

Integrated Oxygen Production and CO₂ Separation through Chemical Looping Combustion with Oxygen Uncoupling

Project DE-FE0025076

Kevin J. Whitty, JoAnn S. Lighty, Andrew Fry

Presenter: Matthew A. Hamilton

The University of Utah

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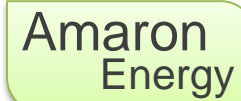
Outline

- Project overview
- Technology background
- Technical approach / project scope
- Progress and current status of project
- Future plans



Project Overview

Participants:



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 – August 31, 2017

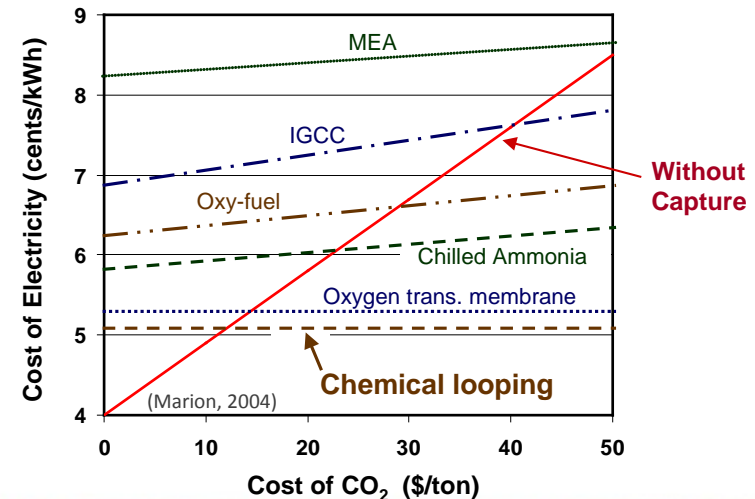
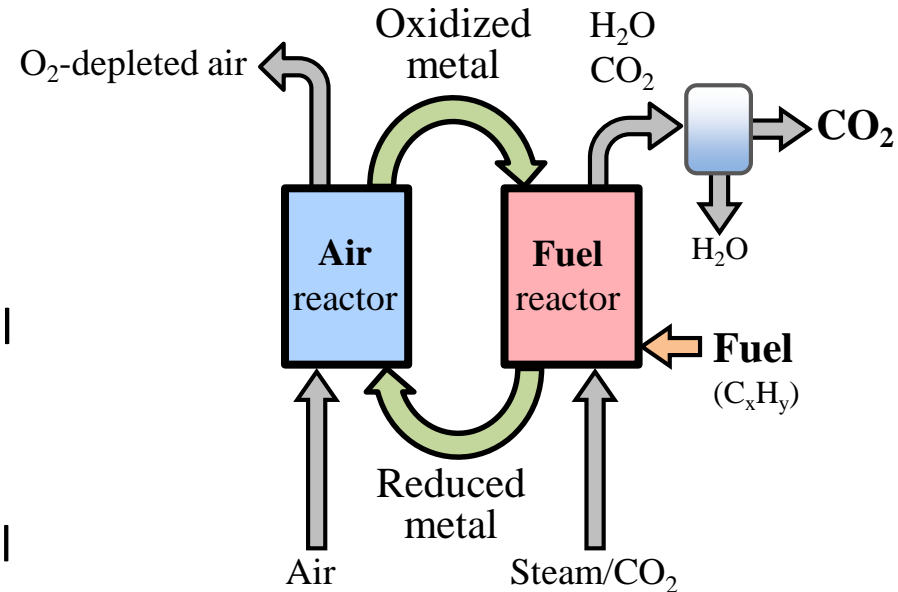
Objectives:

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: Chemical Looping Combustion

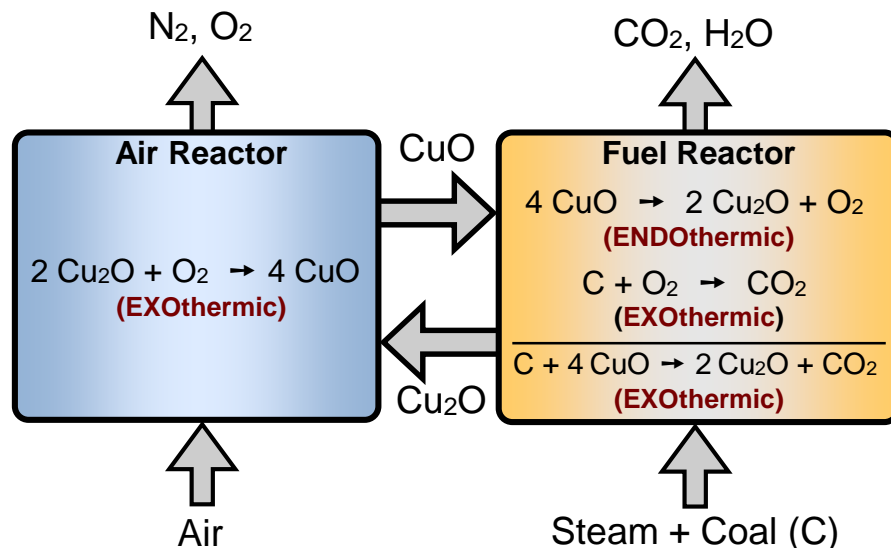
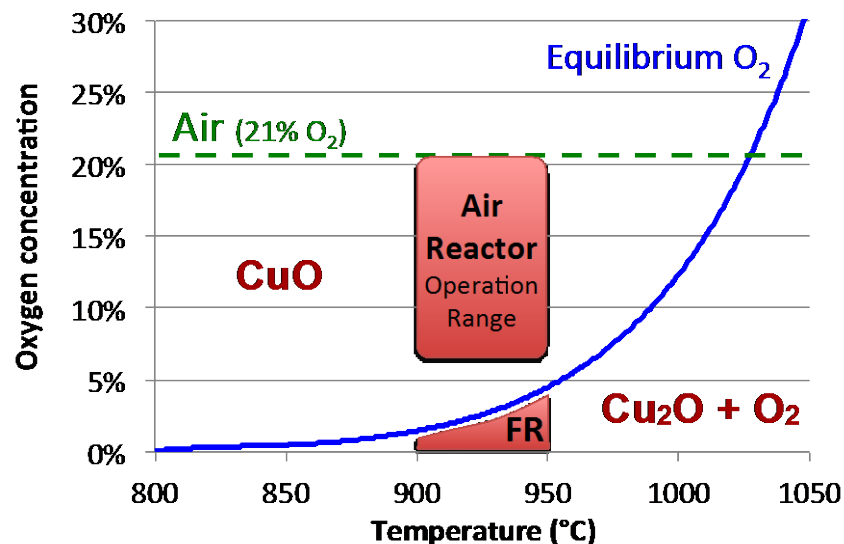
- CLC achieves *in situ* air separation by using a metal to transport oxygen from *air reactor* to *fuel reactor*
- Fuel (e.g. natural gas, coal) fed to fuel reactor is indirectly combusted by oxygen on oxidized metal
- Metal returns to reduced state in fuel reactor and “loops” back to air reactor
- Overall balance same as for conventional combustion
- Economic evaluations indicate CLC yields lowest COE of any CO₂-capture technology



Technology Background: Chemical Looping with Oxygen Uncoupling (CLOU)



- Copper is one of few metals for which oxidation equilibrium ($\text{Cu}_2\text{O}/\text{CuO}$) 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



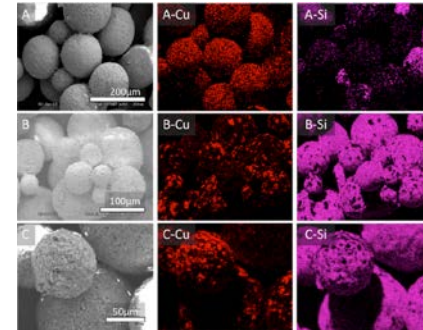
Technology Background: Previous Research and Development

➤ CLC intensively researched worldwide

- UofU researching since 2007
- 10 projects totaling \$5.2 million

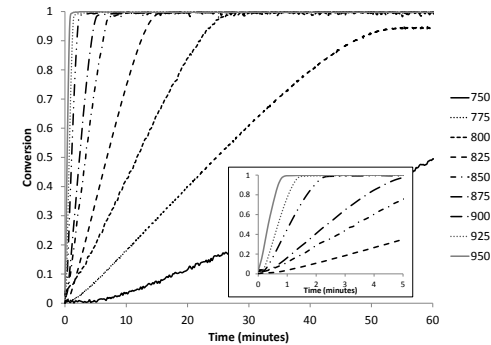
➤ Oxygen carrier development

- Focus on inexpensive copper-based carriers with scalable production
- Dozens of alternatives tested
- Current focus is CuO-on-SiC



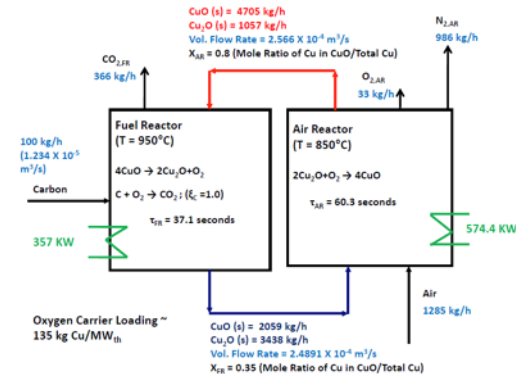
➤ Reactor and process development

- Fundamental studies of CLOU reaction kinetics
- Lab-scale experiments of coal conversion
- Design and initial construction of 200 kW PDU



➤ Process modeling and reactor simulation

- Aspen Plus modeling of CLC system
- Barracuda VR[®] modeling of integrated fluidized bed system



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

- CO₂ capture (target min. 90%)
- CO₂ purity (target min. 95%)
- Coal conversion (target min. 99%)

Work plan / Tasks

1. Project management
2. Construction of pilot-scale rotary kiln for 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 CO₂ capture at pilot scale
8. Carbon stripper design and operation
9. Design of pilot/demo scale CLOU reactors



Project Scope (Project Management Plan)

➤ Technical milestones

- 2.1 Complete pilot rotary kiln
- 3.1 Complete CLC PDU
- 3.2 Start CLOU testing
- 8.1 Carbon stripper installed
- 9.1 Large CLC system design

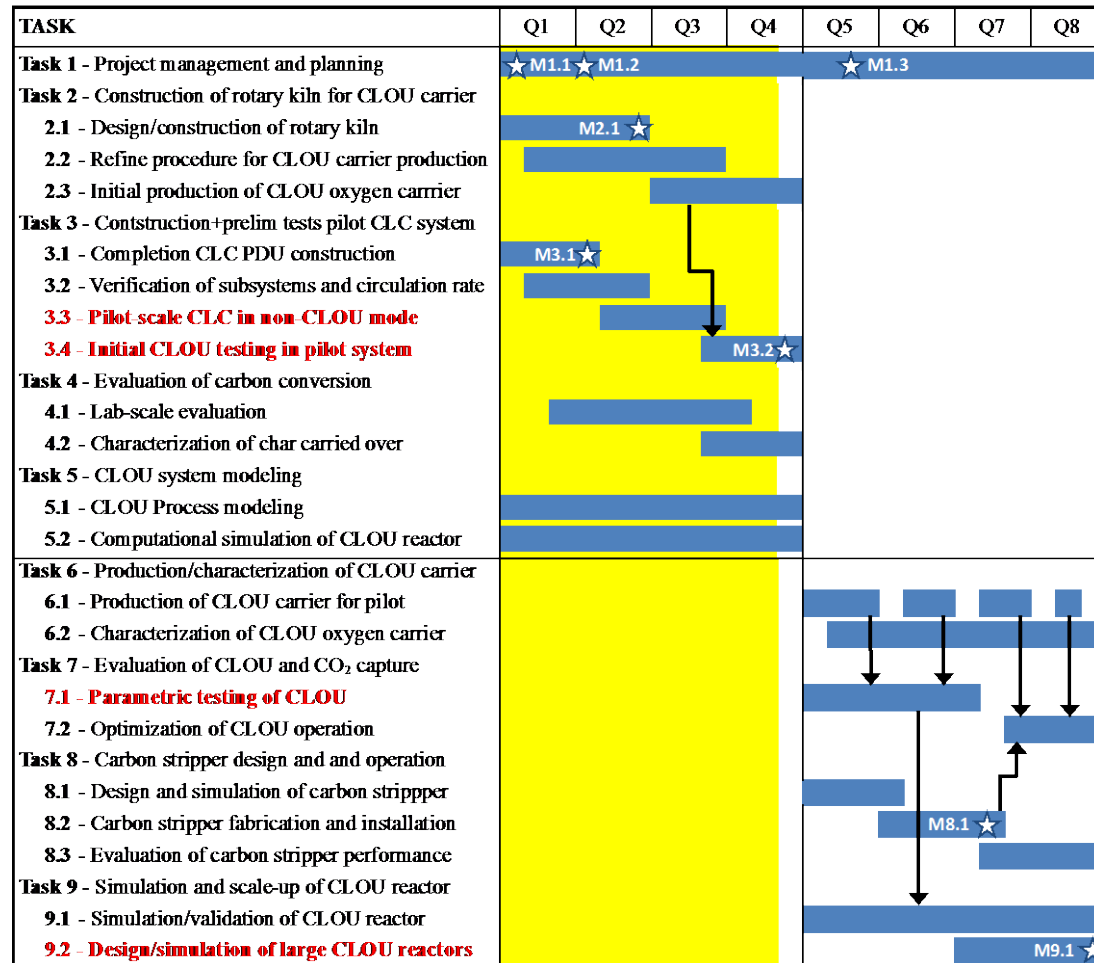
➤ Success criteria focused on pilot system

- Key operation steps (tasks in red) 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

2015				2016				2017															
S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A



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

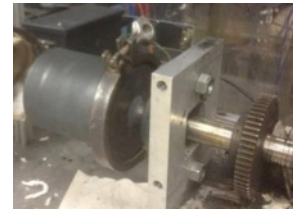
➤ Procedure

- Incipient wetness with copper nitrate
- Current support: SiC
 - Best based on previous screening
- Research focuses on identifying optimum production “recipe”
 - $\text{Cu}(\text{NO}_3)_2$ concentration
 - Number of additions
 - Calcining time
 - Solvent
 - Support pretreat

➤ Equipment

- Rotary evaporator for screening
- Three scales of rotary kiln
 - 1 kg lab scale
 - 10 kg bench scale
 - 100 kg pilot built by Amaron Energy

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	500°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



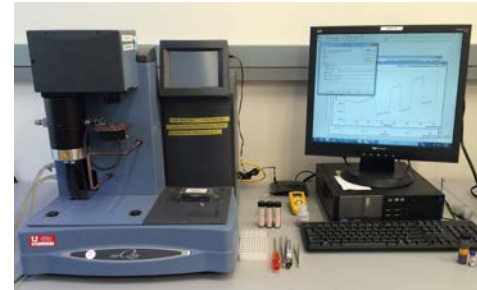
Progress and Current Status: Scale-up of CLOU Oxygen Carrier Production (2)

➤ Characterization

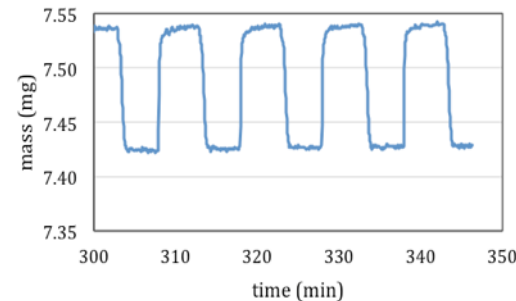
- TGA for oxygen loading/rates
- BET for available surface area
- SEM for morphology
- Crush strength
- Lab-scale fluidized bed for long-term performance in a cycling fluidized bed reactor

➤ Current Status

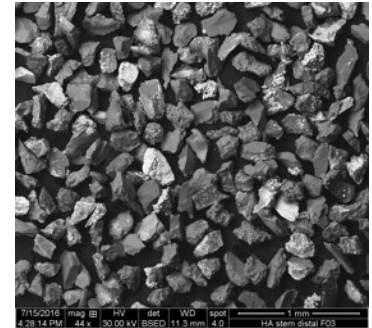
- Over 35 different carriers produced and characterized
- Test batch of 50 kg CuO-on-SiC successfully produced in RK-100 pilot kiln



TGA for oxygen capacity and rate tests



Sustained cyclability of UofU carrier



CuO-on-SiC oxygen carrier



BET surface area analyzer



Lab-scale fluidized bed system



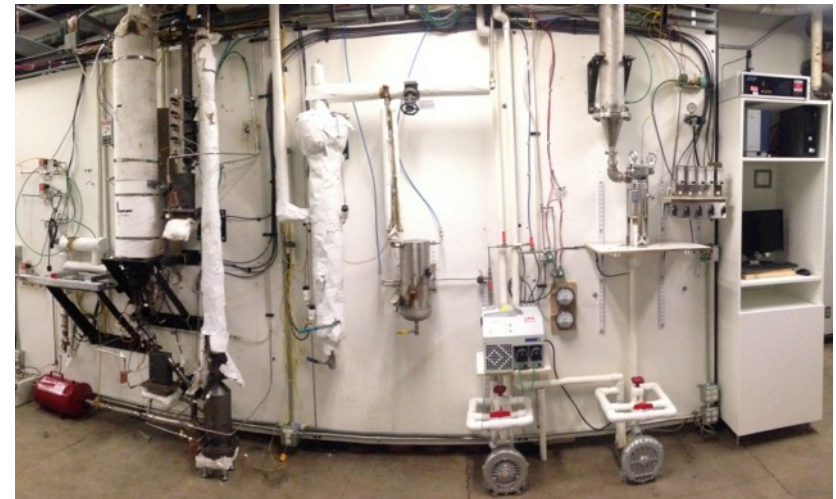
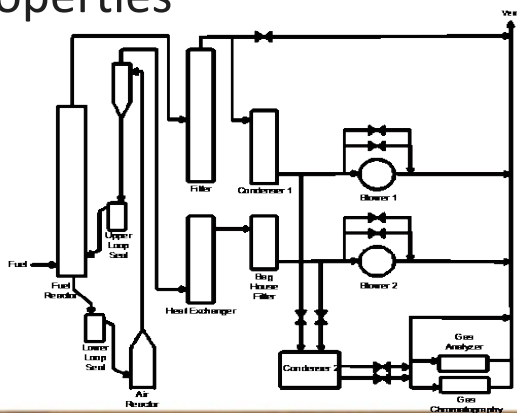
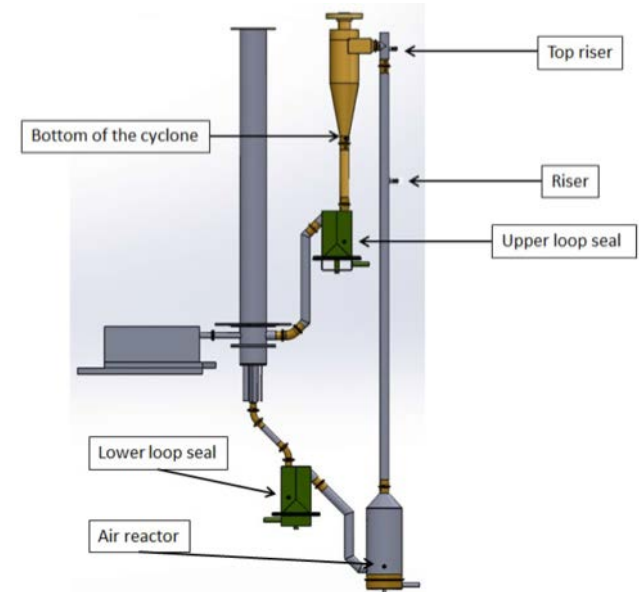
Progress and Current Status: CLOU Experiments and Process Development

➤ Two primary chemical looping reactor systems

- 10 kW bench-scale
- 200 kW semi-pilot scale

➤ 10 kW_{th} bench-scale system

- Electrically heated
- 1.5 kg/hr coal feed rate
- Bubbling bed fuel reactor
- Bubbling bed air reactor
- Riser to lift particles to cyclone
- Used for testing carrier and char properties



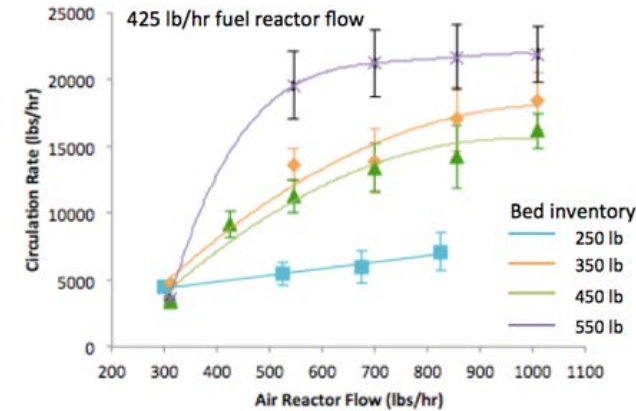
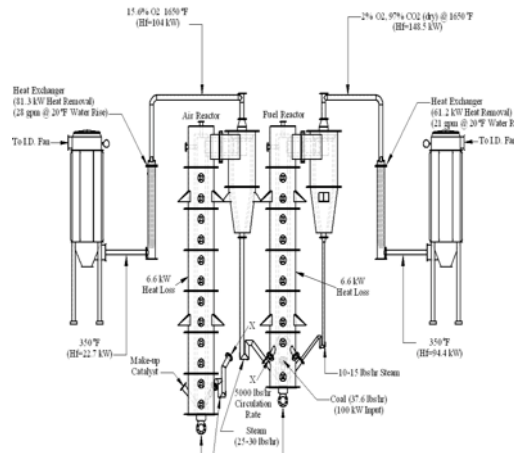
Progress and Current Status: 200 kW_{th} Process Development Unit

➤ PDU Design

- Two interconnected CFBs
- Refractory-lined
- Electric + gas air/steam preheat
- Approx. 175 kg bed inventory

➤ Status

- Construction complete
 - Some rebuilds/repairs were necessary
- Function of subsystems has been confirmed
- Oxygen carrier circulation rates to 12 tons/hr ilmenite achieved
- CLC testing with gas in progress; coal starting soon

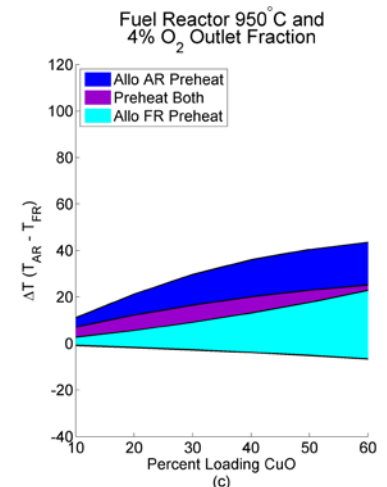
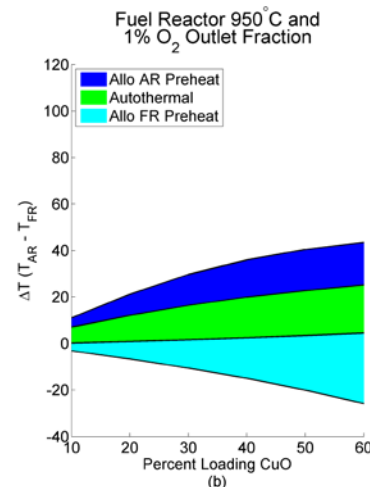
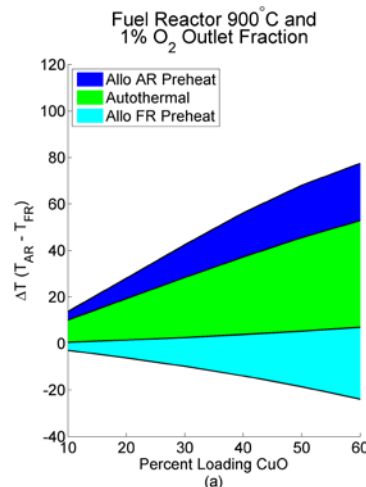
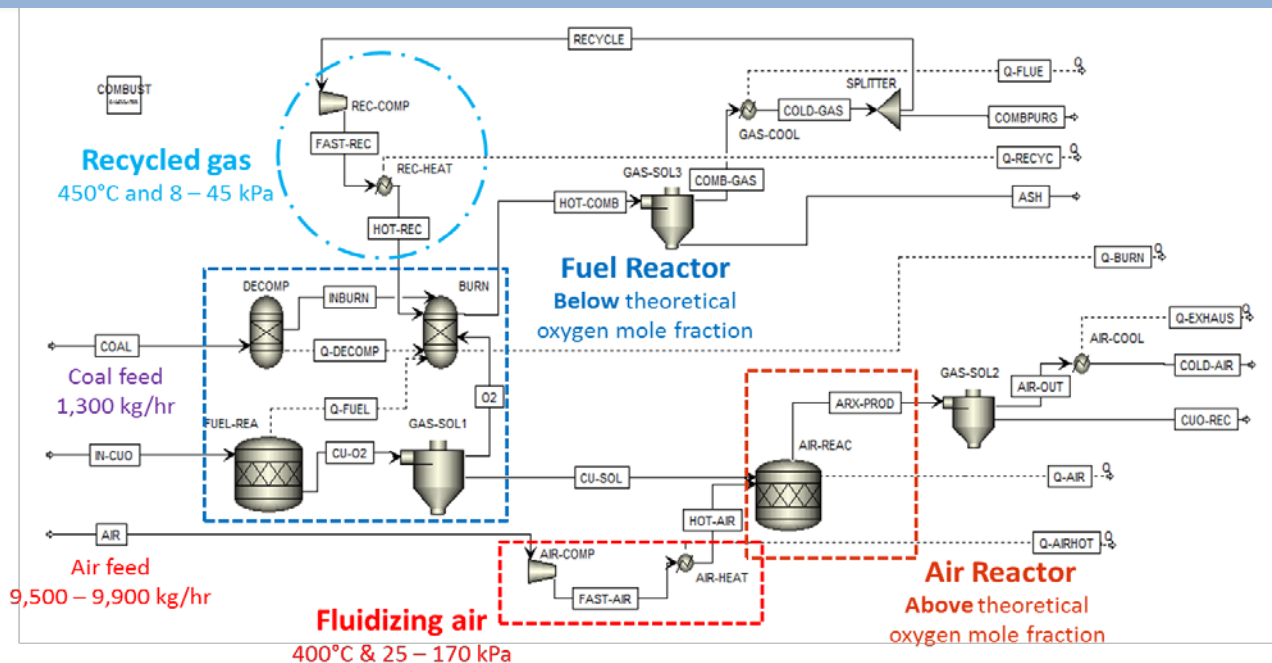


Progress and Current Status: Chemical Looping Process Modeling

➤ **Autothermal:**
Both reactors are exothermic.
Energy transferred from:

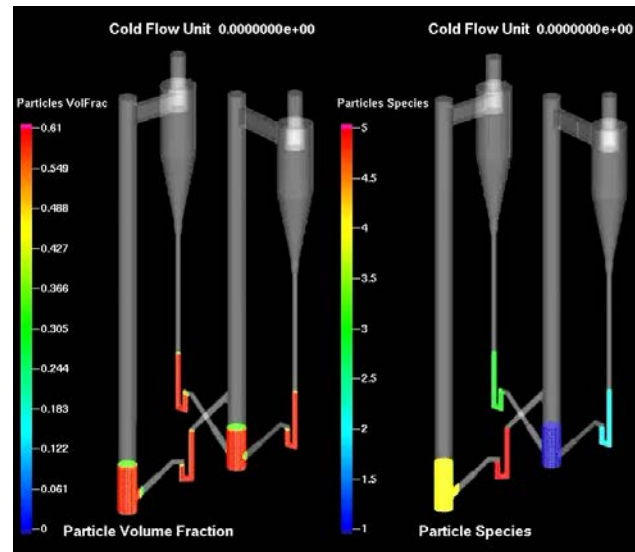
- Reactions
- Oxygen carrier heat capacity
- Heating gases

➤ **Allothermal:** At least one reactor requires external heating (e.g. preheating the fluidizing gas)

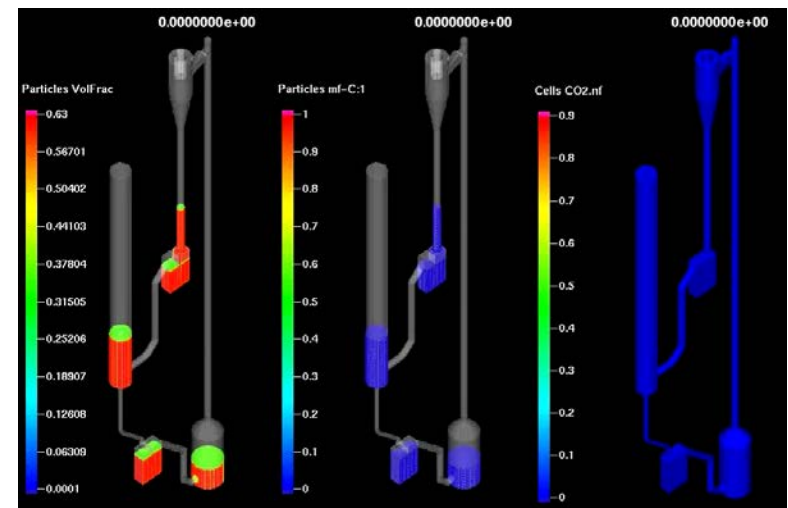


Progress and Current Status: Chemical Looping Reactor Simulation

- Using CFPD Barracuda VR[®]
- Models of 10 kW bench-scale, 200 kW pilot-scale reactors, and cold-flow unit
- Simulations include
 - hydrodynamics
 - heat transfer
 - Oxygen carrier chemistry/kinetics
 - Coal combustion chemistry/kinetics
- Plexiglas cold-flow model of UofU PDU to help validation
- Understanding from simulations has been valuable in starting up and interpreting behavior of pilot-scale system



Cold-flow model of UofU PDU



Progress and Current Status: Significant Accomplishments

- **Successful scale-up of CLOU oxygen carrier production**
 - Can now produce enough material for PDU operation
 - Initial batches of well-performing carrier to 20% CuO loading produced
- **Successful commissioning of 200 kW PDU**
 - All systems now function properly
 - Measured oxygen carrier circulation rates exceed design
 - Already 200+ hours of hot operation with circulation
- **Successful development of PDU simulation model**
 - Incorporation of kinetics for oxygen carrier reactions
 - Incorporation and improvement of coal combustion reaction kinetics
 - Over 20 different conditions have been simulated, each with at least 60 seconds of operation



Future Plans

➤ This project

- Produce CuO-based CLOU carrier for PDU testing
 - Initial batch targets 20% CuO to ensure no agglomeration
 - Eventually target 40-45% 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 CO₂ capture, CO₂ purity, fuel conversion, overall performance
 - Design, install and test carbon stripper to improve coal conversion and CO₂ capture.
- 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
- Pursue opportunities for larger pilot (3-10 MW) system



Acknowledgments

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