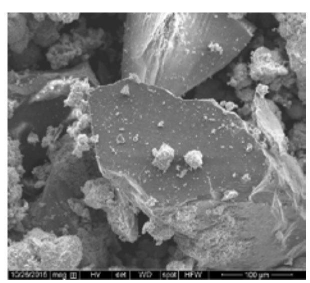

Lab-scale fluidized bed system

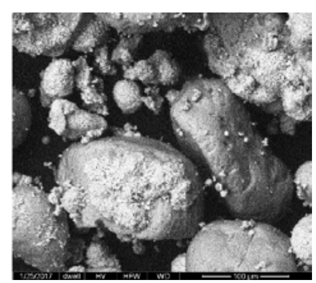


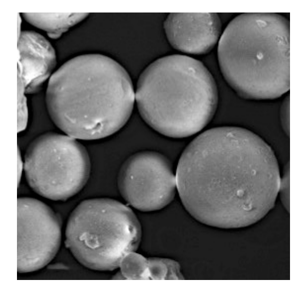


Support Material Cost vs. Performance

Metric	SiC	Ilmenite	Engineered SiO_2
Strength	+ +	+	+
Sphericity	– –	–	+ +
Porosity	– –	– –	+ +
Internal surface area	– –	– –	+ +
Cu loss (attrition)	–	–	+
Uniformity	–	–	+
Impregnability	– –	–	+ +
Cost	+	+ +	– –



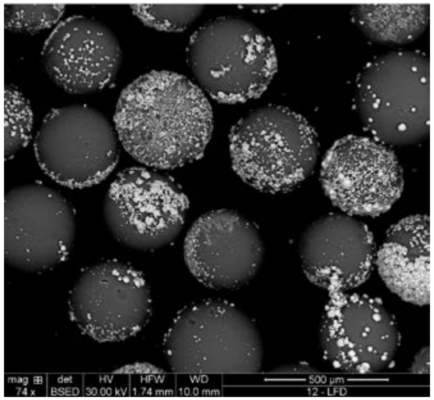


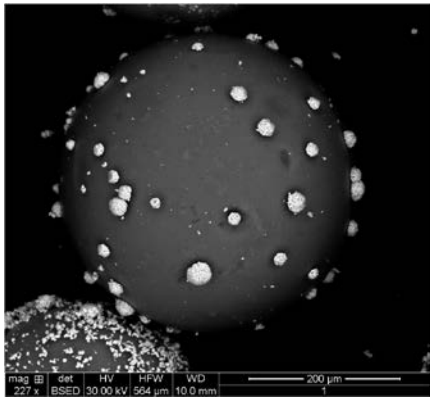


Advances in Impregnation Precursor

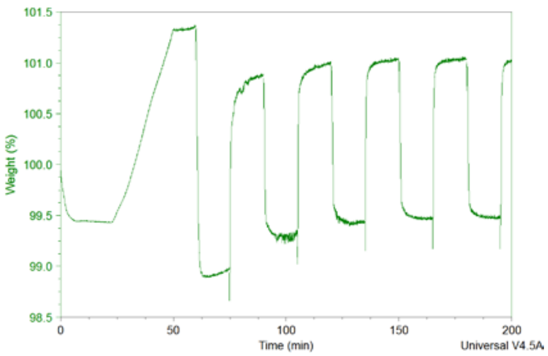
SiO_2 Support

Copper Nitrate
(1M)
20wt% CuO

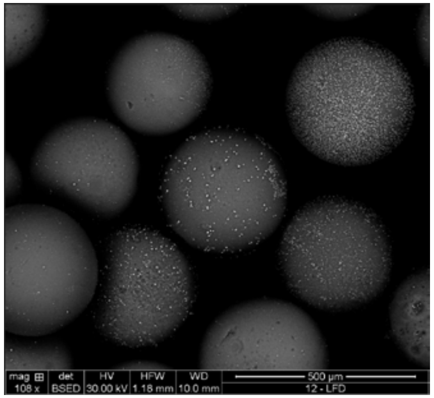


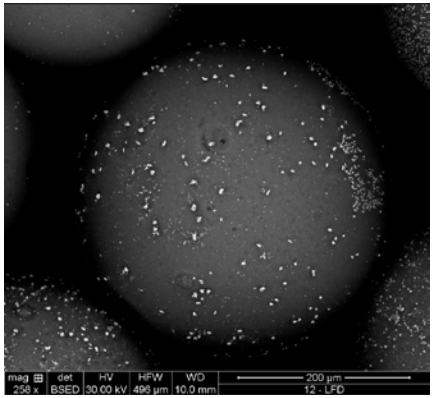


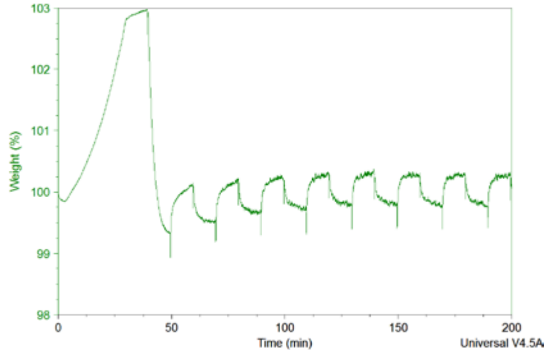
TGA curve (900°C)



Tetraamine
Copper Nitrate
(0.45M)
32wt% CuO







Select Oxygen Carriers

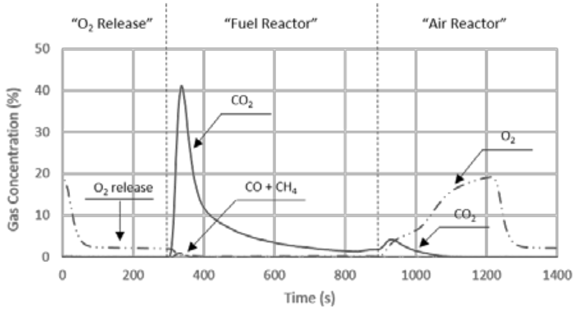
Support	CuO loading (wt%)	Preparation Method	BET Area (m^2/g)	Attrition Rate (%/h)	Agglomeration Temperature (°C)
Titania (Poland)	43	Mechanical mixing	NA	1.3	850
Zirconia (Chalmers)	43	Freeze Granulation	NA	1.5	925
SiC	20	WI (1M) 4 additions	<0.1	-	925
Silica	19	WI, CN, 2 additions	160	0.5	875
Silica	23	WI, CN, 3 additions	219	-	950
Silica	38	WI, TACN, 5 additions	270	0.3	>975

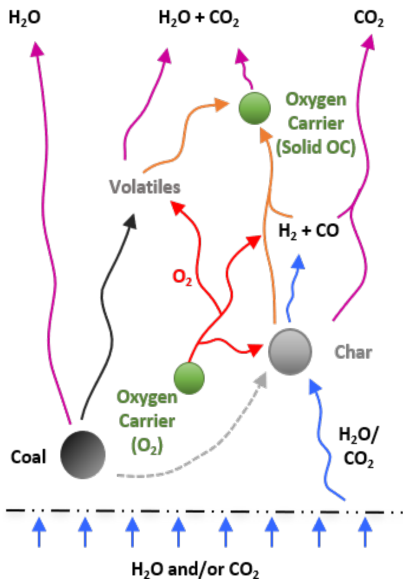
Progress and Current Status

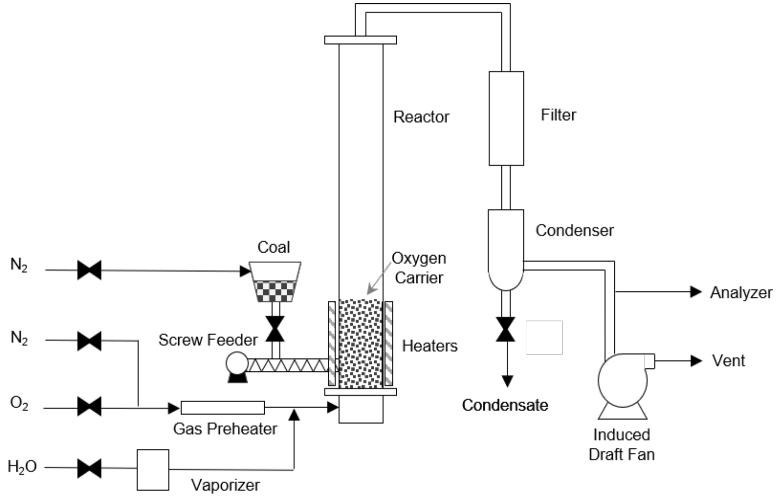
- Oxygen carrier production scale-up
- **Evaluation of carbon conversion**
- Pilot system operation
- Reactor simulation

Evaluation of Carbon Conversion

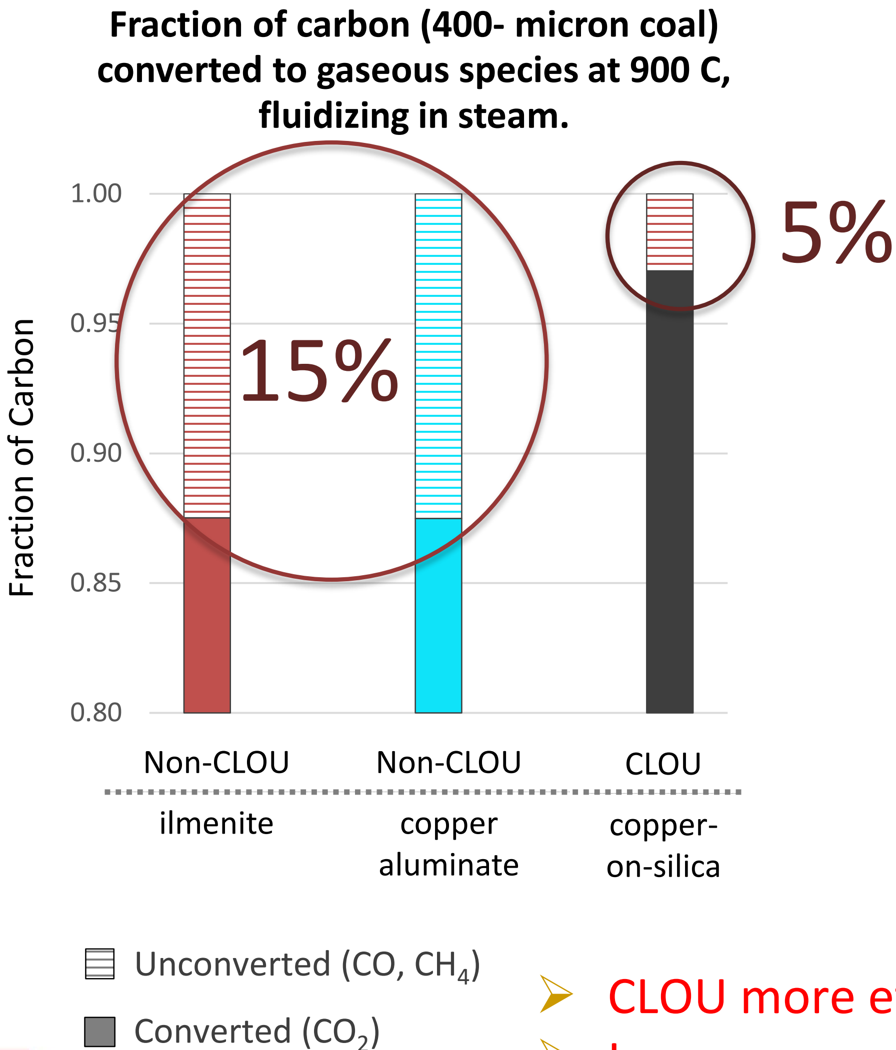
- 9 possible pathways for carbon
  - 6 to CO_2
- Evaluate conversion mechanism in 10 kW reactor
  - Steam vs. N2
  - Coal vs. char
  - CLOU vs. non-CLOU
  - Fuel particle size

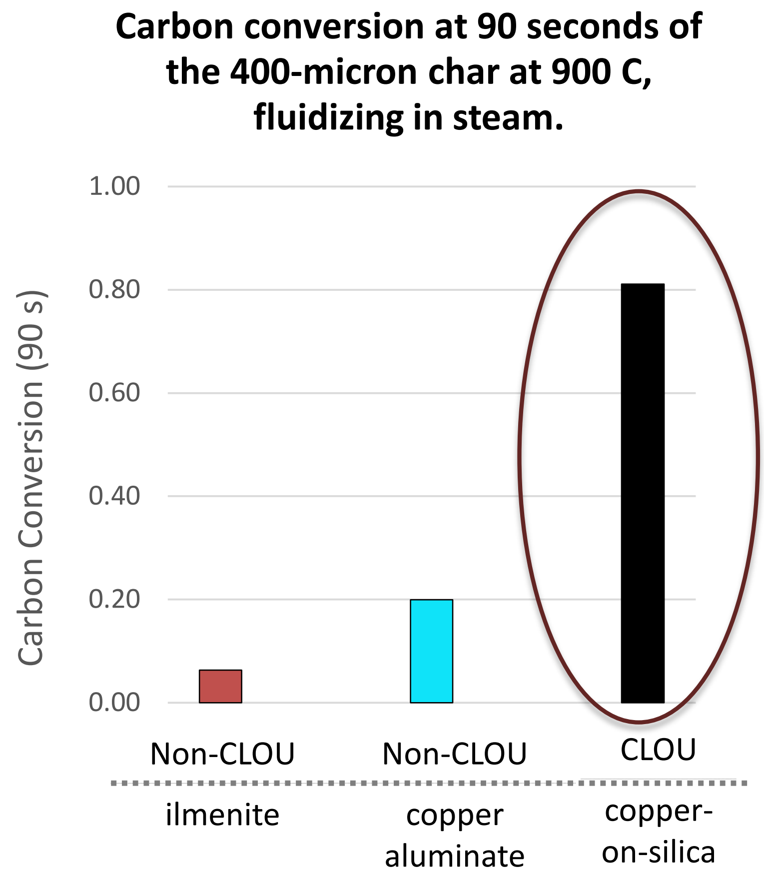






Carbon Conversion: CLOU vs non-CLOU





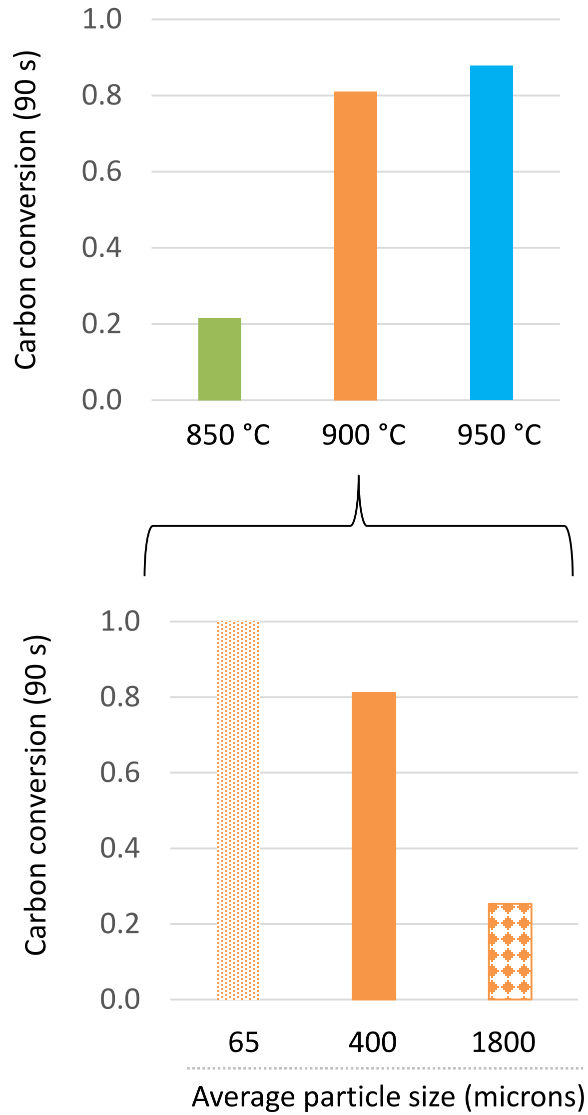
- CLOU more effective at converting carbon in coal
- Less unconverted gases when using a CLOU carrier

CLOU Carbon Conversion

Influence of Temperature and Fuel Particle Size

Carbon conversion at 90 seconds of the 400-micron char fluidizing in steam.

Carbon conversion of char at 90 seconds at 900 C fluidizing in steam.



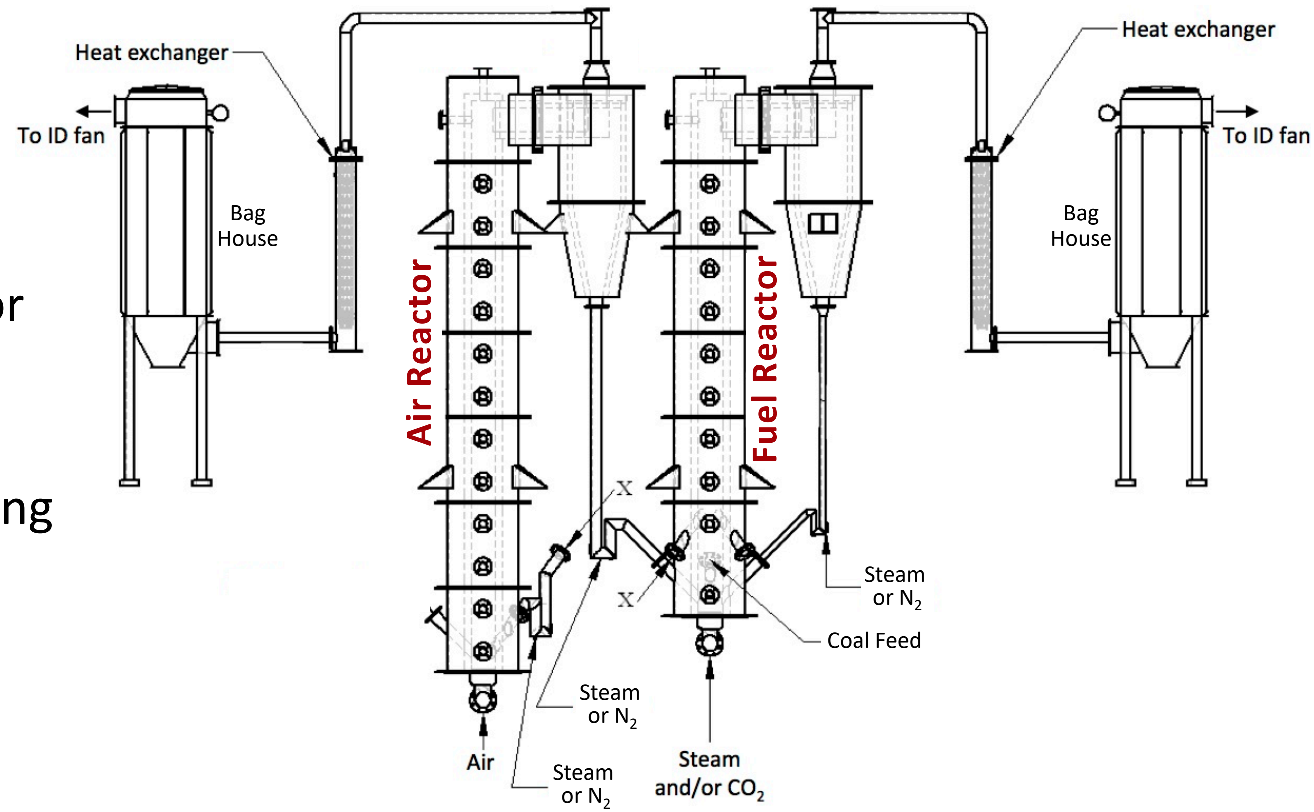
- Carbon conversion increases at elevated temperatures.
- Smaller coal particles convert at a faster rate than the larger particles.
- Smaller coal particles exit the reactor more readily.

Progress and Current Status

- Oxygen carrier production scale-up
- Evaluation of carbon conversion
- **Pilot system operation**
- Reactor simulation and scale-up

CLC Process Development Unit

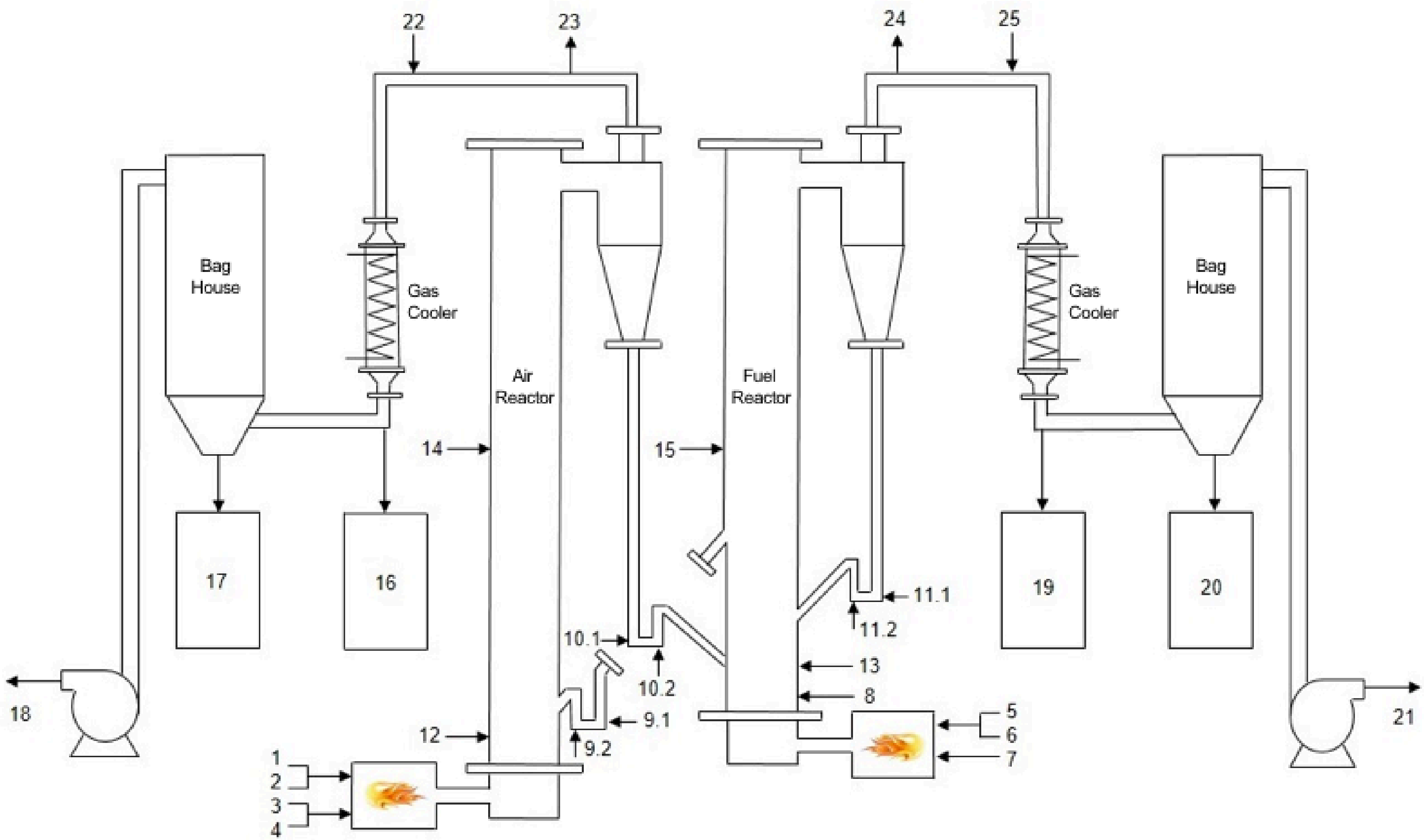
- Design 220 kW_{th}
- Refractory-lined
- CFB air reactor
  - All material to FR
- CFB or BFB fuel reactor
  - Internal recycle
  - Overflow to AR
- Gravimetric coal feeding
  - 2-stage auger-fed
  - Fed to bottom of FR
- Preheating
  - Electric gas heaters
  - Combustors on incoming gases
  - In-bed lances for C_3H_8 or CH_4



Progress and Current Status:
PDU Operation

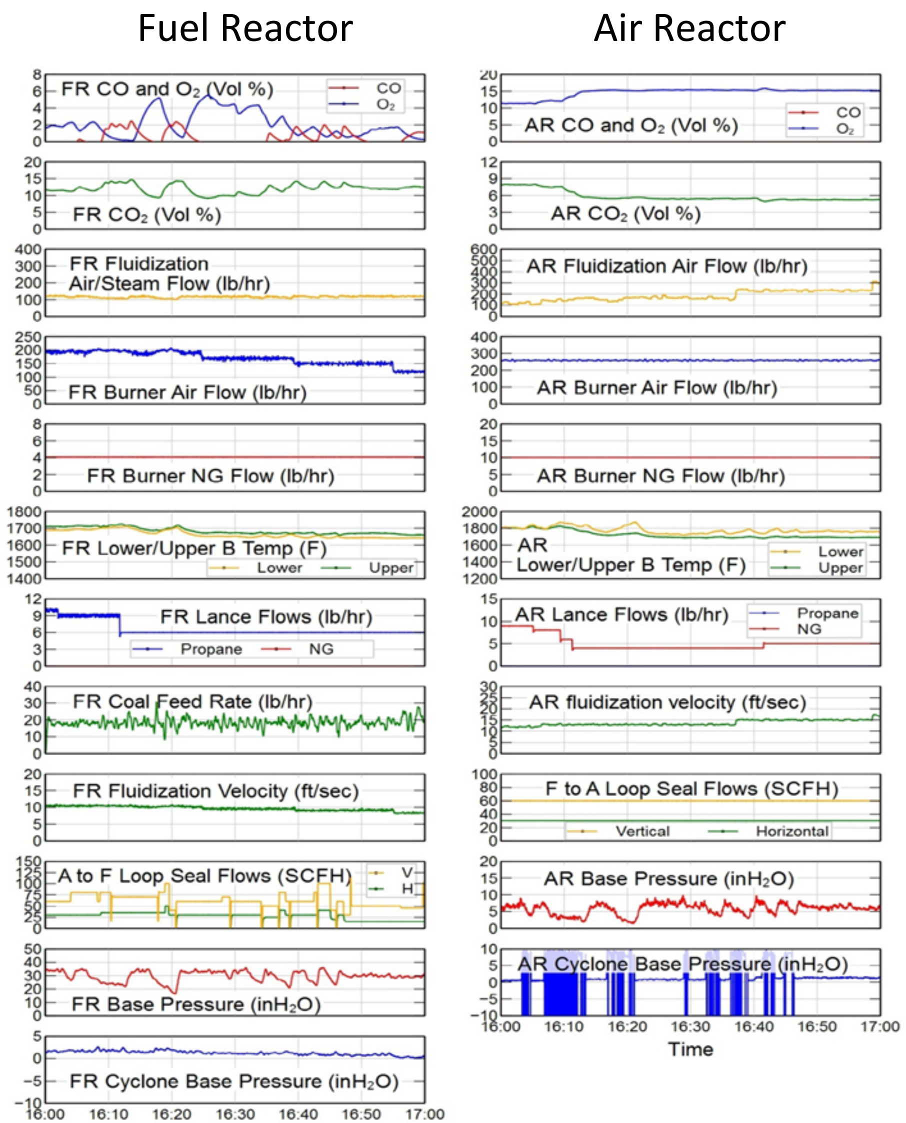
- Preliminary testing
  - Cold flow circulation rates
  - Hot flow circulation rates
  - Ilmenite as oxygen carrier
- Operation progression
  - CLC of natural gas
    - ilmenite
    - Cu-on-Al_2O_3
  - iG-CLC of coal
    - ilmenite
    - Cu-on-Al_2O_3
  - CLOU of coal
    - CLOU carrier

Analysis of PDU Performance: Input and Output Streams



1	Burner Air	(AR)
2	Natural Gas	(AR)
3	Fluidizing Air	(AR)
4	O2	(AR)
5	Burner Air	(FR)
6	Natural Gas	(FR)
7	Steam	(FR)
8	Coal	(FR)
9	Fluidizing Gas- Loop Seal	(FR to AR)
	1 Horizontal	
	2 Vertical	
10	Fluidizing Gas- Loop Seal	(AR to FR)
	1 Horizontal	
	2 Vertical	
11	Fluidizing Gas- Loop Seal	(FR recycle)
	1 Horizontal	
	2 Vertical	
12	Propane/ Natural Gas	(AR)
13	Propane/ Natural Gas	(FR)
14	Pressure Tap Purge	(AR)
15	Pressure Tap Purge	(FR)
16	H2O + Bed Material	(AR)
17	Elutriated Bed Material	(AR)
18	Exiting Gases	(AR)
19	H2O + Bed Material	(FR)
20	Elutriated Bed Material	(FR)
21	Exiting Gases	(FR)
22	Air	(AR)
23	Gas Sample	(AR)
24	Gas Sample	(FR)
25	Air	(FR)

Data Acquisition over 1 Hour



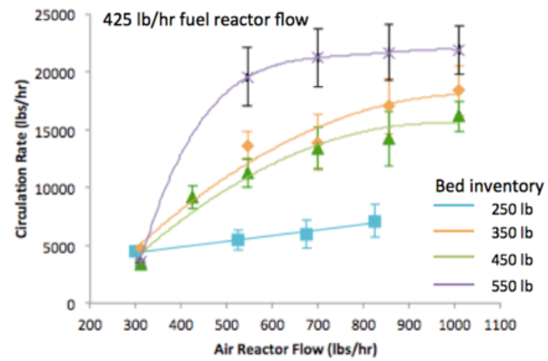
Progress and Current Status:
PDU Operational Experience

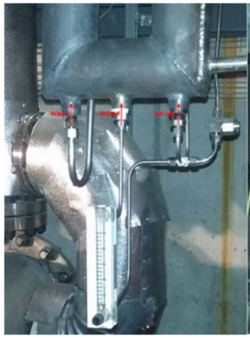
Status

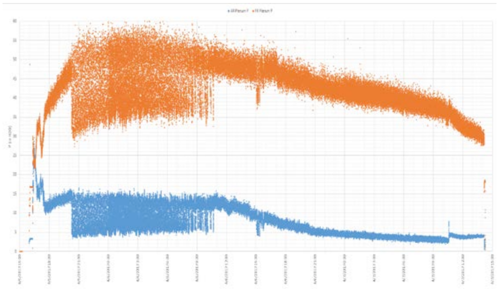
- Construction complete
- Shakedown complete
  - Gas flow + preheat
  - Controllable coal feed
  - Circulation rates > 10 ton/hr
- Over 800 hours of hot circulation
- Temps to 1700°F achieved
- Operators comfortable

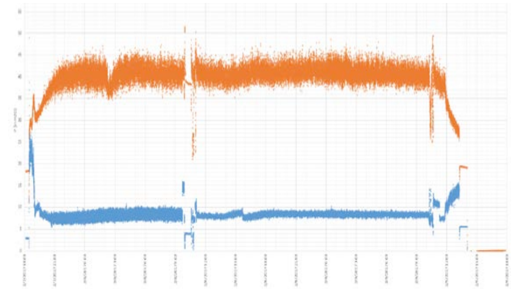
Challenges

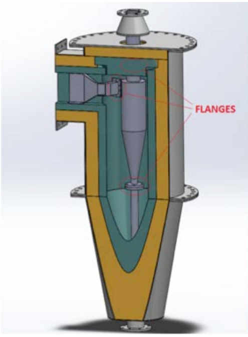
- Preheat
  - electric, burners, propane, nat gas
- Cyclones and bed loss
  - Geometry vs wall roughness
  - Loop seal operation
  - Loop seal sensors
  - Particle size
- “Normal” things
  - Leaks, etc.





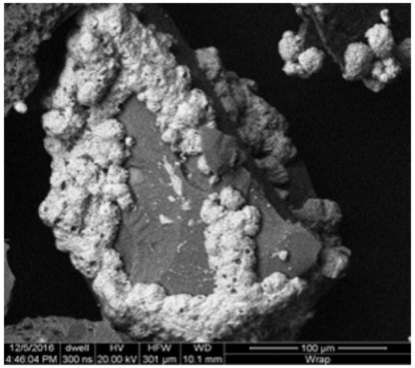


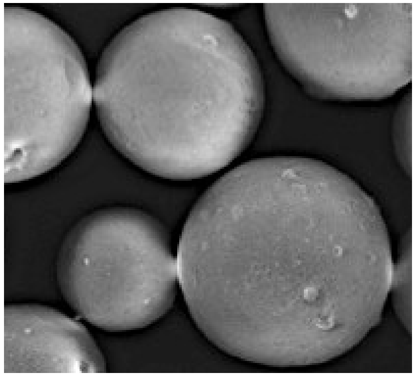




Progress and Current Status:
Oxygen Carrier for PDU

- Oxygen carriers tested to date
  - Ilmenite (non-CLOU)
  - CuO on silicon carbide
  - CuO on ilmenite
- Experience with low-cost CLOU carriers
  - Unacceptable Cu loss
  - Agglomeration tendency
- Future testing will be with superior CLOU carrier
  - CuO on engineered SiO_2 support
  - Good performance in 10 kW unit
    - Reactivity
    - No agglomeration
    - “Fluidizability”
  - Downside is high cost



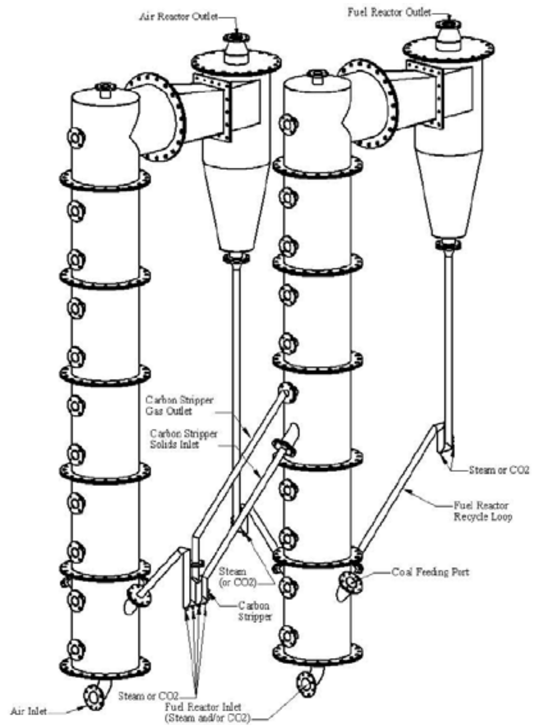


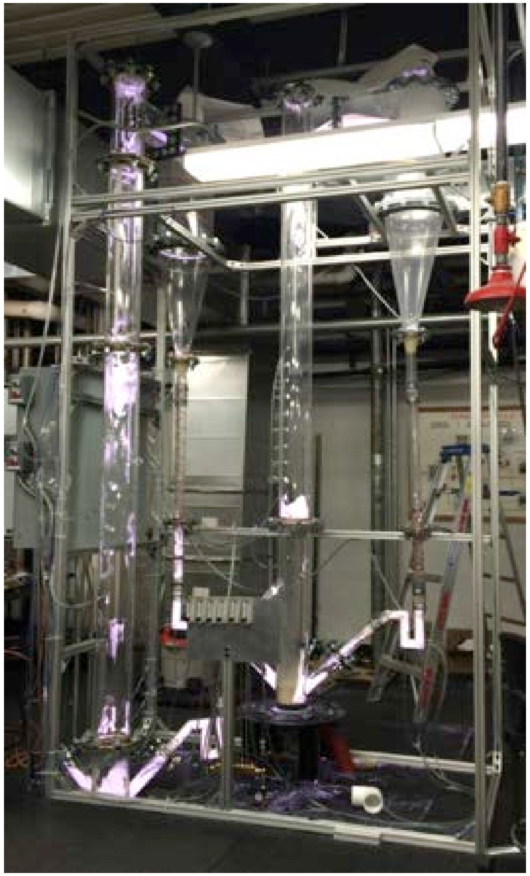
Progress and Current Status

- Oxygen carrier production scale-up
- Evaluation of carbon conversion
- Pilot system operation
- **Reactor simulation and scale-up**

Progress and Current Status:
Process Modeling and Simulation

- **Experimental modeling**
  - Plexiglas cold flow system
  - Scaled properly to represent PDU
  - 60% scale
  - Air for fluidization
  - Glass beads
  - Pressure profiles
  - Circulation rates
- **Computational simulation**
  - CPFD Barracuda VR®

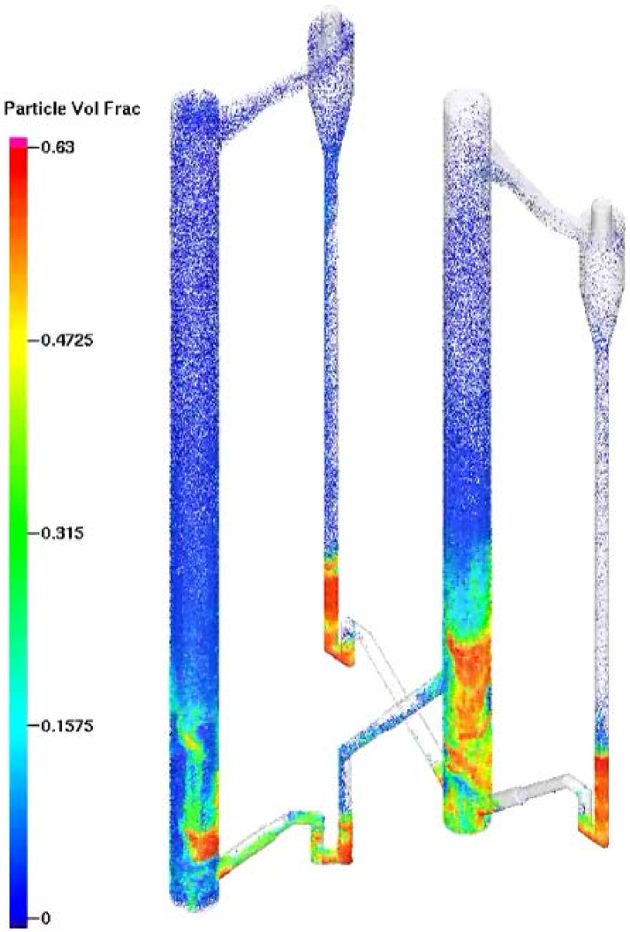




Cold-flow model of UofU PDU

Progress and Current Status:
Chemical Looping Reactor Simulation

- Models of 10 kW bench-scale, 200 kW pilot-scale reactors, and cold-flow unit
- Simulations include
  - hydrodynamics
  - heat transfer
  - Chemistry/kinetics
    - Oxygen carrier
    - Coal combustion
    - Gas phase
- Understanding from simulations valuable for interpreting behavior of pilot-scale system



Progress and Current Status:
Significant Accomplishments

- **Successful scale-up of CLOU oxygen carrier production**
  - Can now produce enough material for PDU operation
  - Material with up to 20% CuO loading produced
- **Successful commissioning of PDU**
  - All systems now function properly
  - Measured oxygen carrier circulation rates exceed design
  - 800+ hours of hot operation with circulation
  - Stable coal feeding achieved
- **Successful development of PDU simulation model**
  - Incorporation of kinetics for oxygen carrier reactions
  - Incorporation and improvement of coal combustion reaction kinetics
  - Over 55 different conditions have been simulated, each with at least 60 seconds of operation

Future Plans

- **This project**
  - Continue improving CLOU carrier performance
    - Improve physical and chemical stability
    - Target 40+ % CuO to increase load
  - Parametric testing of PDU with CuO (CLOU) carrier and coal
    - Vary coal, coal particle size, air reactor flow rate (circulation rate),
    - Measure CO_2 capture, CO_2 purity, fuel conversion, overall performance
  - Advance computational simulation
    - Validate simulation of PDU with operational data
    - Simulate larger (e.g. 10 and 100 MW) reactors

- **Future development**
  - Continued operation and experience with PDU
  - Evaluate PDU performance with different oxygen carriers
  - Pursue opportunities for larger pilot (3-10 MW) system

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