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Chemical Looping with Oxygen Uncoupling (CLOU)

JoAnn S. Lighty, Professor
Philip Smith, Professor
Kevin Whitty, Assoc. Professor
Ted Eyring, Professor (Retired)
Adel Sarofim, Presidential Professor (Deceased)

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Institute for Clean and Secure Energy
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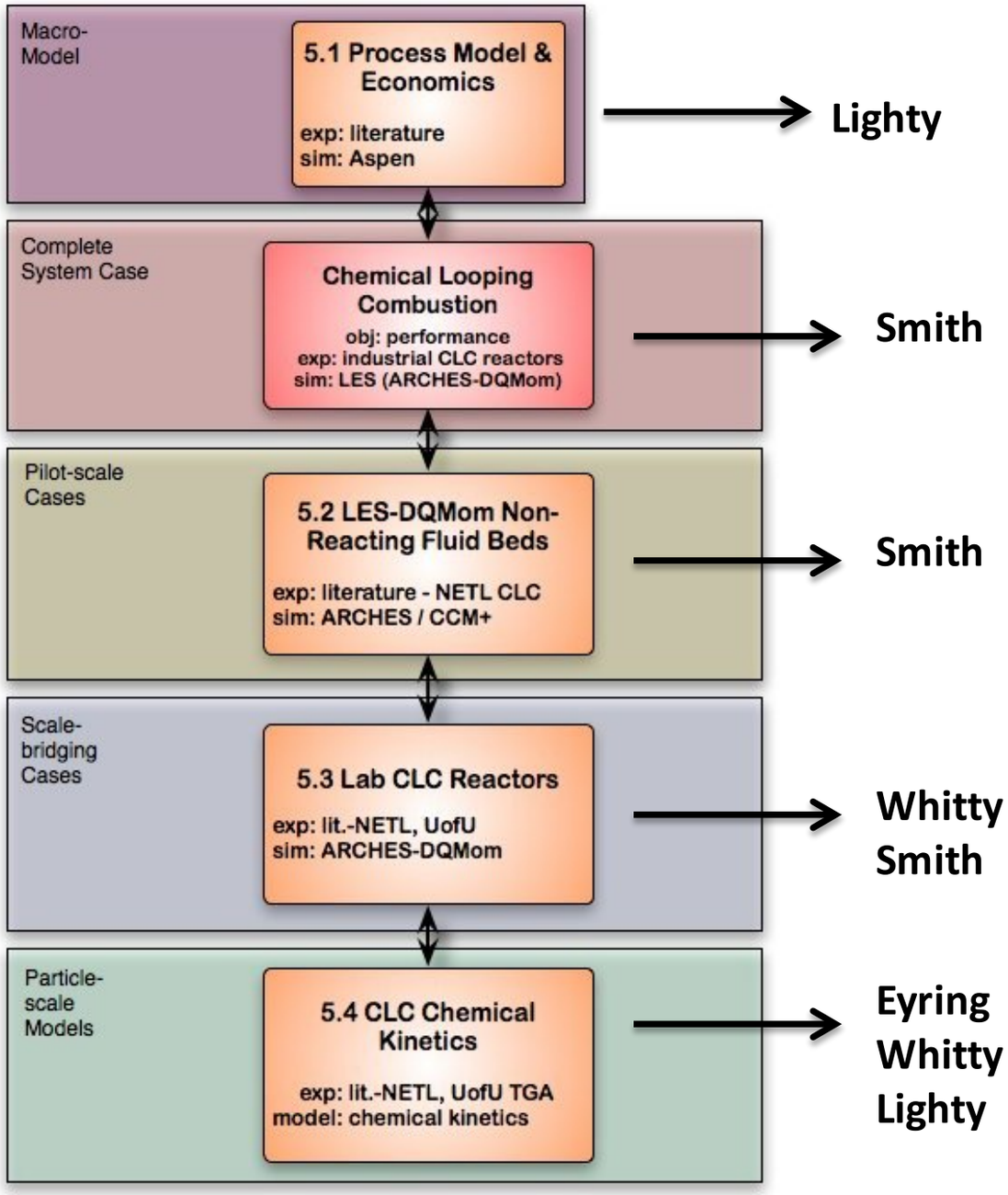
Program Overview

- **Major thrust is the use of complementary theoretical and experimental studies to provide simulation tools with error quantification, in order to reduce time to and risk in commercialization. The problems under study are:**
  - **The impact of CO_2 on flame stability, ash transformation, NOx and SOx emissions for both pulverized and fluidized bed oxyfuel combustion**
  - **The entrained-flow gasification of coal with emphasis on coal pyrolyis, soot formation, char and soot burnout and slag/refractory interactions**
  - **Chemical looping combustion for solid fuels with ASPEN system modeling and CFD detailed modeling**
  - **Underground coal thermal treatment to gasify/liquefy coal in-situ with capture of CO_2 in the residual char**
  - **CO_2 sequestration with experimental in-house studies of kinetics of CO_2 and SO_2 reactions with rock formations.**
- **The above technical activities are complemented by policy and legal studies assessing regulatory gaps in CCS.**

Overall Project Objectives

- Integrated use of process models, simulation, and experiments facilitates scale up, reduces deployment time, and reduces risk



Project Objectives

- Carrier development / production
  - Support material selection
  - Copper addition and particle formation techniques
  - Degree of copper loading
- Carrier characterization
  - Carrier capacity over multiple cycles
  - Oxidation and reduction kinetics
  - Fluidized bed performance (attrition, sintering, agglomeration)
- Simulation and Process
  - Fluidized bed simulations
  - Process material and energy balances
- Future: Process development and evaluation

Funding & Participants

10/2009 to 8/2013 Participants

Edward Eyring, Gabor Konya, Robert Lewis, Sean Peterson, Richard Baracki

Kevin Whitty, Chris Clayton, Crystal Allen

JoAnn Lighty, Asad Sahir, Nick Tingey, James Dansie, Artur Cadore

Philip Smith, Michal Hradisky, John Parra

Funding Amount

Edward Eyring

10/2008 to 8/2013

DOE $370,769

Cost Share $92,692

Kevin Whitty

DOE $255,157

Cost Share $63,789

JoAnn Lighty

DOE $264,968

Cost Share $66,242

Philip Smith

DOE $258,814

Cost Share $64,704

Outline

- Background of Chemical Looping with Oxygen Uncoupling (CLOU)
- Oxygen Carrier Characterization
- Fluidized Bed Simulations
- Process Modeling and System Scale-Up
- Conclusions

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Background: CLC and CLOU

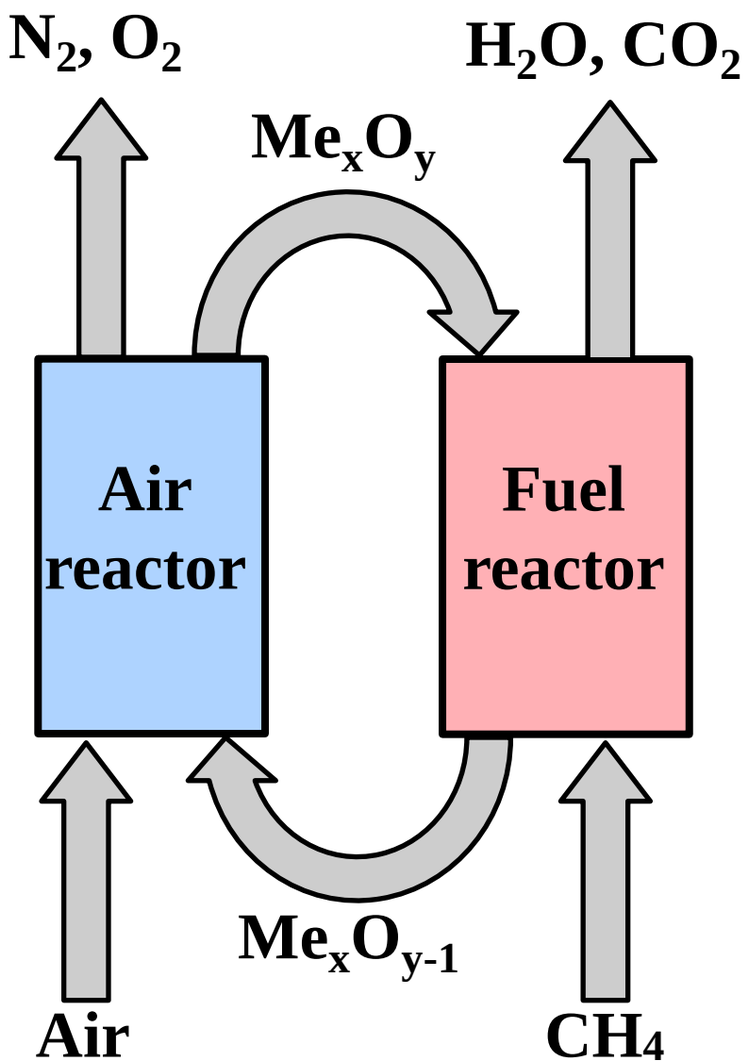
CLC with Natural Gas

Air Reactor:

$$\frac{1}{2} O_2 + Me_xO_{y-1} \rightarrow Me_xO_y$$

Fuel Reactor:

$$CH_4 + 4\ Me_xO_y \rightarrow Me_xO_{y-1} + 2\ H_2O + CO_2$$



(Indirect) CLC with Solid Fuel

Air Reactor:

$$\frac{1}{2} O_2 + Me_xO_{y-1} \rightarrow Me_xO_y$$

Gasifier:

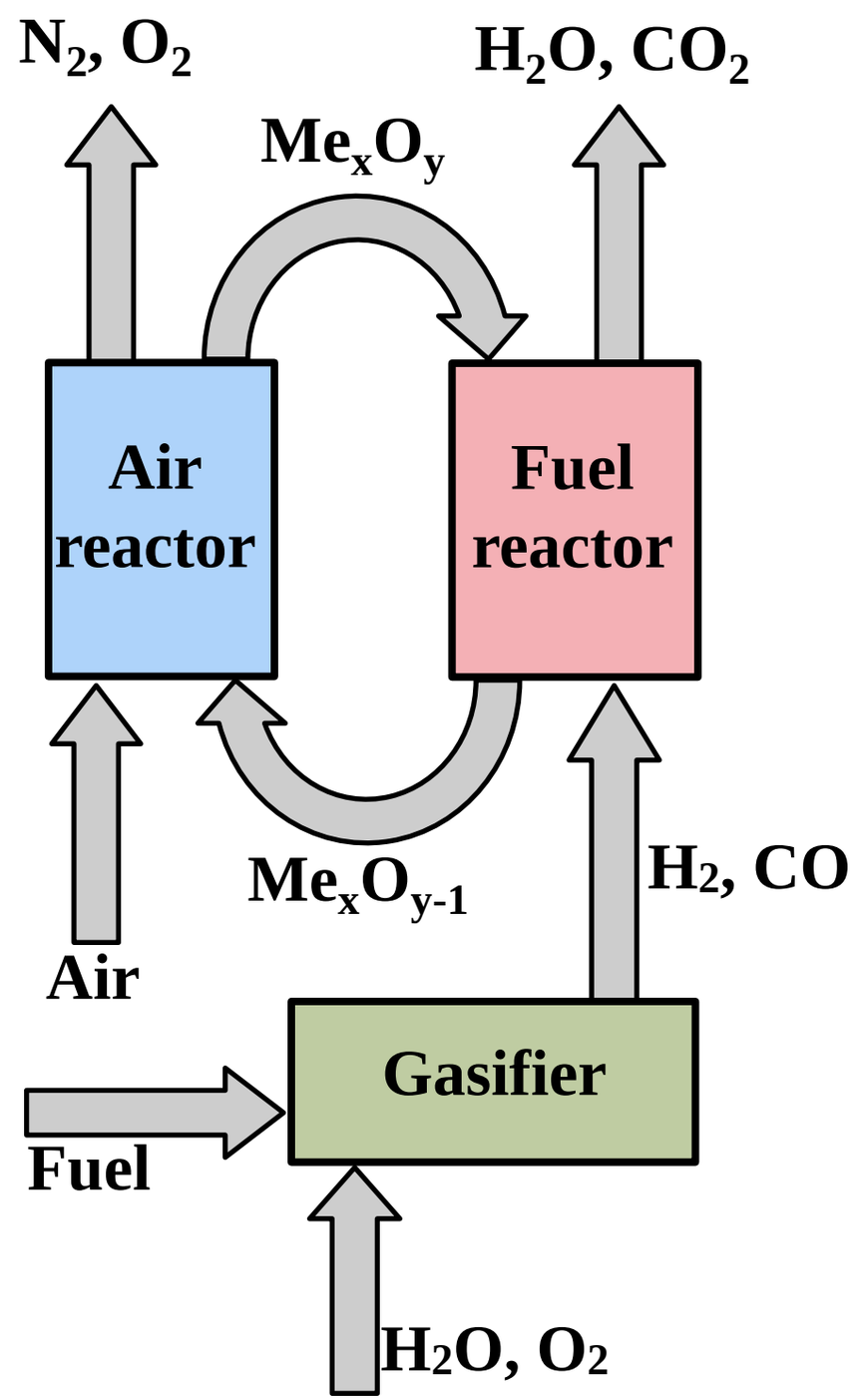
$$C + H_2O \rightarrow H_2 + CO$$

$$C + \frac{1}{2} O_2 \rightarrow CO$$

Fuel Reactor:

$$CO + Me_xO_y \rightarrow Me_xO_{y-1} + CO_2$$

$$H_2 + Me_xO_y \rightarrow Me_xO_{y-1} + H_2O$$



(Direct) CLC with Solid Fuel

Air Reactor:

$$\frac{1}{2} O_2 + Me_xO_{y-1} \rightarrow Me_xO_y$$

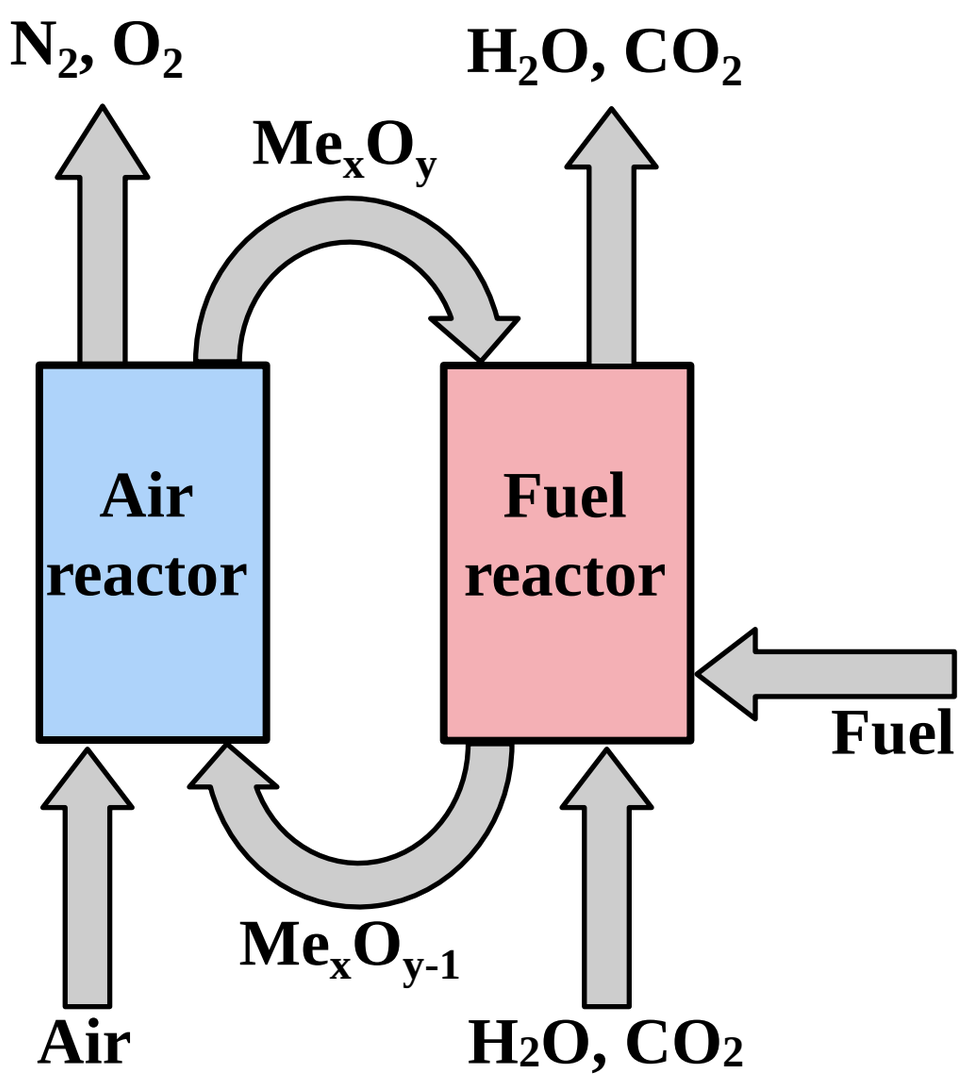
Fuel Reactor:

$$C + H_2O \rightarrow H_2 + CO$$

$$C + CO_2 \rightarrow 2\,CO$$

$$CO + Me_xO_y \rightarrow Me_xO_{y-1} + CO_2$$

$$H_2 + Me_xO_y \rightarrow Me_xO_{y-1} + H_2O$$



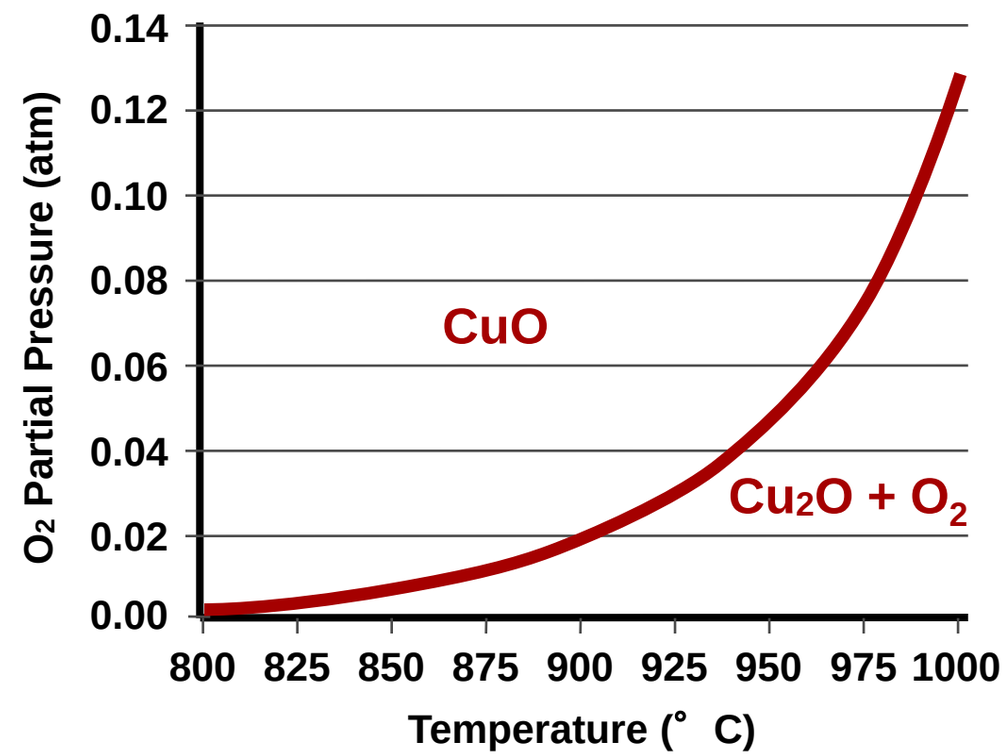
Chemical Looping with Oxygen Uncoupling (CLOU)

- Oxygen (O_2) is spontaneously liberated in the fuel reactor
- Allows for direct processing of solid fuels
- Selection of oxygen carrier combination is key
- University of Utah is focusing on copper

Why Does CLOU Work?

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

- **Thermodynamics**
  - At high temperature, equilibrium of the metal oxidation reaction favors Cu_2O
  - Equilibrium partial pressure of O_2 is about 0.05 atm at combustion temperatures



- **Reactor system configuration**
  - Air reactor: high concentration of O_2 forces reaction to the right
  - Fuel reactor: low concentration of O_2 forces reaction to the left

- **Very few metal/metal oxide combinations exhibit CLOU behavior**

CLOU with Solid Fuel
(Chemical Looping with Oxygen Uncoupling)

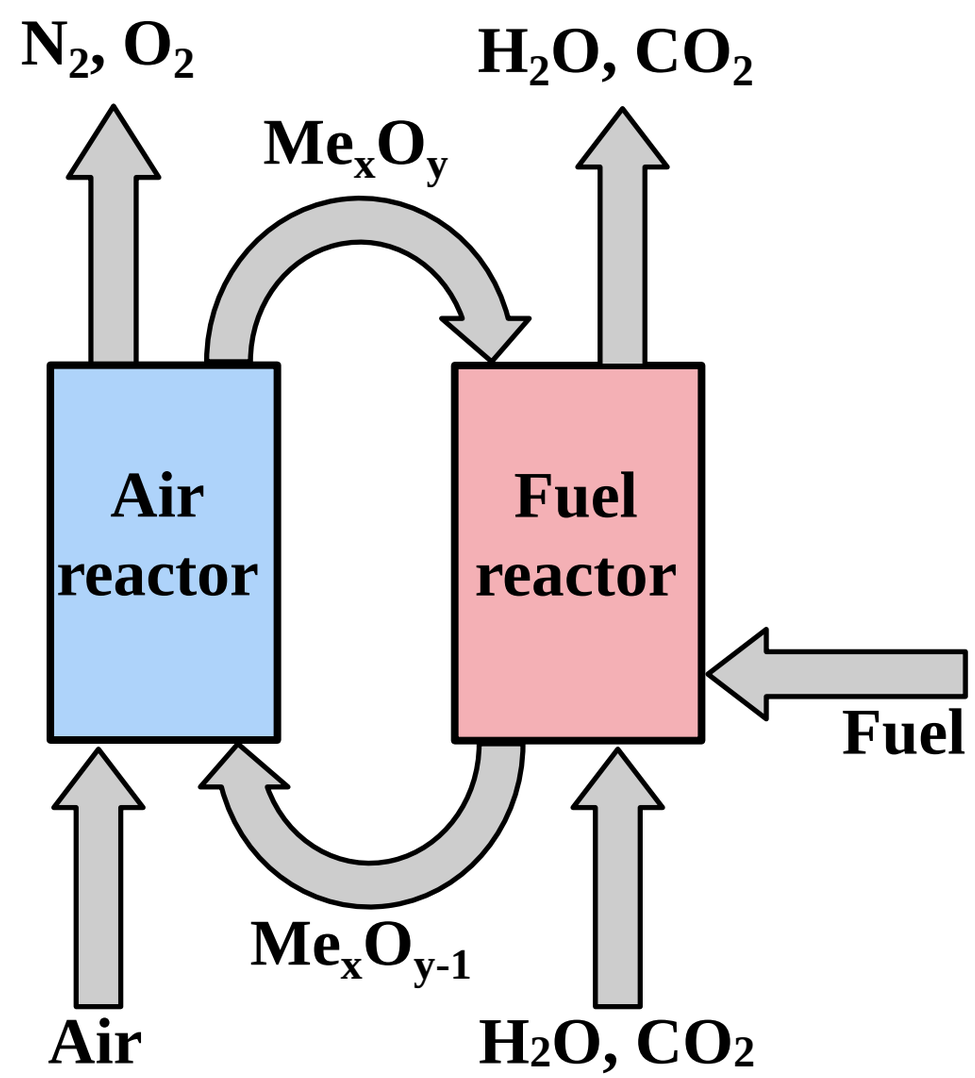
Air Reactor:

$$\tfrac{1}{2}\,O_2 + Me_xO_{y-1} \leftrightarrow Me_xO_y$$

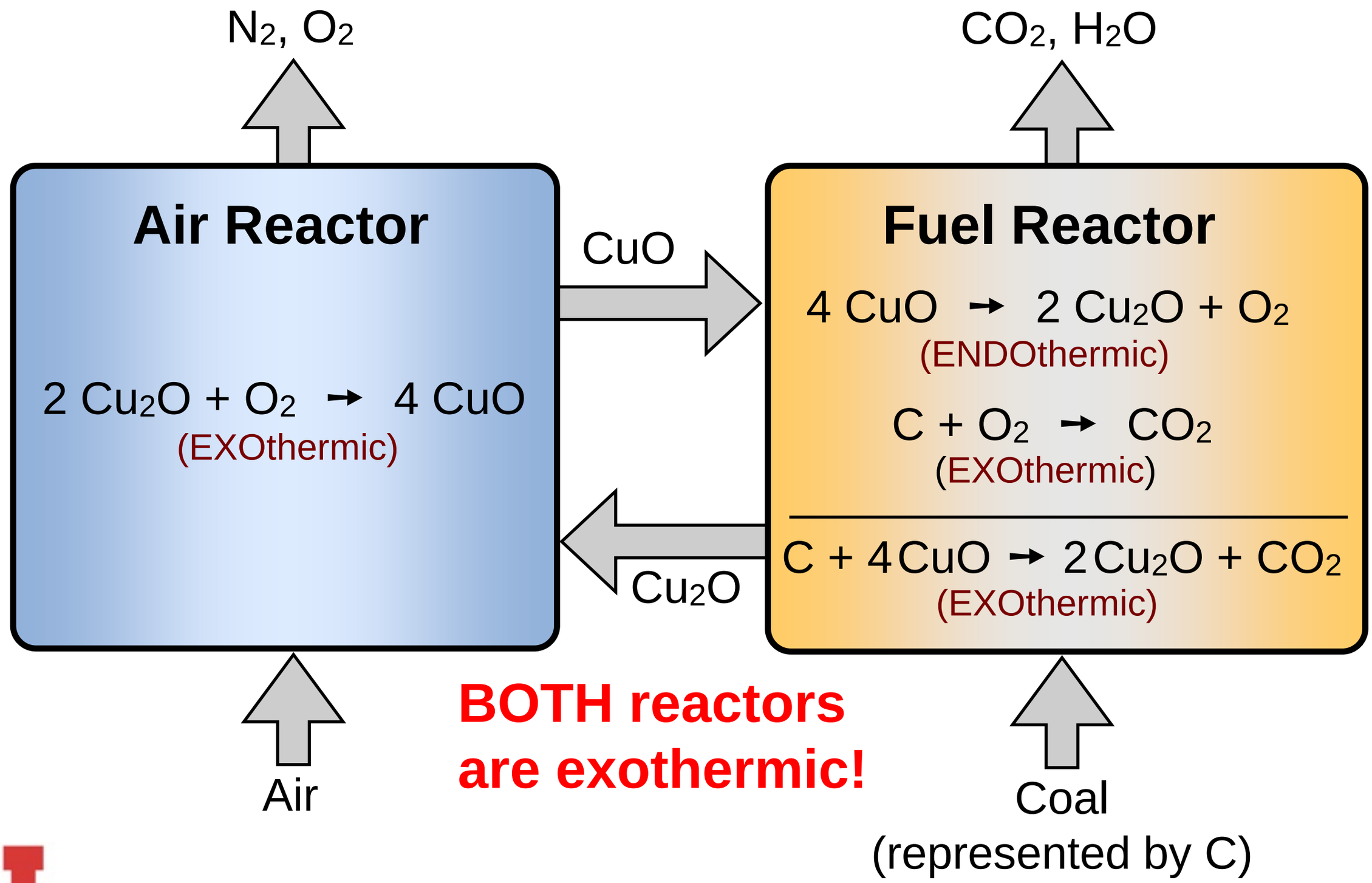
Fuel Reactor:

$$Me_xO_y \leftrightarrow Me_xO_{y-1} + \tfrac{1}{2}\,O_2$$

$$C + O_2 \rightarrow CO_2$$



Copper-Based CLOU



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Oxygen Carrier Whitty (and Eyring)

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Oxygen Carrier Development and Performance Analysis

Kevin Whitty, Edward Eyring, Chris Clayton,
Gabor Konya, Sean Peterson, Crystal Allen, Richard Baraki

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March 6, 2014

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Tasks within CASE Program

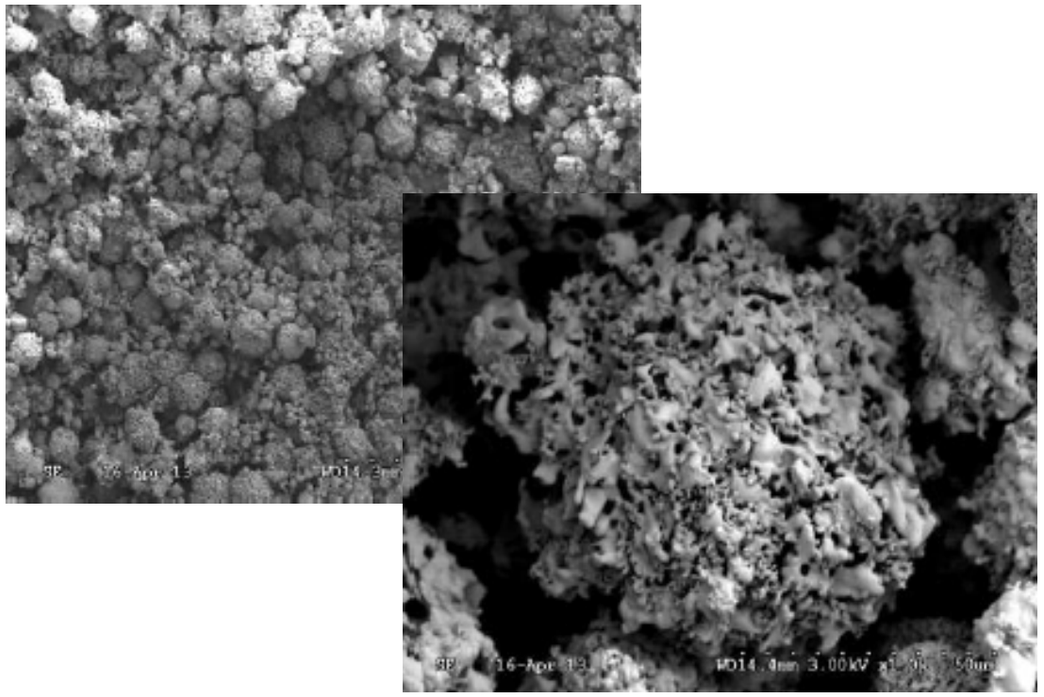
- Focus: Copper-based carriers for CLOU
  - Evaluate range of oxygen carrier materials
    - Carriers provided by outside parties
    - Home-cooked carriers developed at U. Utah
  - Investigate carriers produced by different techniques
    - Mechanical mixing/extrusion
    - Freeze granulation
    - Incipient wetness (wet impregnation)
- Subtask 5.4 – CLC kinetics (Eyring)
  - Decomposition ("uncoupling") kinetics
  - Oxidation kinetics
- Subtask 5.3 – Laboratory-scale CLC studies (Whitty)
  - Characterization of carrier properties
  - Evaluation of performance in lab-scale fluidized bed system
    - Oxygen transport capacity
    - Oxidation and reduction kinetics
    - Agglomeration

Outline

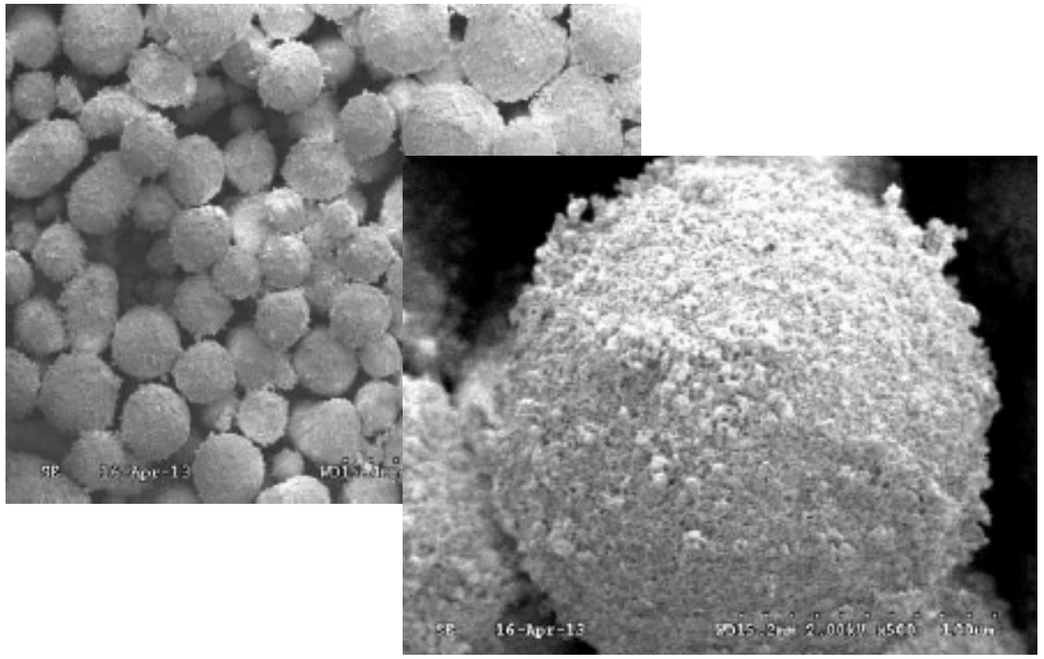
- Oxygen carrier properties and development
- Experimental systems
- Evaluation of carrier performance
  - Oxygen carrying capacity
  - Measurement and modeling of reaction rates
    - Oxidation
    - Reduction ("uncoupling")
  - Conversion of coal in a lab-scale fluidized bed
  - Attrition resistance

Oxygen Carriers: "Off the shelf"

- 50_TiO2_MM
  - 50% CuO by weight
  - TiO_2 support
  - Mechanically mixed,
    then extruded, calcined, sieved
  - Provided by ICPC, Poland

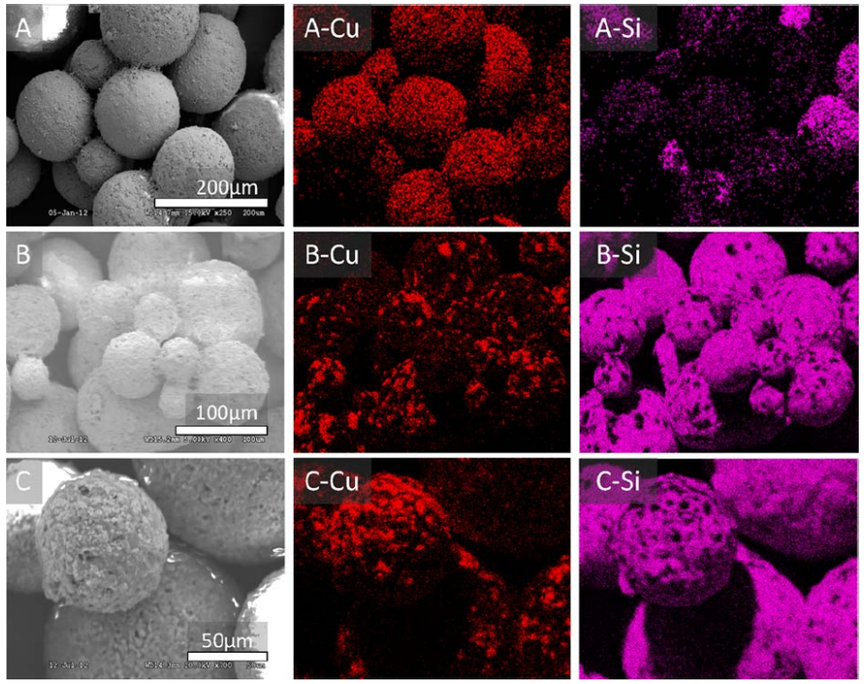


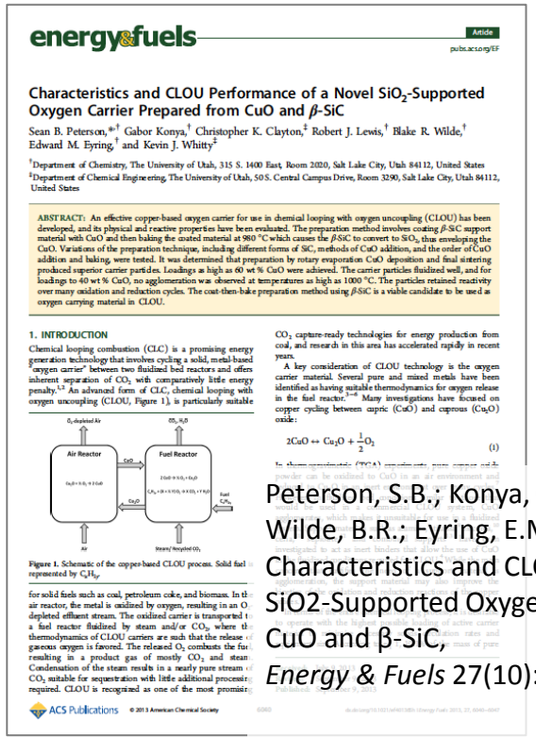
- 45_ZrO2/MgO_FG
  - 45% CuO by weight
  - MgO-stabilized ZrO_2 support
  - Mechanically mixed,
    then freeze granulated, calcined
  - Provided by Chalmers U, Sweden



Oxygen Carriers: UofU SiO_2-based

- SiO_2 support
  - Formed by starting with SiC, then calcining
  - Two forms of SiC used
    - SiC powder (abrasive grit)
    - SICAT SiC spheres (catalyst support)
- CuO added by wet impregnation
  - Rotary evaporator technique
  - Bake-then-coat vs coat-then-bake
  - 15, 20, 40 and 60% CuO loadings
  - Number of CuO impregnation cycles was varied from 1 to 10

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Article

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Characteristics and CLOU Performance of a Novel SiO_2-Supported Oxygen Carrier Prepared from CuO and β-SiC

Sean B. Peterson,*[†] Gabor Konya,[†] Christopher K. Clayton,[‡] Robert J. Lewis,[†] Blake R. Wilde,[†] Edward M. Eyring,[†] and Kevin J. Whitty[‡]

[†]Department of Chemistry, The University of Utah, 315 S. 1400 East, Room 2020, Salt Lake City, Utah 84112, United States

[‡]Department of Chemical Engineering, The University of Utah, 50 S. Central Campus Drive, Room 3290, Salt Lake City, Utah 84112, United States

ABSTRACT: An effective copper-based oxygen carrier for use in chemical looping with oxygen uncoupling (CLOU) has been developed, and its physical and reactive properties have been evaluated. The preparation method involves coating β-SiC support material with CuO and then baking the coated material at 980 °C which causes the β-SiC to convert to SiO_2, thus enveloping the CuO. Variations of the preparation technique, including different forms of SiC, methods of CuO addition, and the order of CuO addition and baking, were tested. It was determined that preparation by rotary evaporation CuO deposition and final sintering produced superior carrier particles. Loadings as high as 60 wt % CuO were achieved. The carrier particles fluidized well, and for loadings to 40 wt % CuO, no agglomeration was observed at temperatures as high as 1000 °C. The particles retained reactivity over many oxidation and reduction cycles. The coat-then-bake preparation method using β-SiC is a viable candidate to be used as oxygen carrying material in CLOU.

1. INTRODUCTION

Chemical looping combustion (CLC) is a promising energy generation technology that involves cycling a solid, metal-based "oxygen carrier" between two fluidized bed reactors and offers inherent separation of CO_2 with comparatively little energy penalty.[1,2] An advanced form of CLC, chemical looping with oxygen uncoupling (CLOU, Figure 1), is particularly suitable

CO_2 capture-ready technologies for energy production from coal, and research in this area has accelerated rapidly in recent years.

A key consideration of CLOU technology is the oxygen carrier material. Several pure and mixed metals have been identified as having suitable thermodynamics for oxygen release in the fuel reactor.[3−6] Many investigations have focused on copper cycling between cupric (CuO) and cuprous (Cu_2O) oxide:

$$2CuO \leftrightarrow Cu_2O + \frac{1}{2}O_2 \quad (1)$$

Figure 1. Schematic of the copper-based CLOU process. Solid fuel represented by C_xH_y.

for solid fuels such as coal, petroleum coke, and biomass. In the air reactor, the metal is oxidized by oxygen, resulting in an O_2-depleted effluent stream. The oxidized carrier is transported to a fuel reactor fluidized by steam and/or CO_2, where the thermodynamics of CLOU carriers are such that the release of gaseous oxygen is favored. The released O_2 combusts the fuel resulting in a product gas of mostly CO_2 and steam. Condensation of the steam results in a nearly pure stream of CO_2 suitable for sequestration with little additional processing required. CLOU is recognized as one of the most promising

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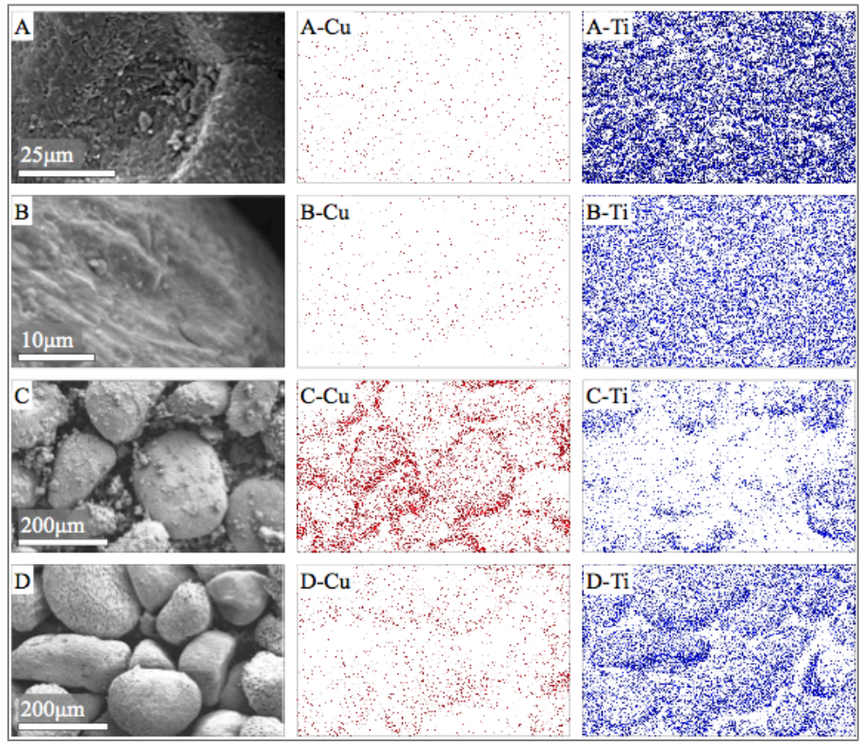
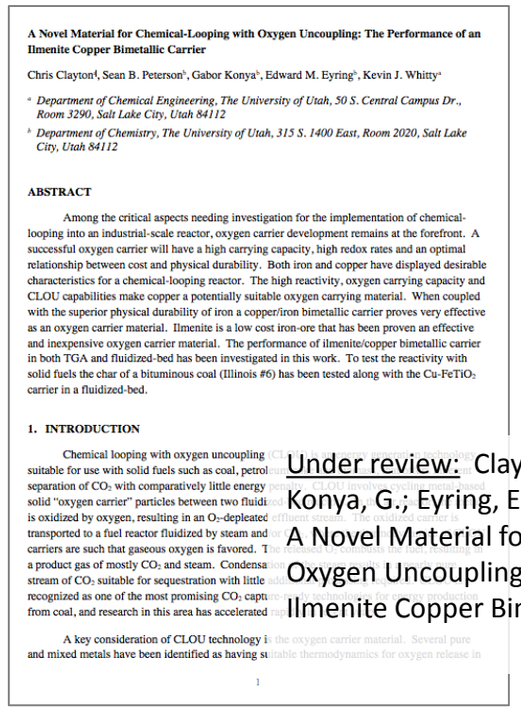
Peterson, S.B.; Konya, G.; Clayton, C.K.; Lewis, R.J.; Wilde, B.R.; Eyring, E.M.; Whitty, K.J. Characteristics and CLOU Performance of a Novel SiO2-Supported Oxygen Carrier Prepared from CuO and β-SiC, *Energy & Fuels* 27(10):6040-6047 (2013).

Oxygen Carriers: UofU Copper-on-Ilmenite

- Ilmenite ($FeTiO_3$) used as support
  - Conventional CLC carrier (Ti/Fe)
  - Well characterized
  - Inexpensive (< $100/ton)
- Wet impregnation
  - Rotary evaporator technique
  - Tested activated and non-activated ilmenite
  - 20 and 30% CuO loadings
  - CuO added in 6 to 9 cycles





A Novel Material for Chemical-Looping with Oxygen Uncoupling: The Performance of an Ilmenite Copper Bimetallic Carrier

Chris Clayton[a], Sean B. Peterson[b], Gabor Konya[b], Edward M. Eyring[b], Kevin J. Whitty[a]

[a] *Department of Chemical Engineering, The University of Utah, 50 S. Central Campus Dr., Room 3290, Salt Lake City, Utah 84112*

[b] *Department of Chemistry, The University of Utah, 315 S. 1400 East, Room 2020, Salt Lake City, Utah 84112*

ABSTRACT

Among the critical aspects needing investigation for the implementation of chemical-looping into an industrial-scale reactor, oxygen carrier development remains at the forefront. A successful oxygen carrier will have a high carrying capacity, high redox rates and an optimal relationship between cost and physical durability. Both iron and copper have displayed desirable characteristics for a chemical-looping reactor. The high reactivity, oxygen carrying capacity and CLOU capabilities make copper a potentially suitable oxygen carrying material. When coupled with the superior physical durability of iron a copper/iron bimetallic carrier proves very effective as an oxygen carrier material. Ilmenite is a low cost iron-ore that has been proven an effective and inexpensive oxygen carrier material. The performance of ilmenite/copper bimetallic carrier in both TGA and fluidized-bed has been investigated in this work. To test the reactivity with solid fuels the char of a bituminous coal (Illinois #6) has been tested along with the Cu-$FeTiO_3$ carrier in a fluidized-bed.

1. INTRODUCTION

Chemical looping with oxygen uncoupling (CLOU) is a promising technology for energy production suitable for use with solid fuels such as coal, petroleum coke, and biomass. CLOU involves cycling metal based separation of CO_2 with comparatively little energy penalty. CLOU involves cycling metal based solid "oxygen carrier" particles between two fluidized beds. The oxygen carrier is is oxidized by oxygen, resulting in an O_2-depleated effluent stream. The oxygen carrier is transported to a fuel reactor fluidized by steam and fuel. The released O_2 combusts the fuel, leaving a carriers are such that gaseous oxygen is favored. The released O_2 combusts the fuel, leaving a a product gas of mostly CO_2 and steam. Condensation of the steam leaves a pure CO_2 stream of CO_2 suitable for sequestration with little additional energy. CLOU is recognized as one of the most promising CO_2 capture energy technologies for energy production from coal, and research in this area has accelerated rapidly.

A key consideration of CLOU technology is the oxygen carrier material. Several pure and mixed metals have been identified as having suitable thermodynamics for oxygen release in

1

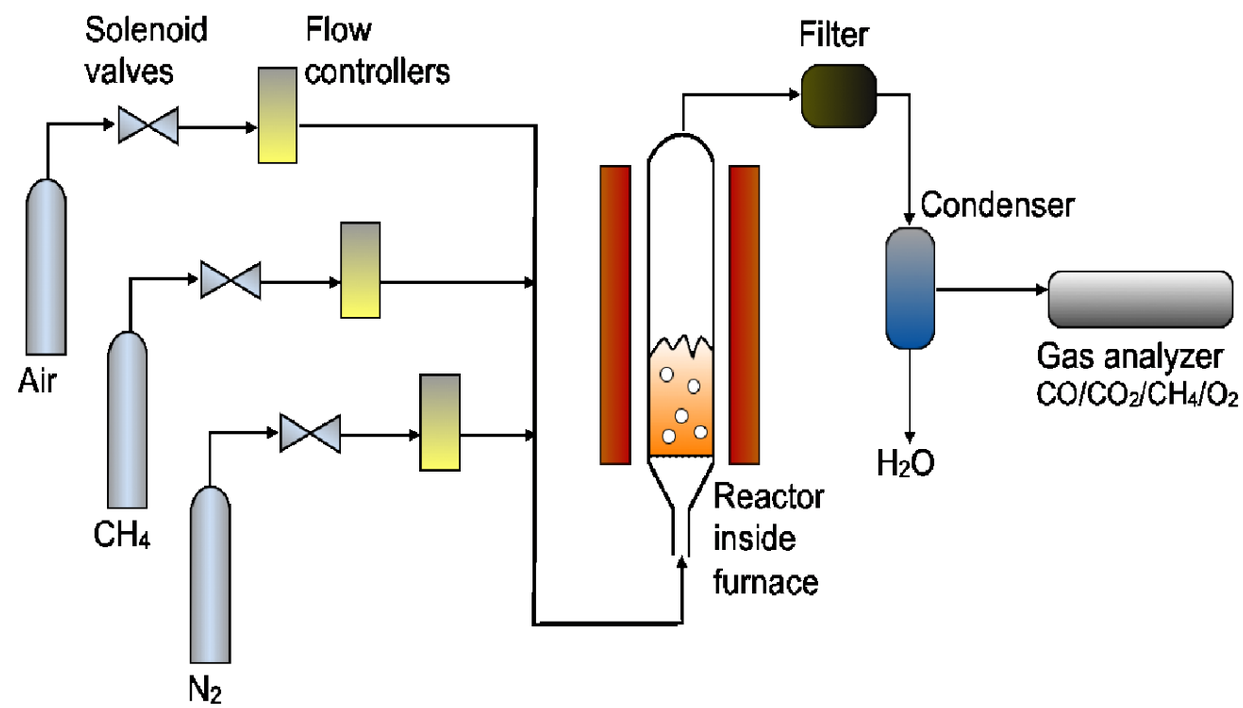
Under review: Clayton, S.K., Peterson, S.B.; Konya, G.; Eyring, E.M.; Whitty, K.J.
A Novel Material for Chemical-Looping with Oxygen Uncoupling: The Performance of an Ilmenite Copper Bimetallic Carrier

Experimental Systems

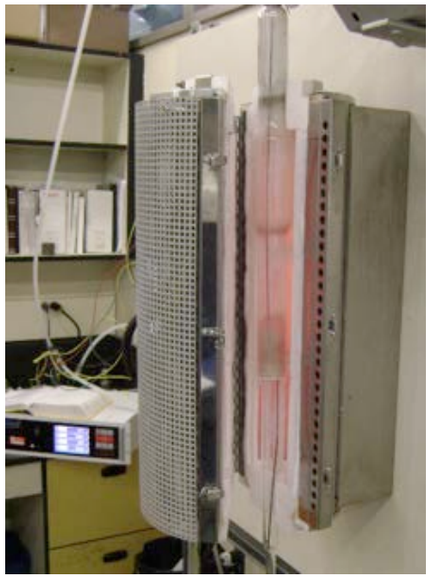
- Three different experimental systems
  - Thermogravimetric apparatus (TGA)
  - Batch fluidized bed reactor (FZB)
  - Batch fixed bed reactor (FXB)
- Thermogravimetric apparatus
  - TA Instruments Q500 or Q600
  - Direct measurement of mass
  - Used for measuring
    - carrier capacity
    - oxidation rates
    - reduction rates

Fluidized and Fixed Bed Systems

- Fluidized bed reactor
  - Similar to Chalmers system
  - 3 cm diam quartz reactor
  - Fluidizing gas switched between air and nitrogen
  - Progression of reaction determined by gas analysis



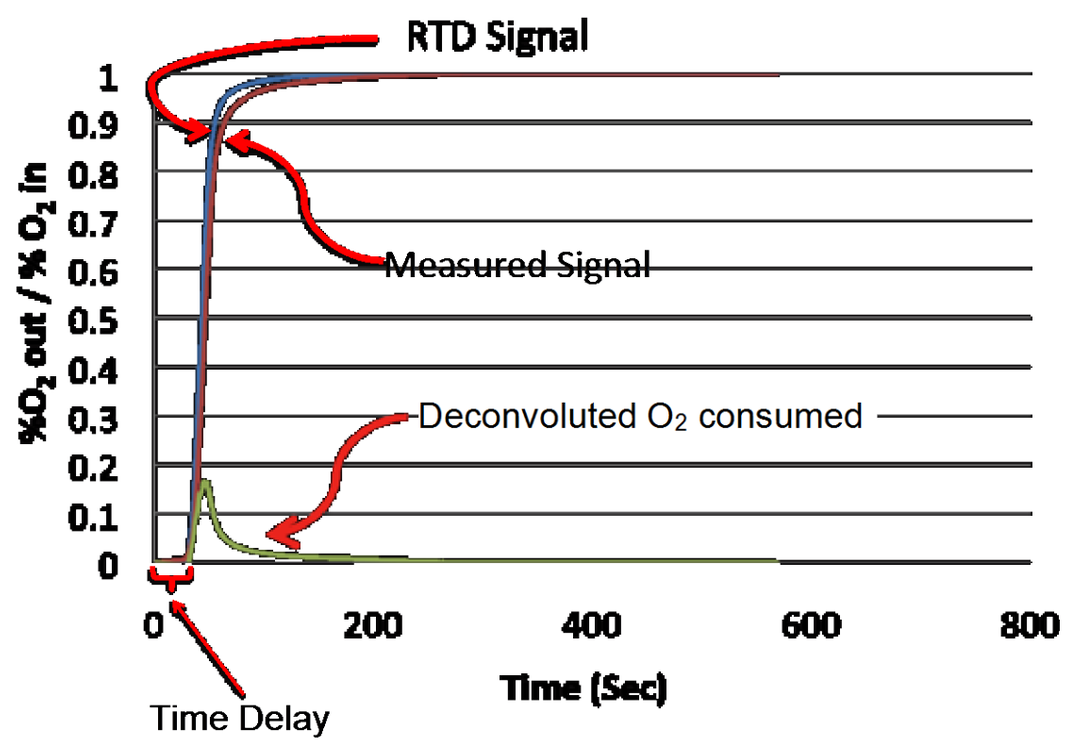
- Fixed bed reactor
  - Same setup as FZB
  - Quartz wool plug above bed to create fixed bed
  - Allows testing with smaller particle sizes than fluidized bed



- For both systems
  - Automated gas switching / cycling
  - Can be operated as integral or differential reactor

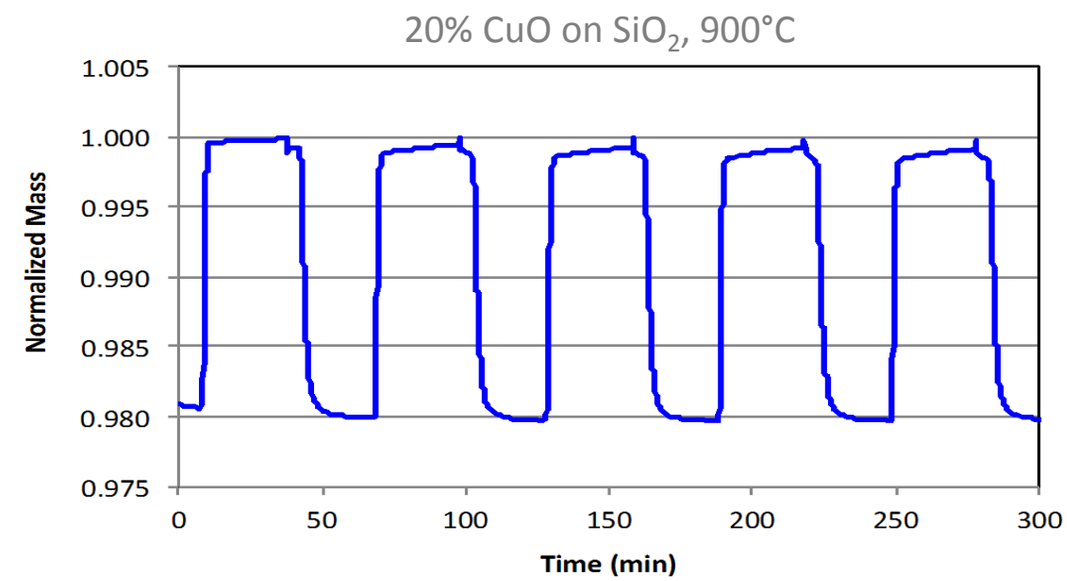
Data Analysis from Fluidized/Fixed Beds

- Only indication of reaction progression is gas composition downstream of reactor
  - Not real-time
  - Reactor non-idealities and axial dispersion skew / convolute gas evolution profile
  - Also need real-time gas flow rate
- Gas composition data should be deconvolved to extract true gas production
  - Typically a challenging analysis involving multiple Laplace transforms
  - For CLOU oxidation and reduction in N_2, can be simplified by subtracting response of step change in inert environment

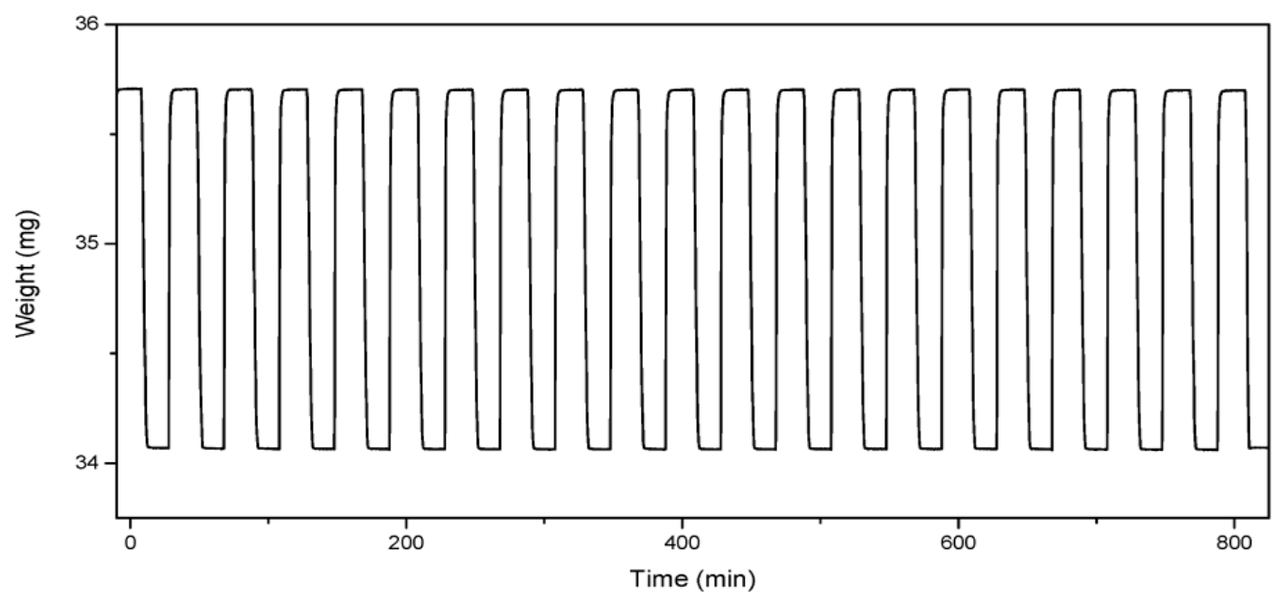


Oxygen Carrying Capacity

- Oxygen carrying capacity evaluated by TGA
  - CuO content thus determined
  - Pure Cu_2O gains 10% mass when converted to Cu



- Stability of carrying capacity evaluated over multiple cycles

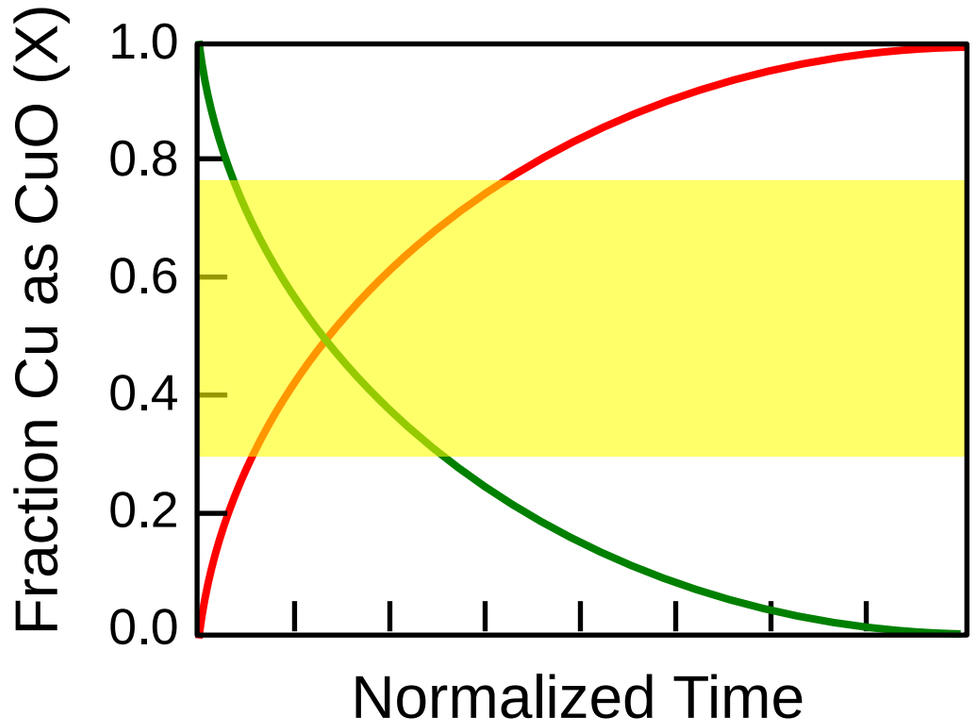


Rate Determination: Overall Objectives

- Develop better understanding of oxidation and reduction mechanisms for Cu-based carriers
  - Work recently performed at e.g. Chalmers, CSIC, Columbia U.
- Evaluate dependence of rates on carrier properties
  - e.g., in the absence of mass transfer limitations, will all carriers with 30% CuO behave the same?
- Ultimately, develop universal rate expressions suitable for incorporation into system models, perhaps of the form
  - For oxidation: $rate = A\exp\left(E_a/RT\right)\left[P_{O2} - P_{O2,eq}\right]^{\alpha}\left[Cu_2O\right]^{\beta}$
  - For reduction: $rate = A\exp\left(E_a/RT\right)\left[P_{O2,eq} - P_{O2}\right]^{\alpha}\left[CuO\right]^{\beta}$

Range of Interest for Reaction Rates

- X = fraction of Cu as CuO, with remainder as Cu_2O
- PDU design assumption: Carrier cycling between X = 0.75 exiting air reactor and X = 0.30 exiting fuel reactor



Oxidation:

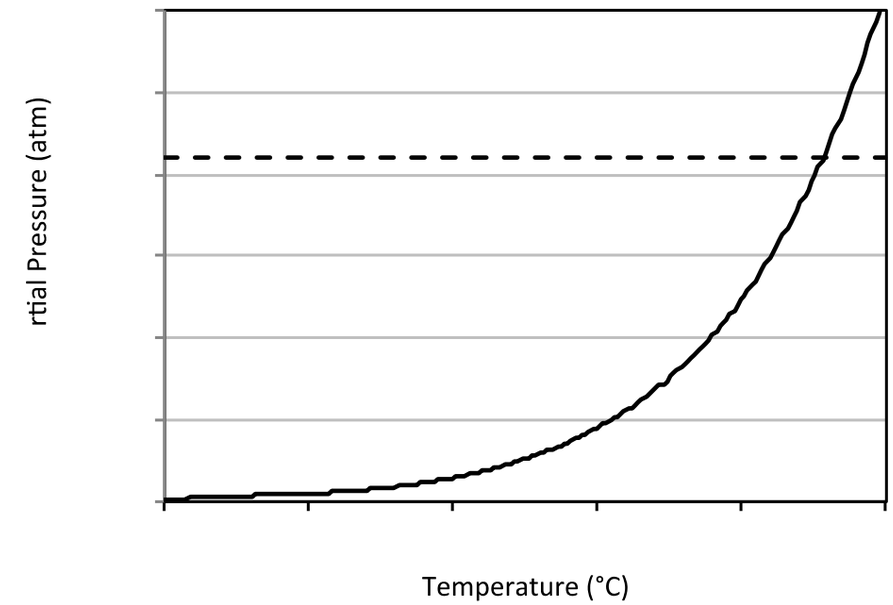
$2\,Cu_2O + O_2 \longrightarrow 4\,CuO$

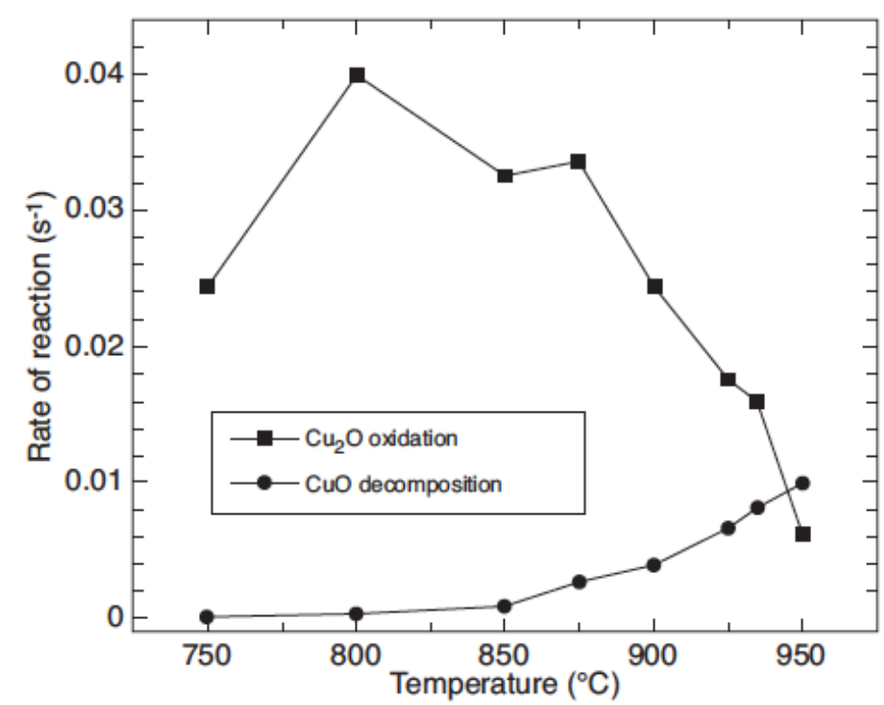
Reduction:

$4\,CuO \longrightarrow 2\,Cu_2O + O_2$

Oxidation of Cu_2O to CuO

- Oxidation experiments present interesting challenge
  - Driving force for oxidation decreases with temperature
  - Fundamental chemical rate increases with temperature (E_a)
  - Possible grain boundary sintering may also contribute to reduced rate at high temperature
- Resulting "oxidation rate peak" observed by many groups
- Deciphering true kinetics is challenging





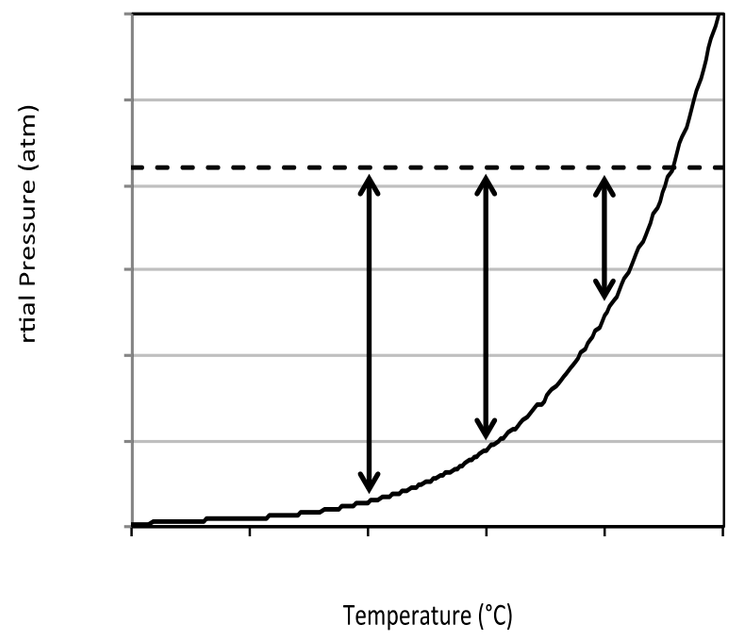
Oxidation: Influence of O_2 Driving Force

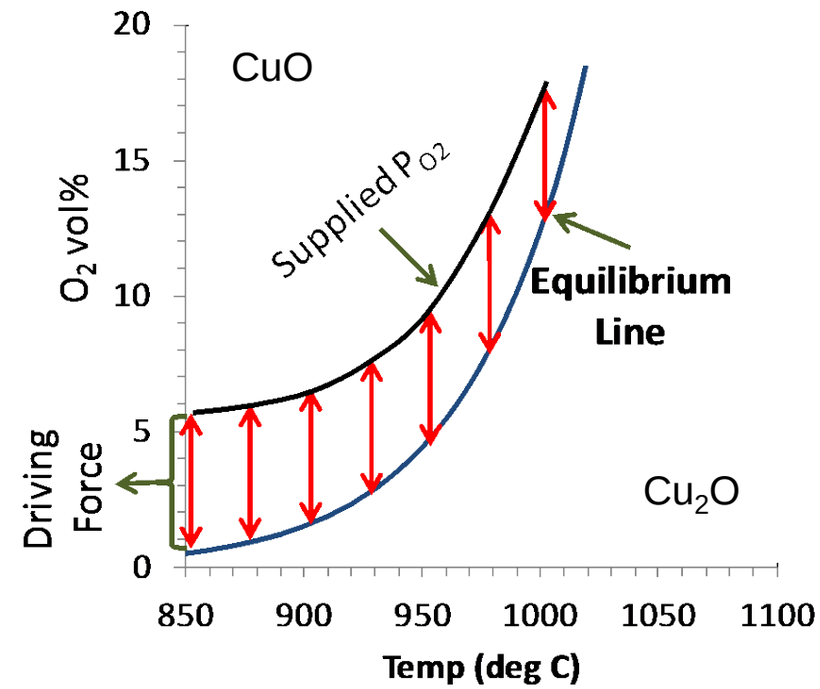
- Constant temperature
- Constant p_{O2},eq
- Vary O_2 concentration in oxidizing gas

Experiment number	Temperature (°C)	Equilibrium O_2 part. press. (atm)	Supplied O_2 part. press. (atm)	O_2 "driving force" (atm)
1	850	0.005	0.050	0.045
2	850	0.005	0.100	0.095
3	850	0.005	0.150	0.145
4	850	0.005	0.210	0.205

Oxidation: Influence of Temperature

- Various temperatures
- Various O_2 partial pressures
- Maintain constant driving force ($p_{O2} - p_{O2,eq}$)

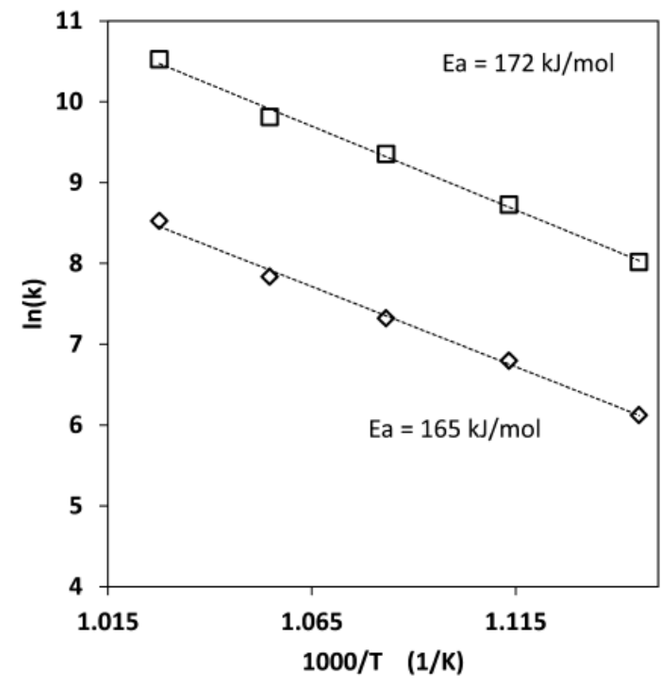


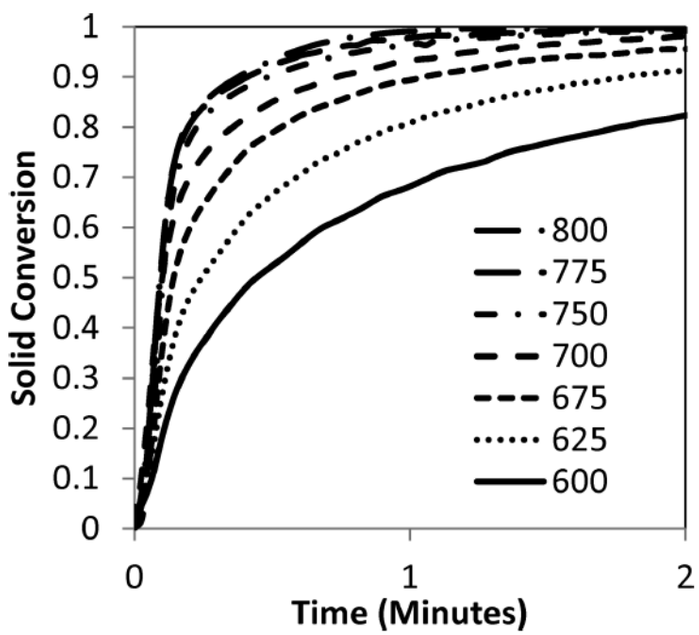


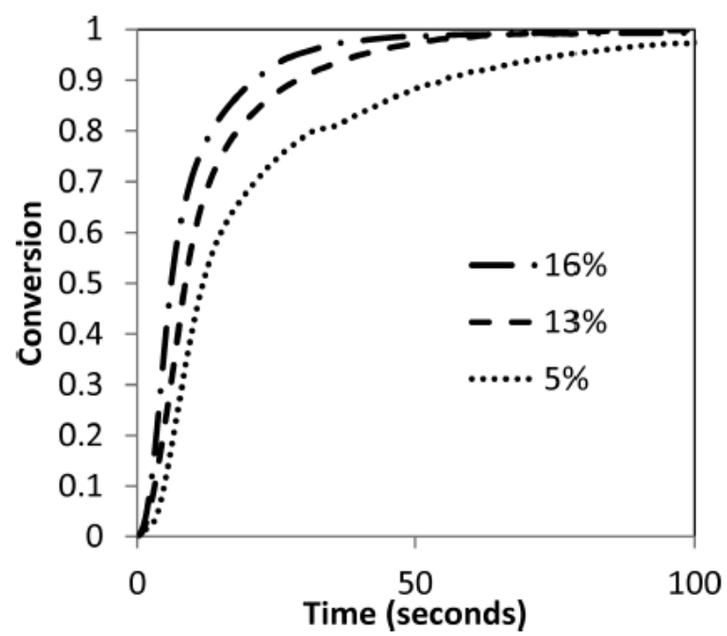
Experiment number	Temperature (°C)	Equilibrium O_2 part. press. (atm)	Supplied O_2 part. press. (atm)	O_2 "driving force" (atm)
1	876	0.010	0.050	0.040
2	962	0.060	0.100	0.040
3	994	0.110	0.150	0.040
4	1017	0.170	0.210	0.040

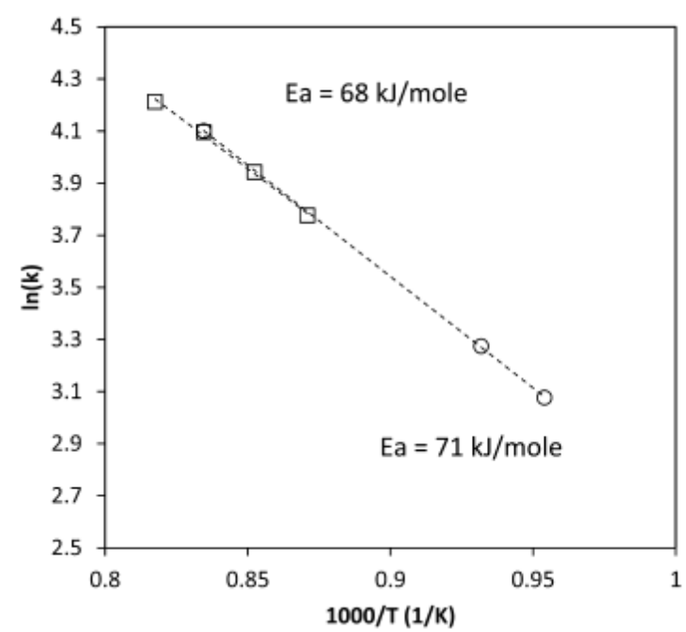
Measured Oxidation Rates

- Range of experimental conditions
  - Temperature
  - Reacting gas composition
- Four types of carrier materials
  - Various production techniques
  - Various CuO loadings









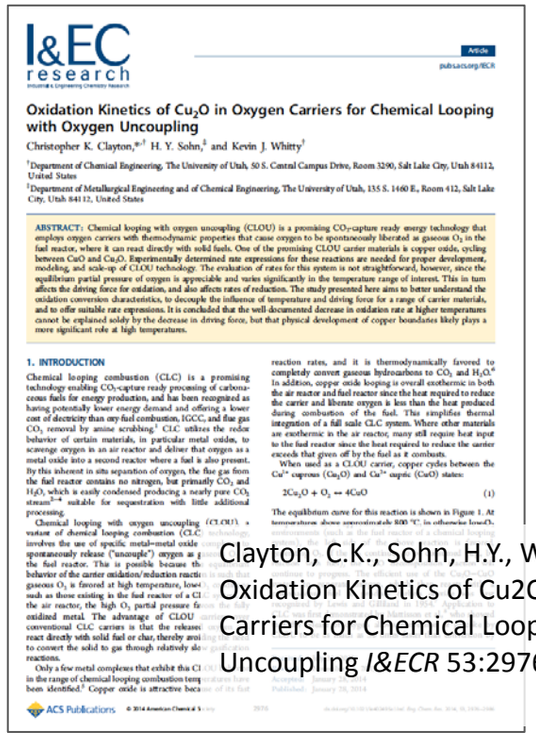
Modeling of Oxidation Rates

- Mechanism determined to be more challenging than simple reversible reaction kinetics
- Two regimes of reaction behavior identified
  - Low temperature, non-CLOU region
    - Best described by pore blocking kinetic mechanism

$$\frac{dX}{dt} = k\frac{1}{\exp\left(\frac{X}{\lambda}\right)}\left[P_{O_2}^{\beta} - P_{O_2,eq}^{\beta}\right]$$

  - High temperature CLOU region
    - Activation energy must be separated into thermodynamic and kinetic barriers
    - Best described by nucleation and growth mechanism

$$[-\ln(1 - X)]^{1/n} = k_{app} \times t$$


I&EC research

Oxidation Kinetics of Cu_2O in Oxygen Carriers for Chemical Looping with Oxygen Uncoupling

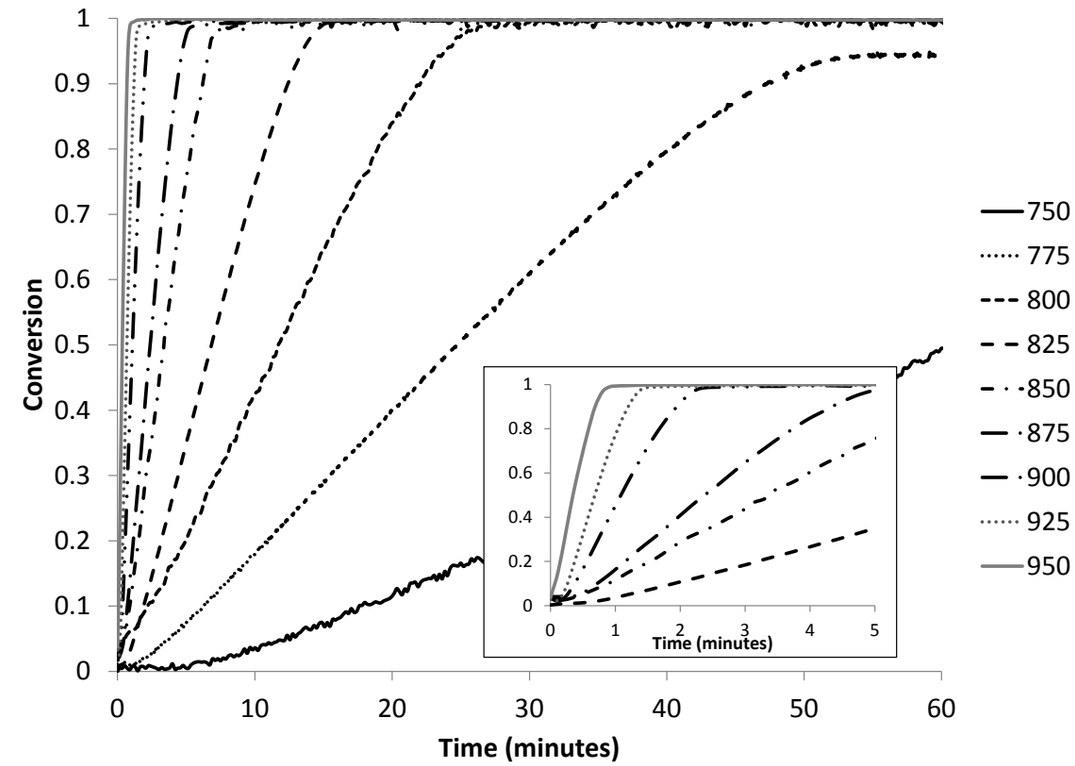
Christopher K. Clayton, H. Y. Sohn, and Kevin J. Whitty

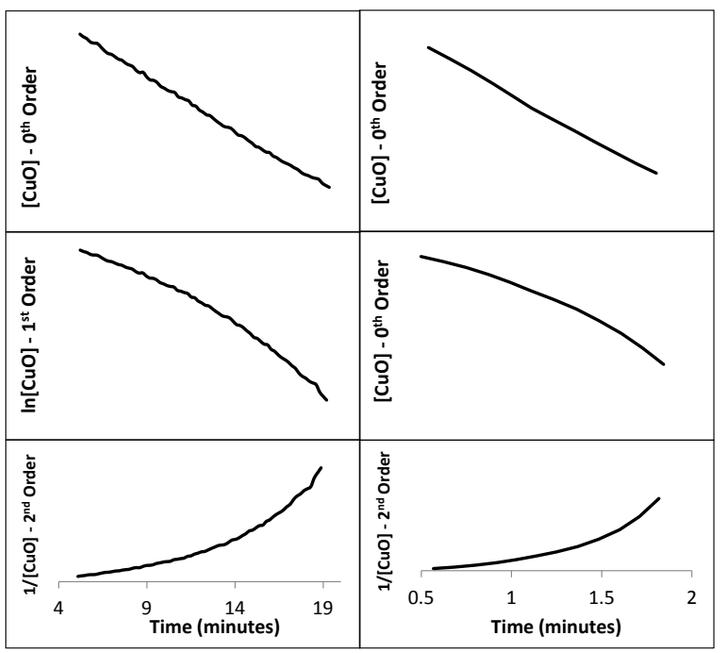
1. INTRODUCTION

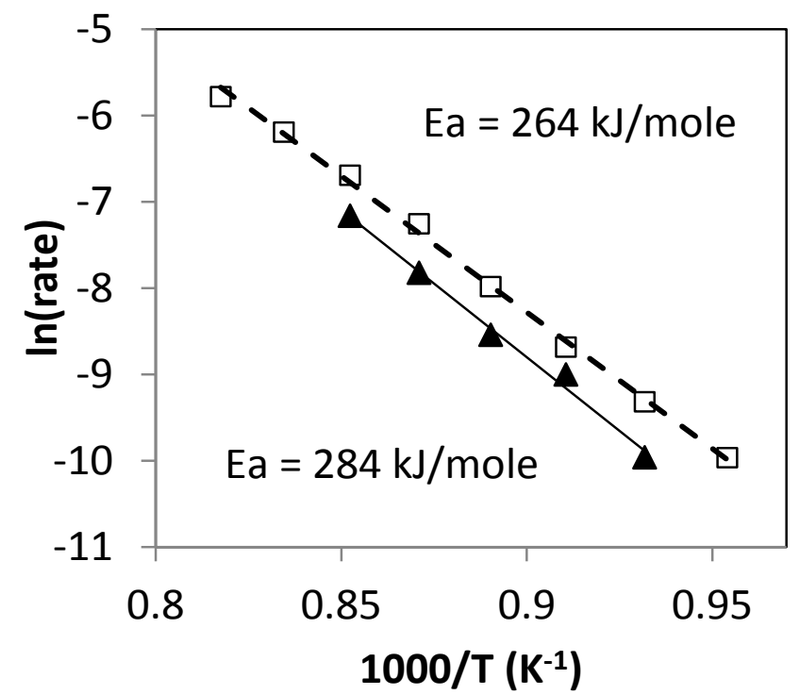
Clayton, C.K., Sohn, H.Y., Whitty, K.J. Oxidation Kinetics of Cu2O in Oxygen Carriers for Chemical Looping with Oxygen Uncoupling *I&ECR* 53:2976-2986 (2013).

Measurement of CuO Reduction Rates

- Similar to oxidation studies
- Range of conditions
  - Temperature
  - Gas composition
- Challenge of having absolutely zero O_2 in gas phase
- Reaction order in CuO = 0
- Apparent activation energy 274 kJ/mol



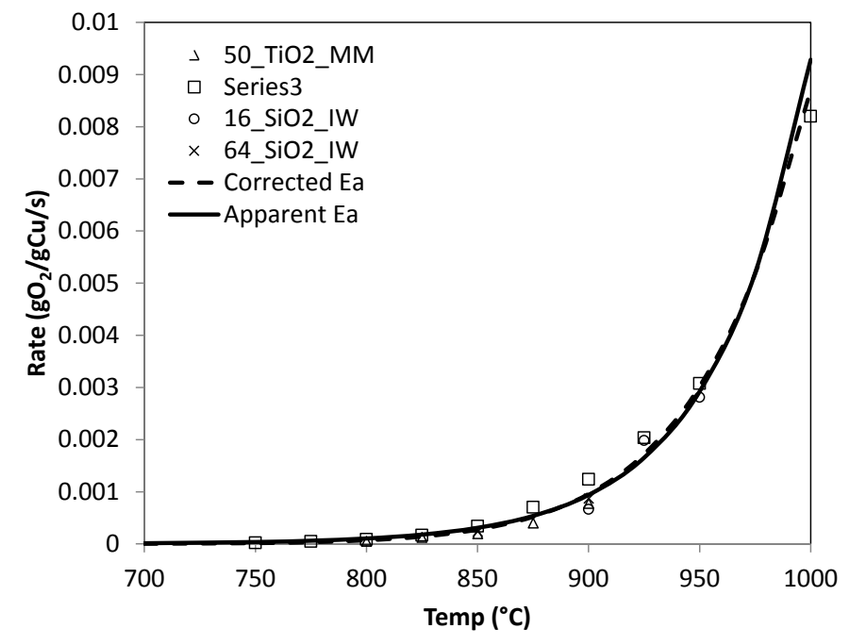




Modeling of Carrier Reduction Rates

- Any oxygen in gas phase reduces driving force for reduction
- Used similar methodology to deciphering specific influences for oxidation
  - Vary ($p_{O2,eq} - p_{O2}$) at constant temperature
  - Hold ($p_{O2,eq} - p_{O2}$) constant at various temperatures
- Could decipher constants in rate expression
- Universal rate expression:

$$\text{rate}\left(\frac{g}{s}\frac{1}{g_{Cu}}\right) = 3.90 \times 10^{-4} \exp\left(-\frac{62,000}{R \times T}\right)[6.057 \times 10^{-11} \exp^{0.02146 \times (T-273)} - P_{O2}]$$



Applied Energy 116 (2014) 416–423

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Measurement and modeling of decomposition kinetics for copper oxide-based chemical looping with oxygen uncoupling

Christopher K. Clayton *, Kevin J. Whitty

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HIGHLIGHTS

- By experimental approach kinetic equations of two copper-based oxygen carriers were defined.
- The dual effects of temperature (kinetic and thermodynamic) were separated.
- The developed kinetic equations were then used to predict the rates of two other carriers.
- It may be reasonable to assume a universal rate equation for all copper-based oxygen carriers.

ARTICLE INFO

Article history:
Received 8 May 2013
Received in revised form 11 September 2013
Accepted 12 October 2013
Available online 6 November 2013

Keywords:
CLOU
Copper oxide
Chemical looping
Decomposition kinetics

ABSTRACT

Chemical looping combustion with oxygen uncoupling (CLOU) is a promising CO_2-capture ready energy technology that employs oxygen carriers with thermodynamic properties that cause oxygen to be spontaneously liberated as gaseous O_2 in the fuel reactor, where it can react directly with solid fuels. One of the promising CLOU carrier metals is copper, cycling between CuO and Cu_2O. Experimentally-determined rate expressions for these reactions are needed for proper development, modeling and scale-up of CLOU technology. The CuO–Cu_2O system presents an interesting challenge in that the rate of decomposition depends on the thermodynamic driving force imparted by the difference between equilibrium and actual partial pressures of oxygen, and the equilibrium partial pressure is strongly temperature dependent in the range useful for combustion. This study investigates decomposition of two different copper-based oxygen carriers, from CuO to Cu_2O oxidation states, to develop a universal kinetic expression to describe the observed rate of reaction as a function of temperature, conversion and gas environment. The kinetic model developed is compared to results of a third support type (silica) using two different CuO wt% loadings (64 wt% CuO and 16 wt% CuO) to demonstrate applicability to other support types and copper oxide loadings.

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1. Introduction

Chemical looping combustion (CLC) is promising technology for CO_2-capture ready processing of carbonaceous fuels for energy production, and has been recognized as having potentially lower energy demand and offering a lower cost of electricity than oxy-fuel combustion, IGCC and flue gas CO_2 removal by amine scrubbing [1,2]. The most common configuration for a CLC system involves two interconnected fluidized beds, the so-called air reactor and fuel reactor, with metal-based "oxygen carrier" particles cycling between them [3]. The metal is oxidized in the air reactor, the product gas of which is oxygen-depleted air. The oxidized carrier particles are transported to the fuel reactor via a loop seal, thus keeping nitrogen from entering the fuel reactor. In the fuel reactor, the oxygen carrier is reduced by a gaseous fuel such as natural gas, effectively combusting the fuel to CO_2 and H_2O, resulting in a product stream of nearly pure CO_2 upon water vapor condensation. Because solid fuels are involved, CLC is not suitable for processing a coal feedstock unless the fuel is converted into a gaseous form prior to processing. Gasification is one way to accomplish this, but it is not ideal because the equilibrium behavior of the carrier oxidation/reduction

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http://dx.doi.org/10.1016/j.apenergy.2013.10.032

Clayton, C.K., Whitty, K.J., Measurement and Modeling of Decomposition Kinetics for Copper-Oxide Based Chemical Looping with Oxygen Uncoupling, *Applied Energy* 116:416-423 (2013).

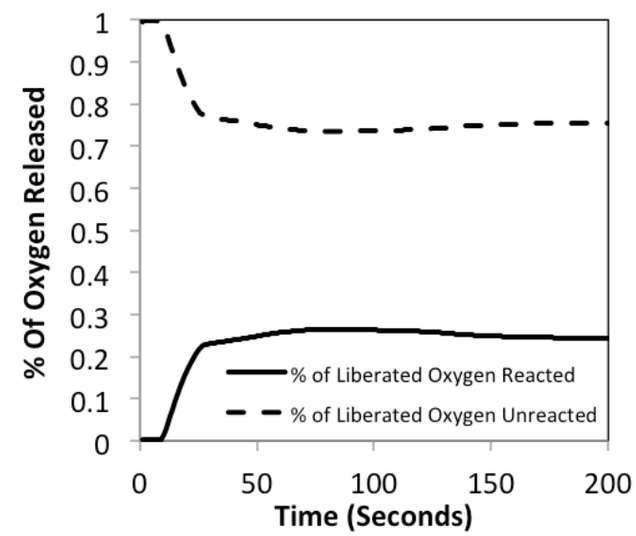
Coal Conversion in Lab-Scale Fluidized Bed

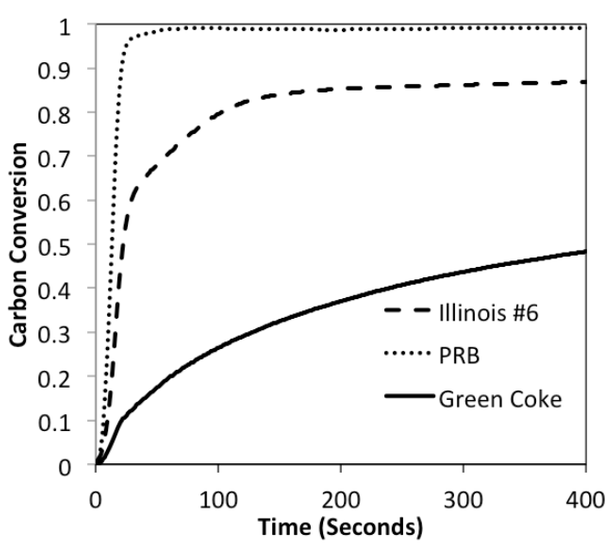
- Three fuels tested
  - Illinois #6
  - Black Thunder PRB
  - Green petcoke
- Two carriers tested
  - 45% CuO on ZrO_2
  - 50% CuO on TiO_2
- Fuel introduced batch-wise
  - Dropped onto top of bed shortly after turning off air
- Conversion performance determined based on concentrations of gases in reactor effluent

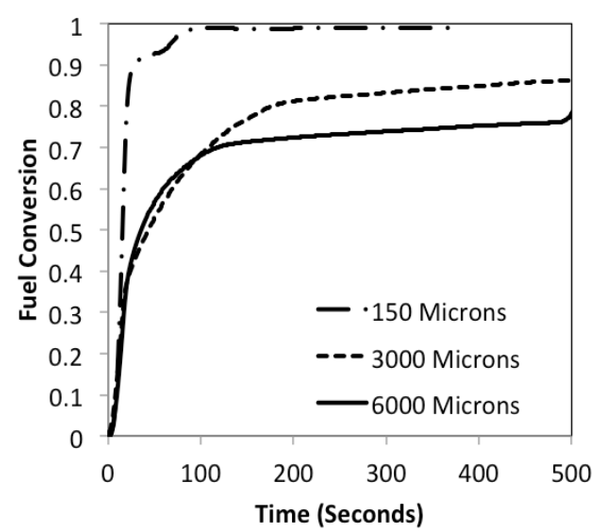
Fuel Type	Illinois #6 Bituminous	Black Thunder PRB Sub-bituminous	Green Coke Petroleum Coke
Proximate Analysis			
Moisture (wt% as received fuel)	2.54	21.30	0.4
Ash (wt% Dry)	12.33	6.46	0.39
Volatile matter (wt% dry)	39.40	54.26	11.03
Fixed carbon (wt% dry)	48.28	39.28	88.01
Ultimate Analysis (wt% dry ash-free)			
Carbon	78.91	74.73	89.21
Hydrogen	5.50	5.40	3.78
Nitrogen	1.38	1.00	1.73
Sulfur	4.00	0.51	5.82
Oxygen	10.09	18.27	4.41
Chlorine	0.11	0.08	-
Heating Value			
HHV, dry (Btu/lb)	12,233	12,815	15,622

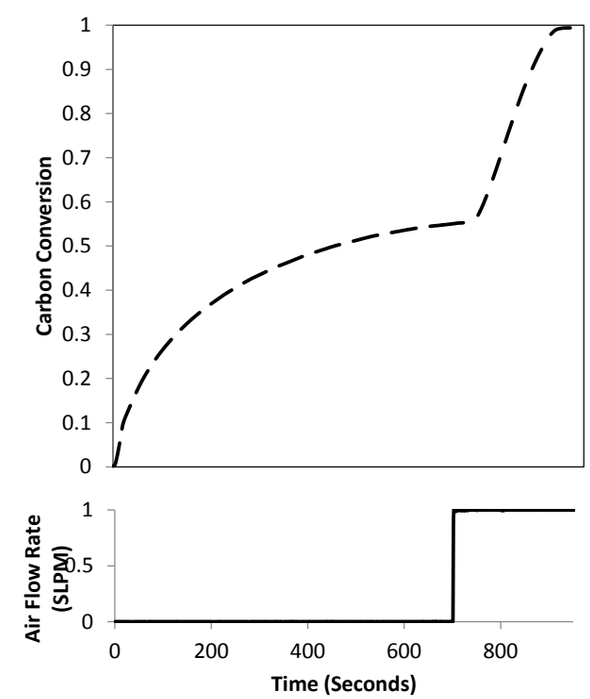
Coal Conversion Performance

- Ranking of fuel conversion
  - PRB > Illinois #6 > petcoke
- Particle size matters
  - Smaller is faster
  - Largest particles not converted in the time needed to release all oxygen from CLOU particles
    - Consequence of batch design



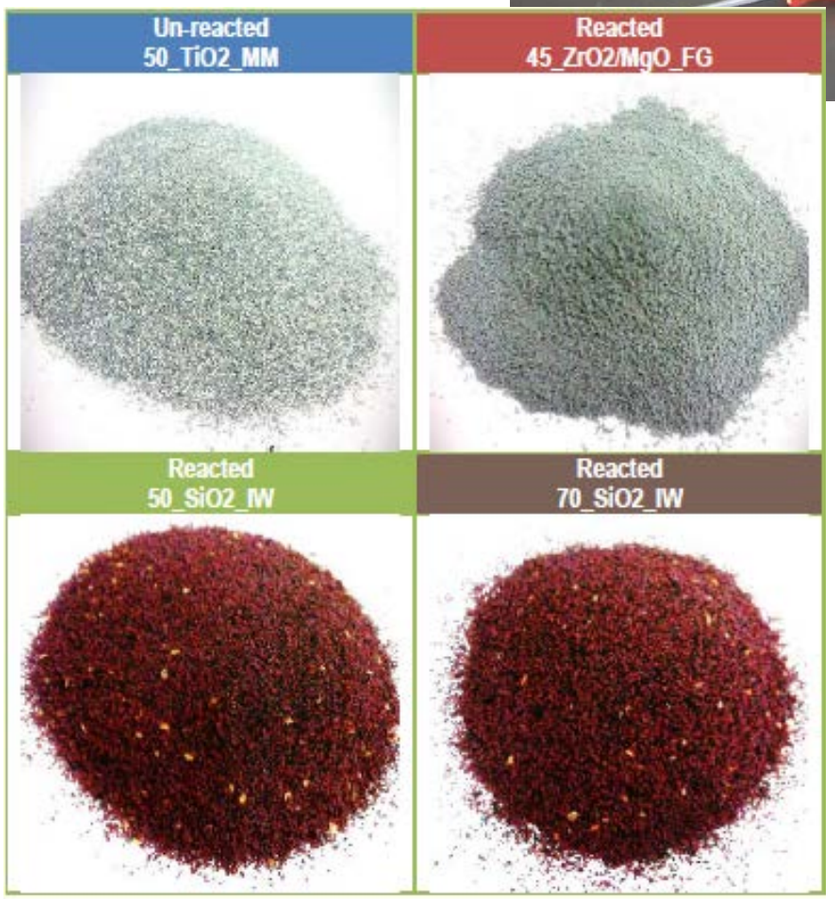




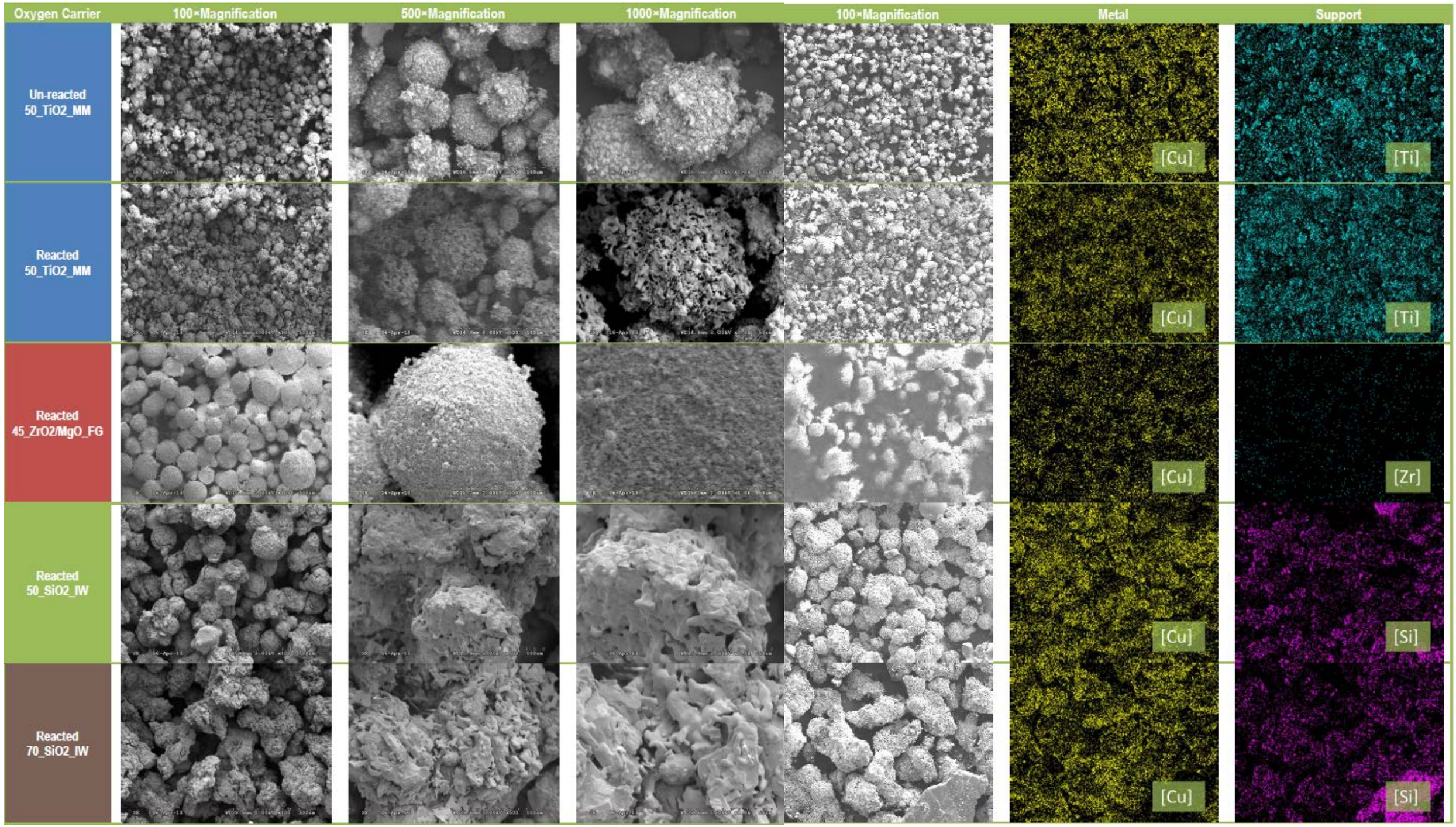


Evaluation of Carrier Particle Durability

- Crushing strength of particles
  - Insight into fluidized bed durability
  - Less than 1 N not considered appropriate
- Hot fluidized bed tests
  - Attrition rates over extended operation, multiple cycles
  - Agglomeration propensity
- Analytical evaluations
  - SEM micrographs
  - BET surface area development



SEM Analysis



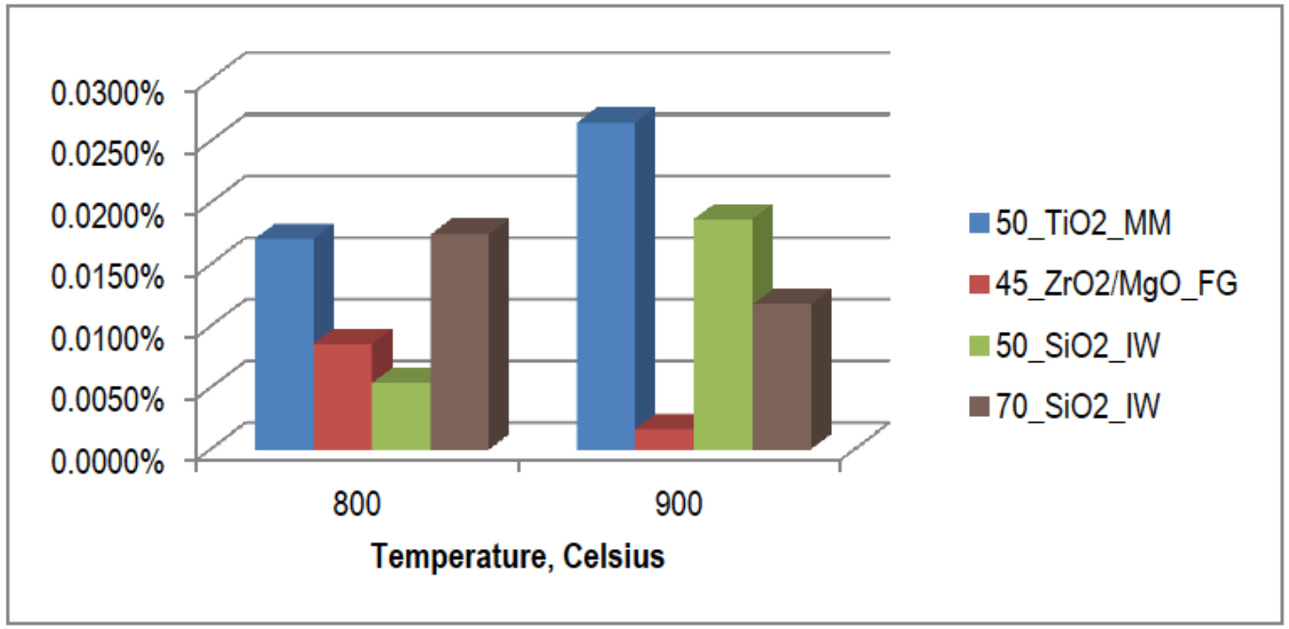
Crushing Strength

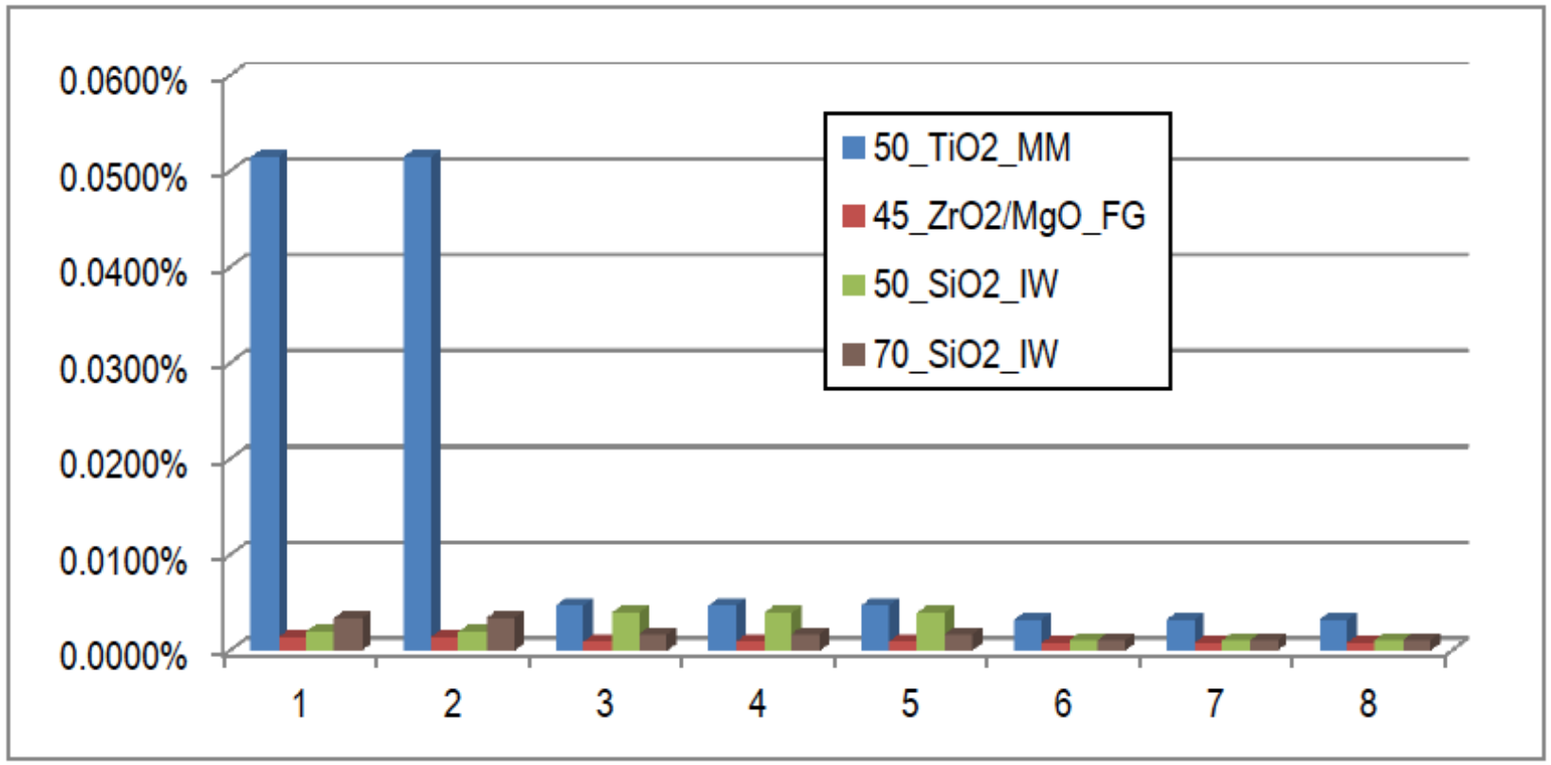
- Particles sieved to 180-250 micron
- Reported values average of 30 tests

Oxygen Carrier	Particle Diameter (μm)	Crushing Strength (N)	Standard Deviation
Un-reacted 50_TiO2_MM	180 – 250	4.45	1.14
Reacted 50_TiO2_MM	180 – 250	3.94	1.28
Reacted 45_ZrO2/MgO_FG	180 – 250	2.21	0.88
Reacted 50_SiO2_IW	180 – 250	4.10	1.26
Reacted 70_SiO2_IW	180 – 250	4.48	1.02

Attrition Rates

- 50_TiO2_MM material displayed highest attrition rates
  - Especially during initial cycles
- 45_ZRO2/MgO_FG had best physical stability
- No correlation between crushing strength and attrition resistance
- No obvious influence of temperature





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Fluidized Bed Modeling

Smith

INSTITUTE FOR
Clean and Secure Energy
THE UNIVERSITY OF UTAH

Task 5.2, simulation task
Chemical Looping Combustion

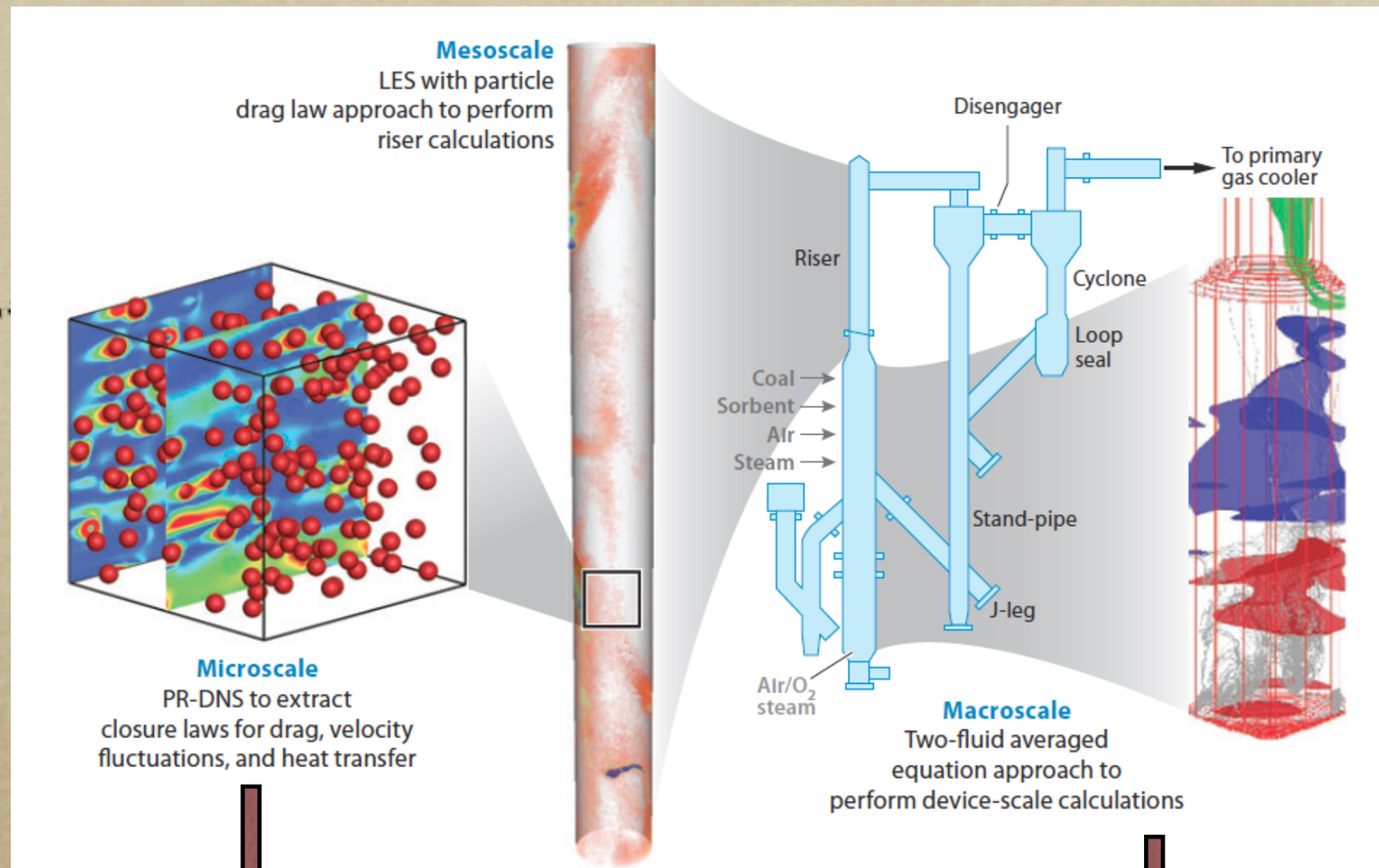
John Milo Parra-Álvarez
Michal Hradisky
Philip J. Smith

Simulation Task

modeling approaches

sensitivity analysis

comparison with experimental data and previous results



Microscale modeling
Resolves all the length and time scales of the fluid flow and the particulate phase. The most accurate and expensive representation of a multiphase flow

Mesoscale modeling
Resolves large length and time scales of the fluid and model the small ones. Resolves the interaction between the scales of the fluid flow and the particulate phase

Macroscale modeling
Model all the scales of the fluid flow and their interactions with the particulate phase

figure from: *Particle-resolved direct numerical simulation for gas-solid flow model development*. S. Tenneti, S. Subramaniam., Annu. Rev. Fluid Mech. 2014. 46:199-230

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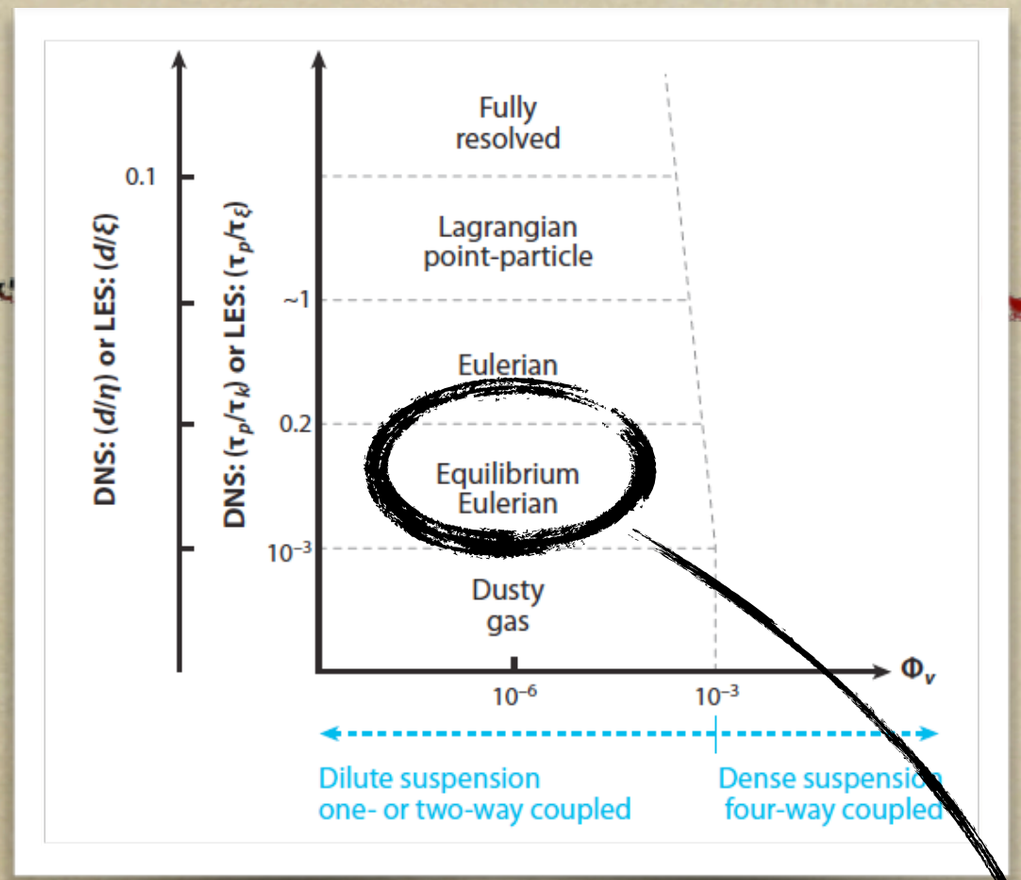
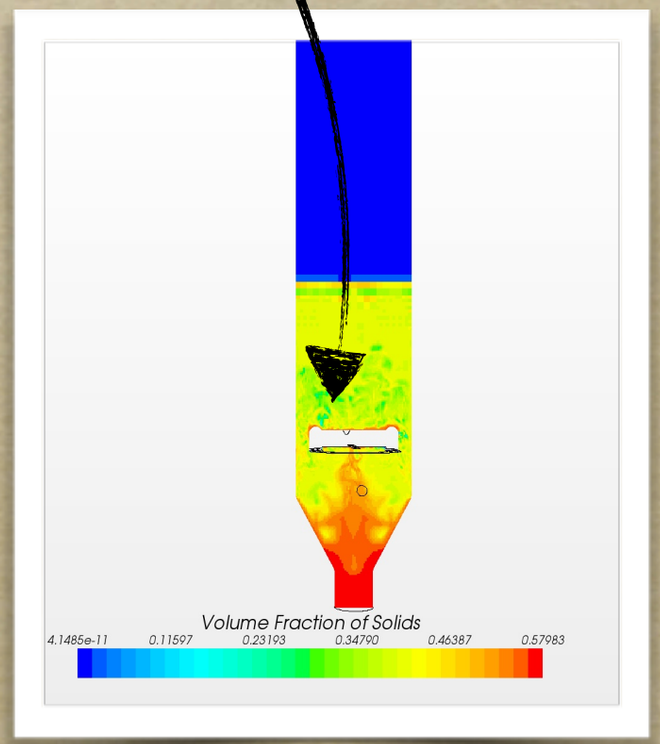


figure from: *Turbulent Dispersed Multiphase Flow*. S. Balachandar, J. K. Eaton., Annu. Rev. Fluid Mech. 2010. 42:111-133

COST

In general the computational cost increases as the ratio of lengths and time scales increases Although we are working on mesoscale simulations of multiphase flows we have have focused on this project on an eulerian macroscale formulation to represent the fluidization system



Simulation Task

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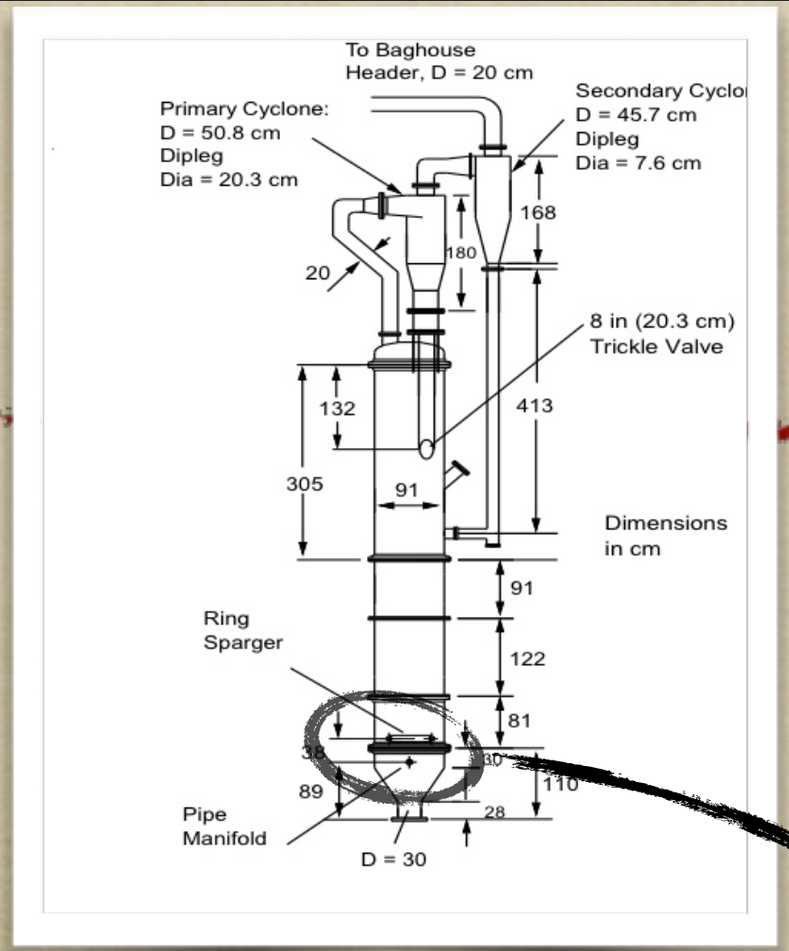

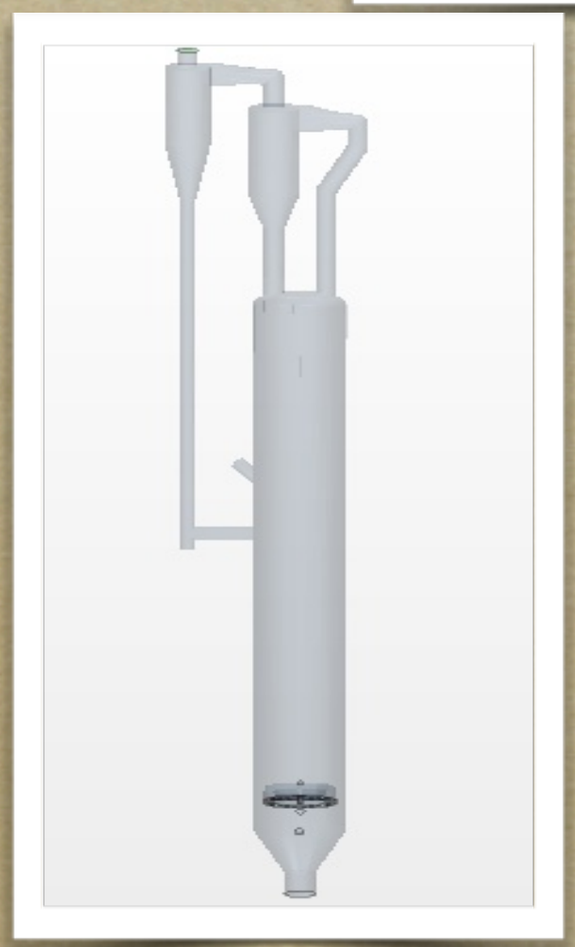

Schematics and CAD from:
Shadle, L., Shahnam, M., Cocco, R., Issangya, A., Guenther, C., Syamlal, M., et al. (2011, May 03). *Challenge Problem III. CFB X Workshop presentation* . Oregon: NETL-PSRI.

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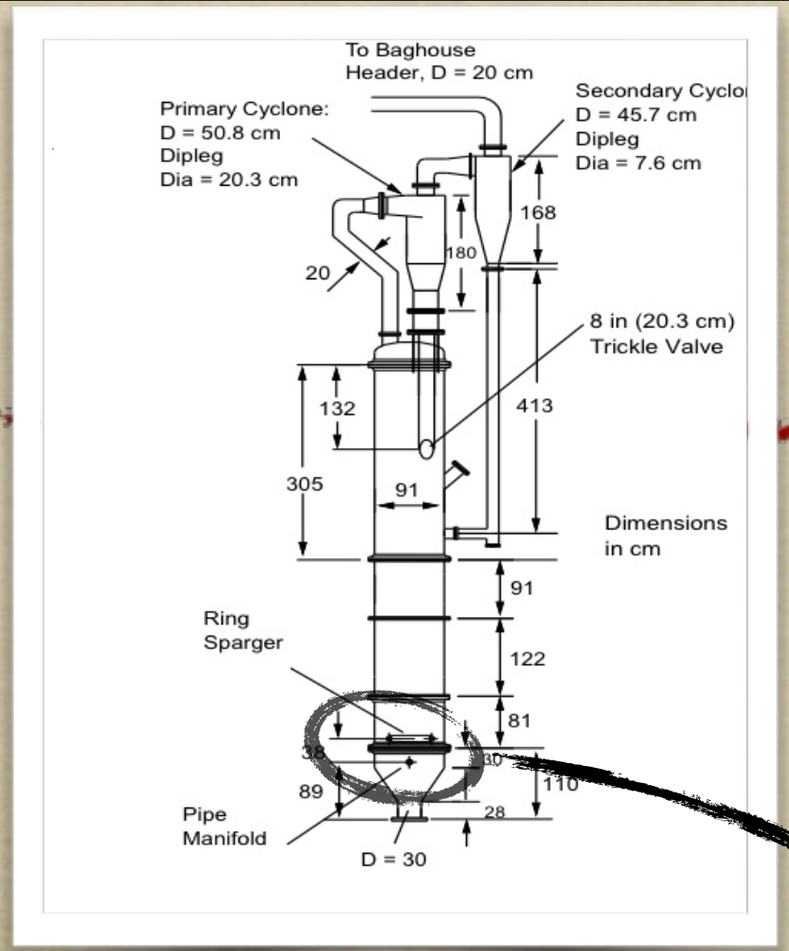

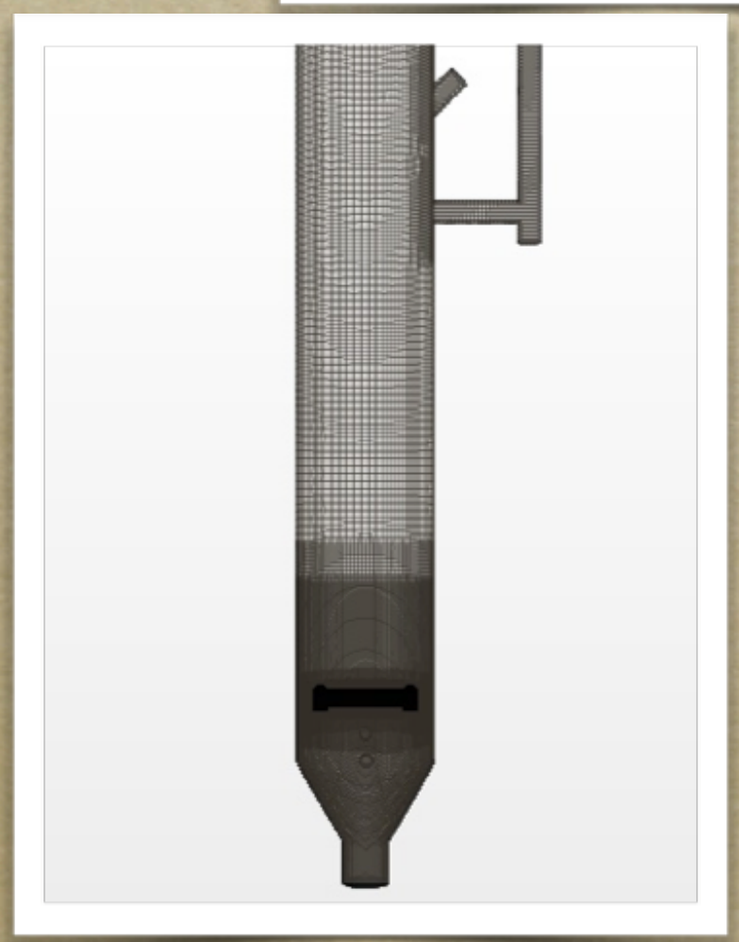

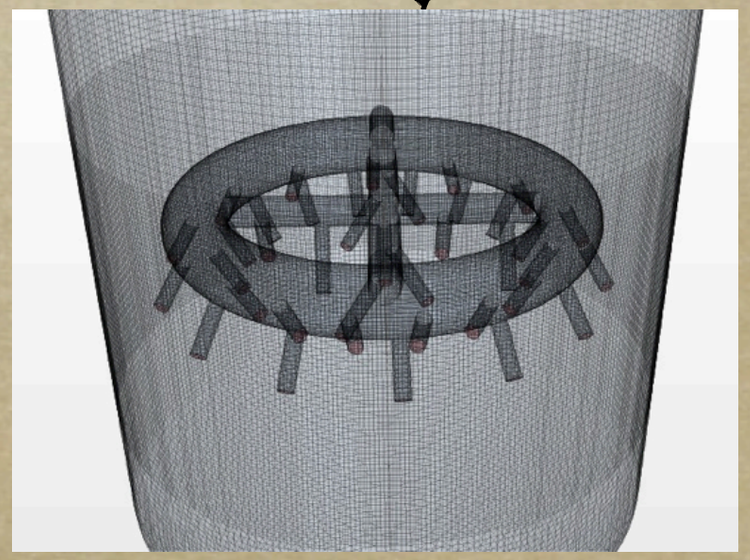

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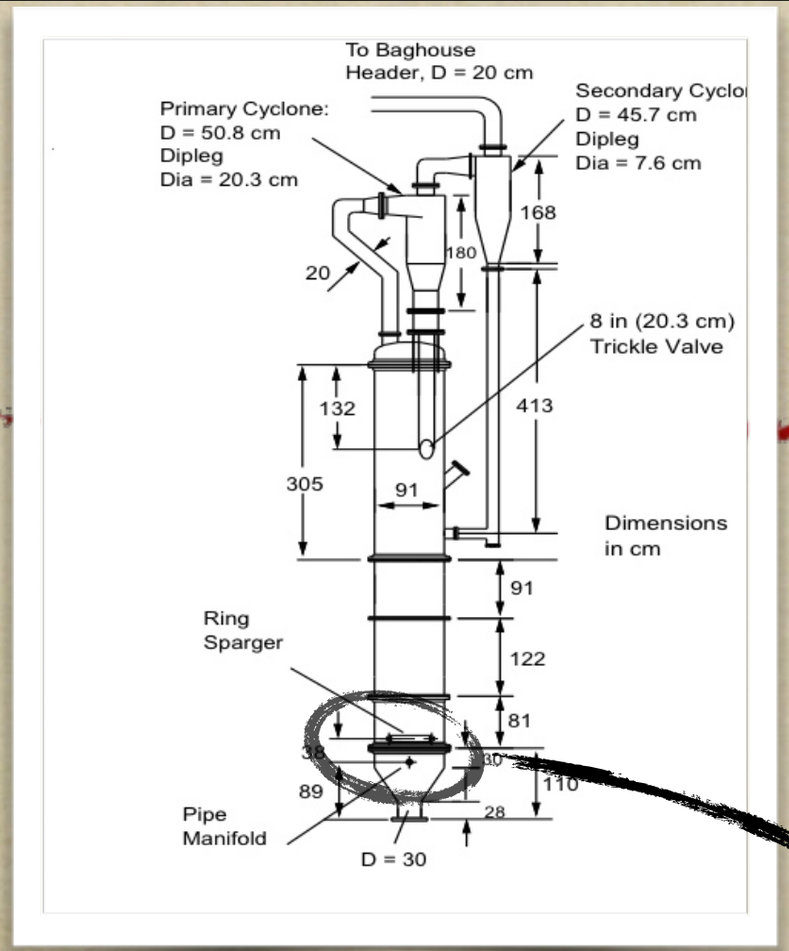

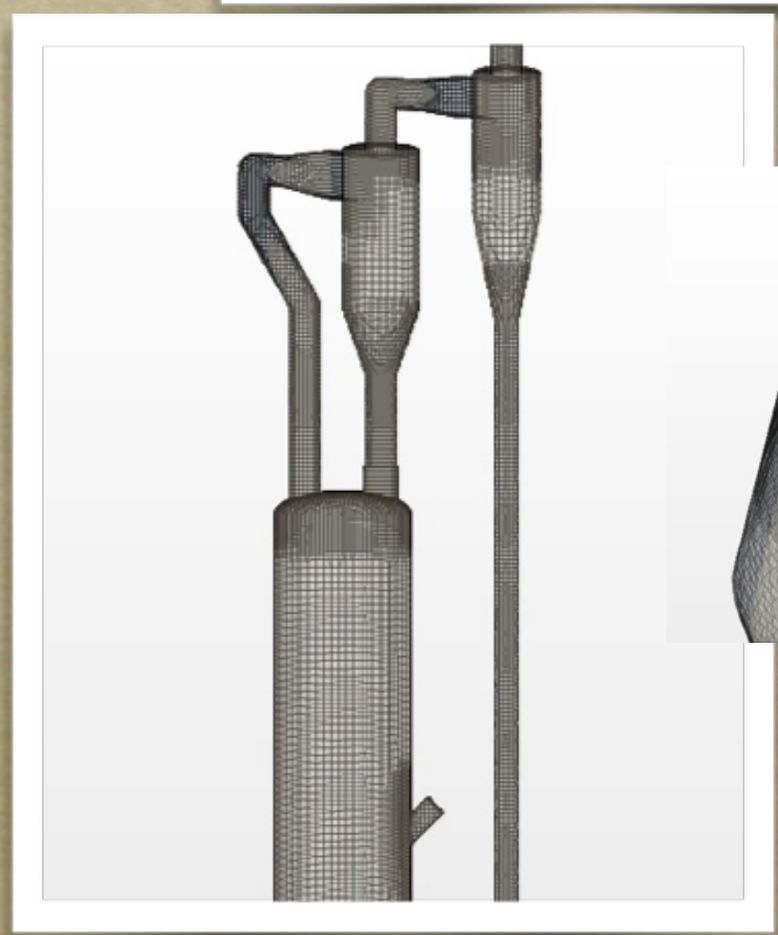

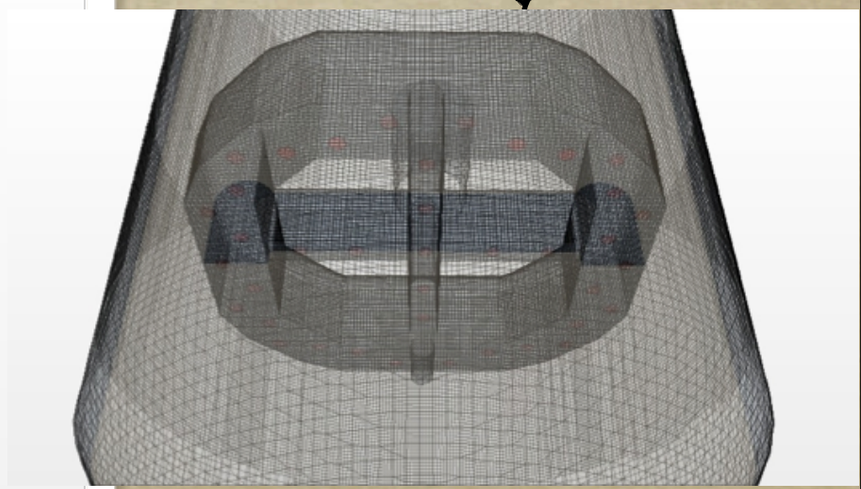

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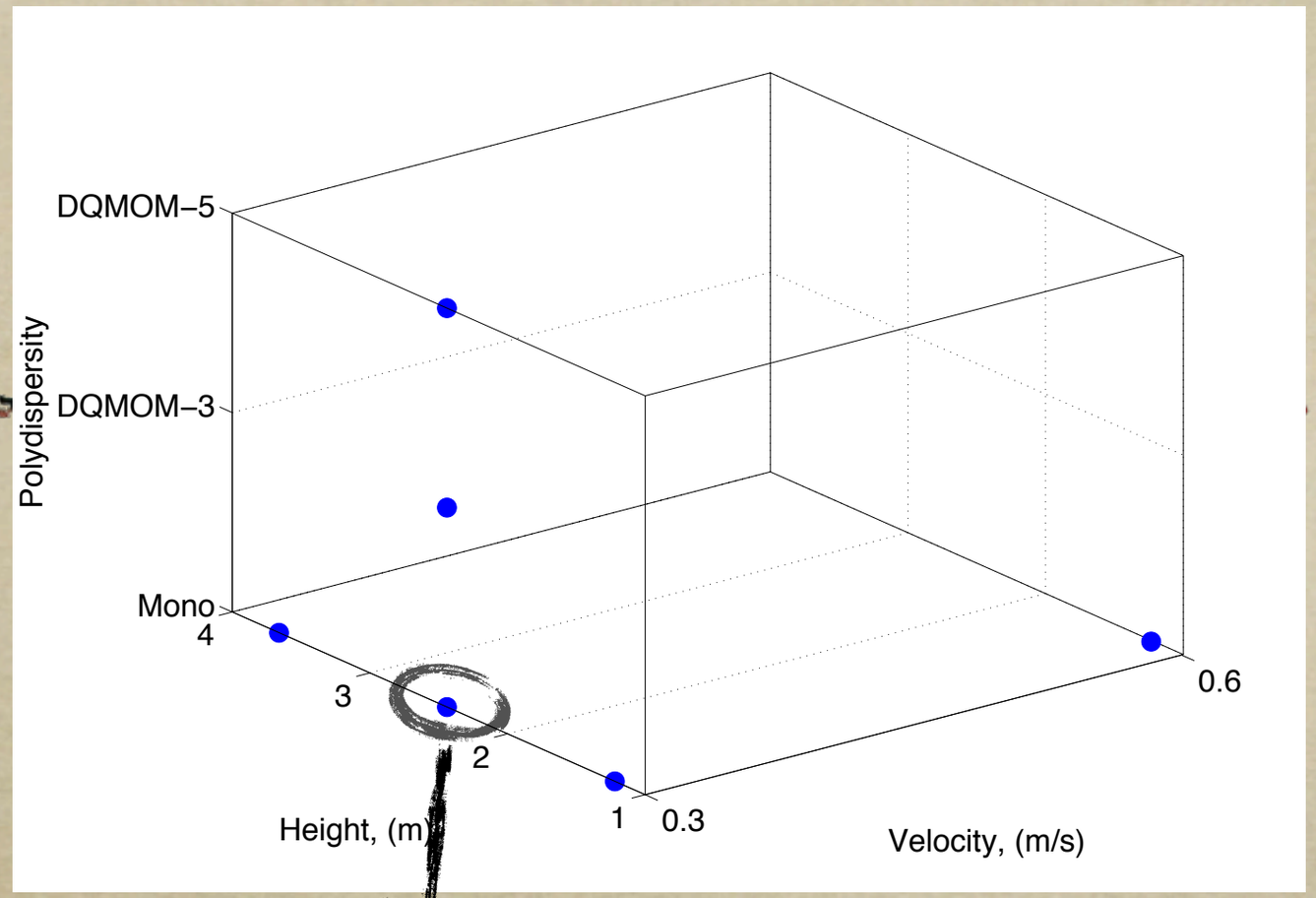

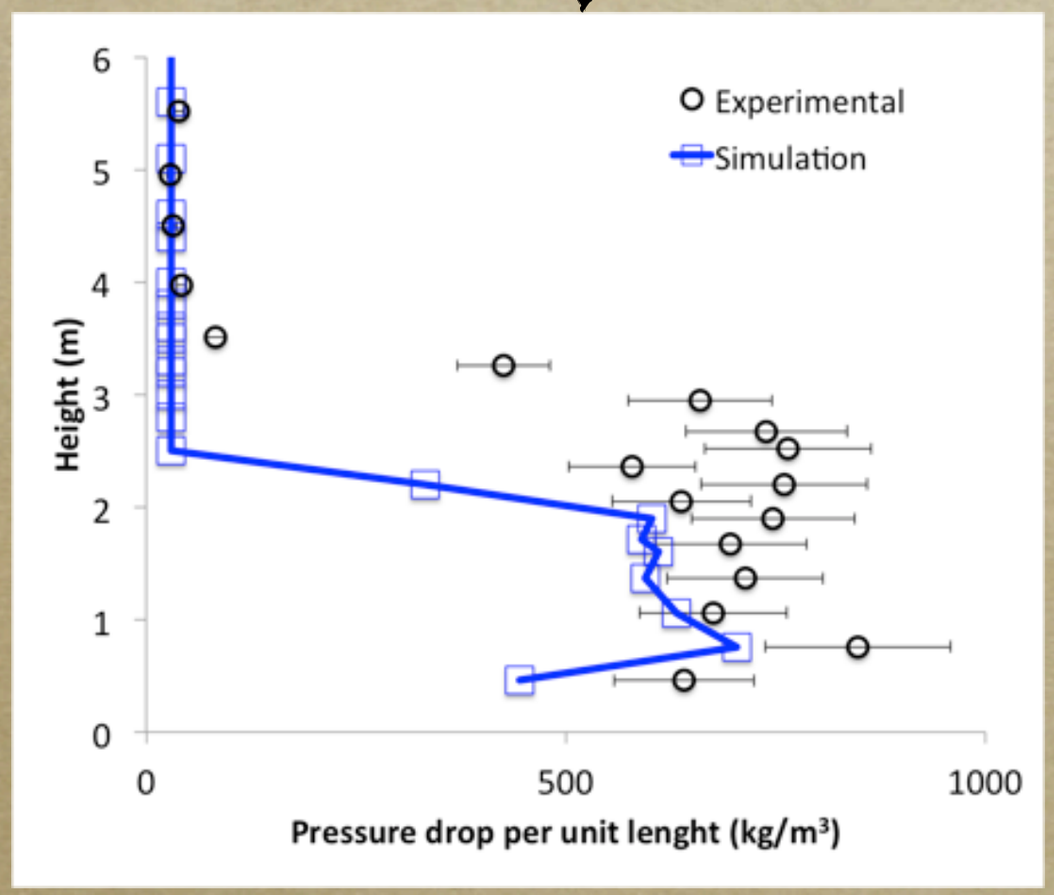

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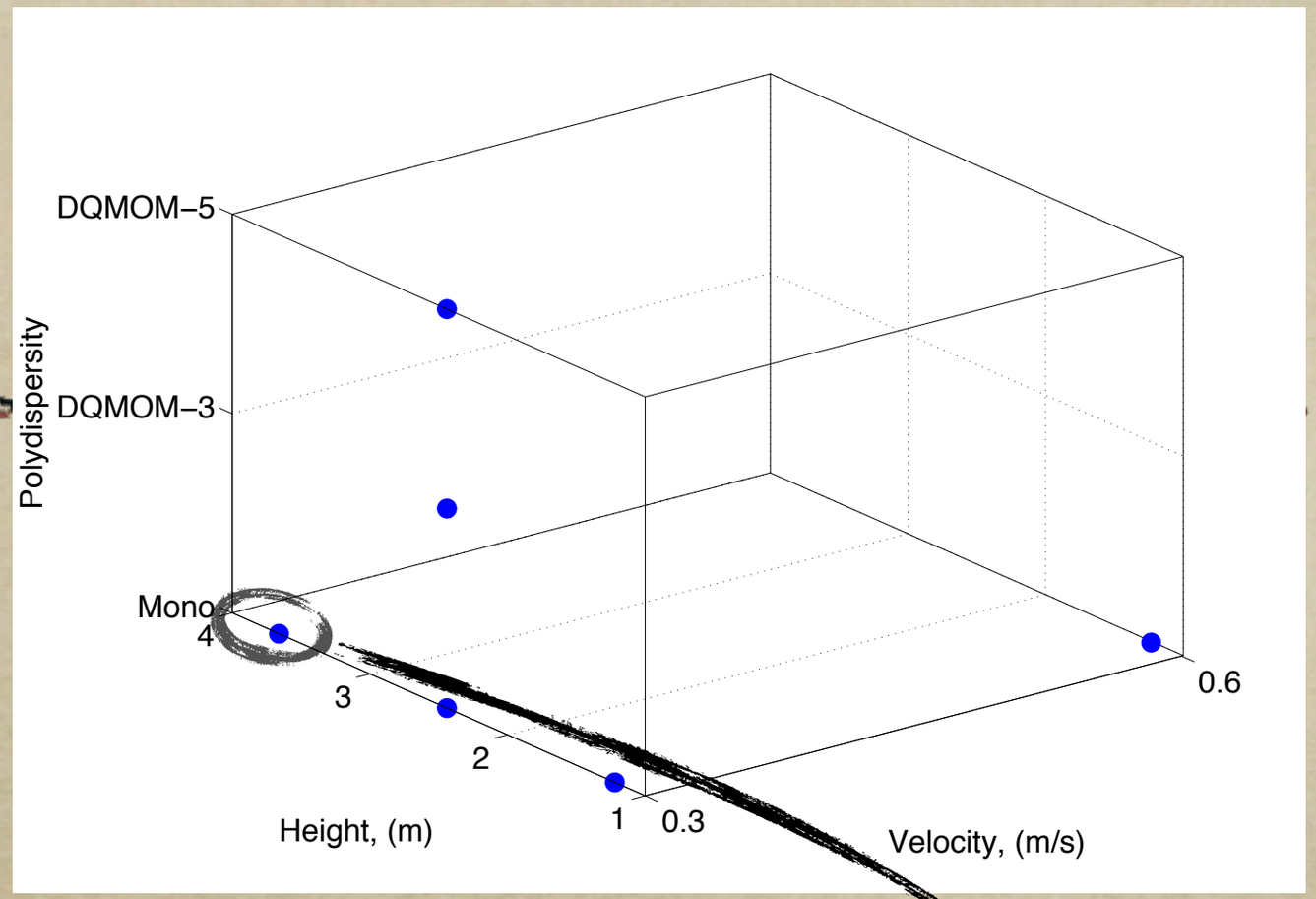

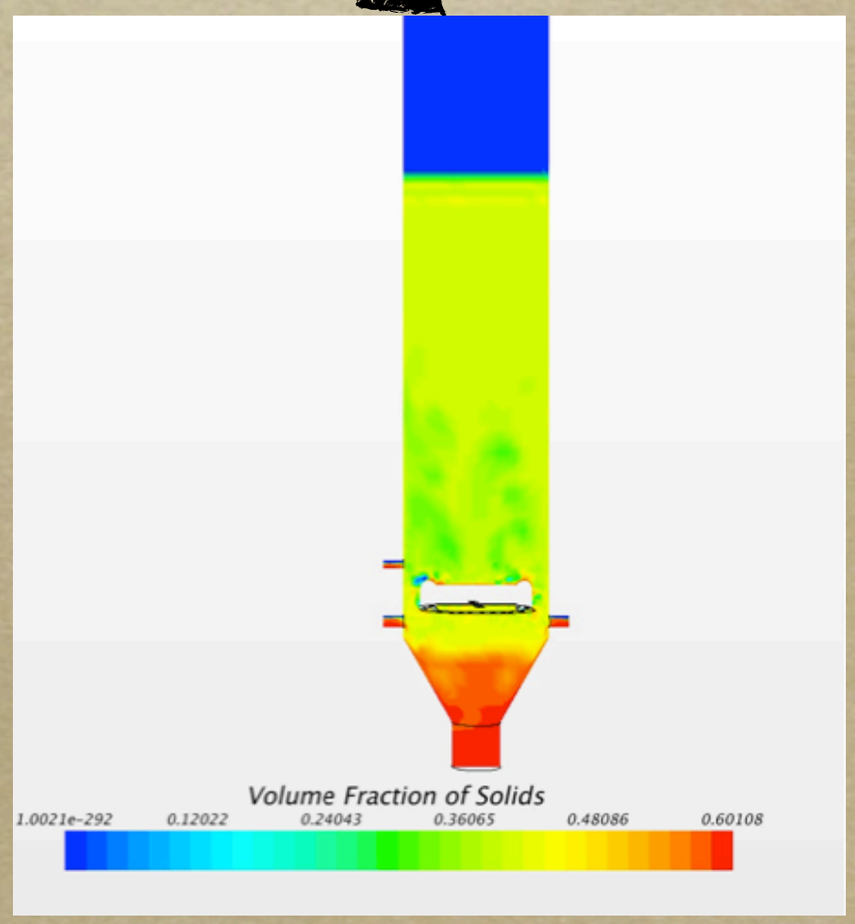

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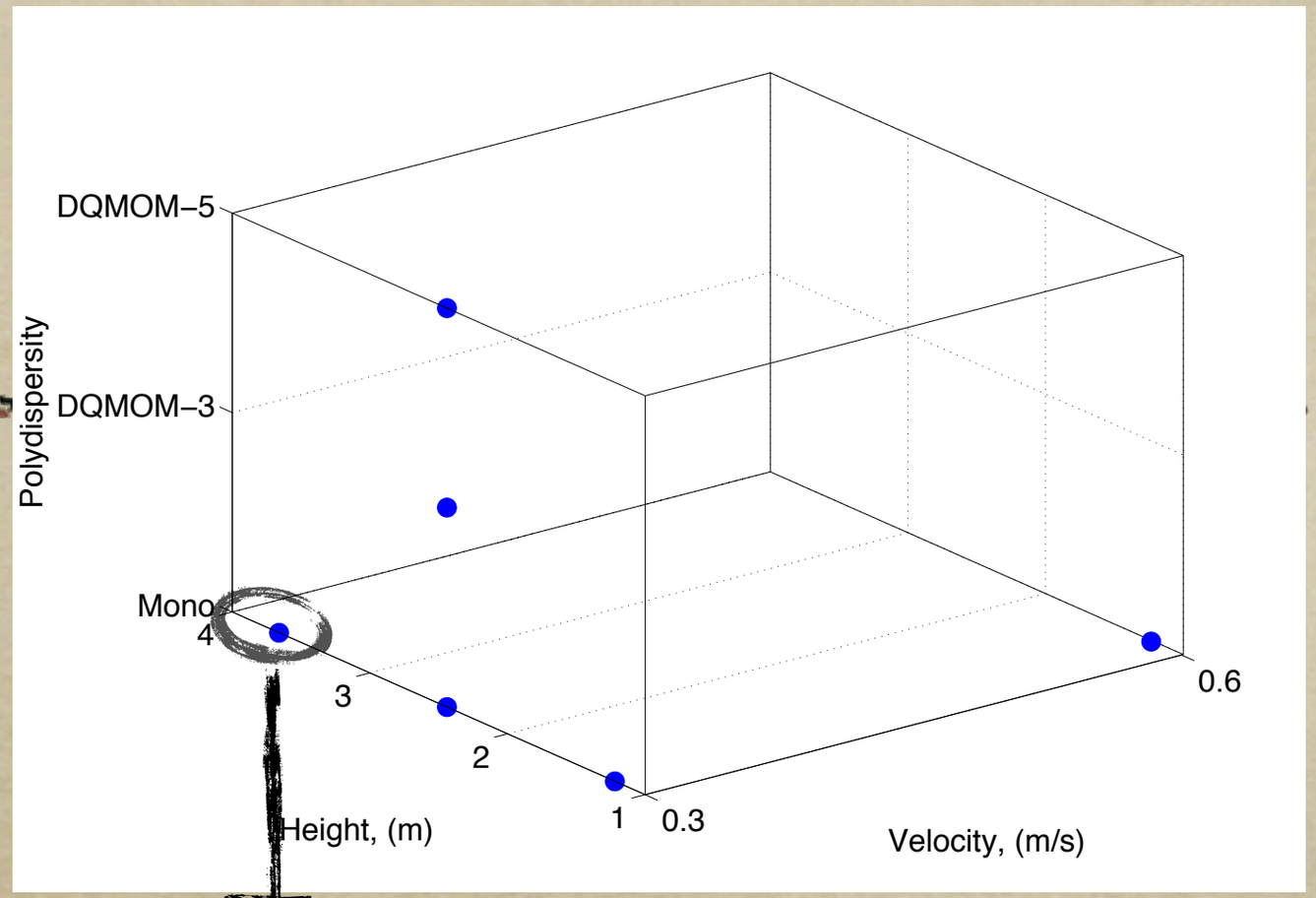

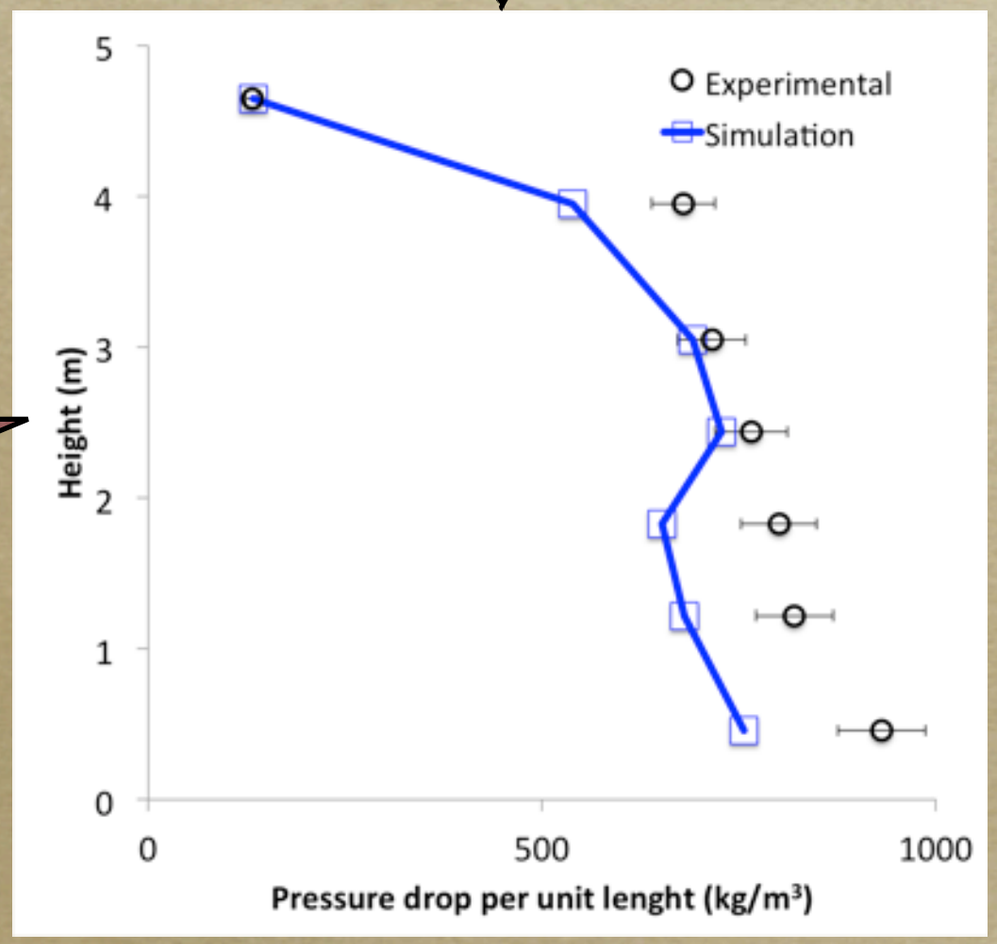

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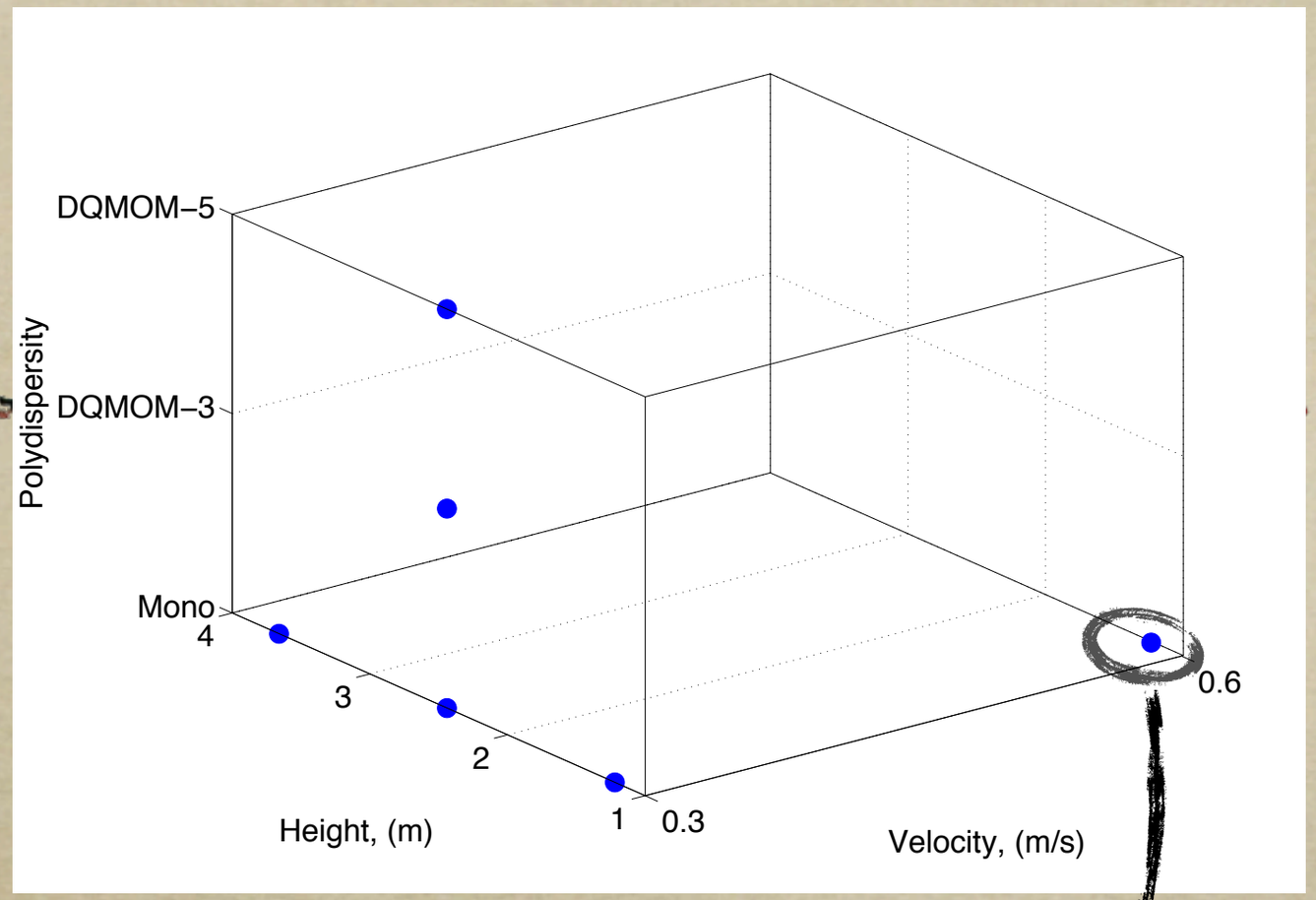

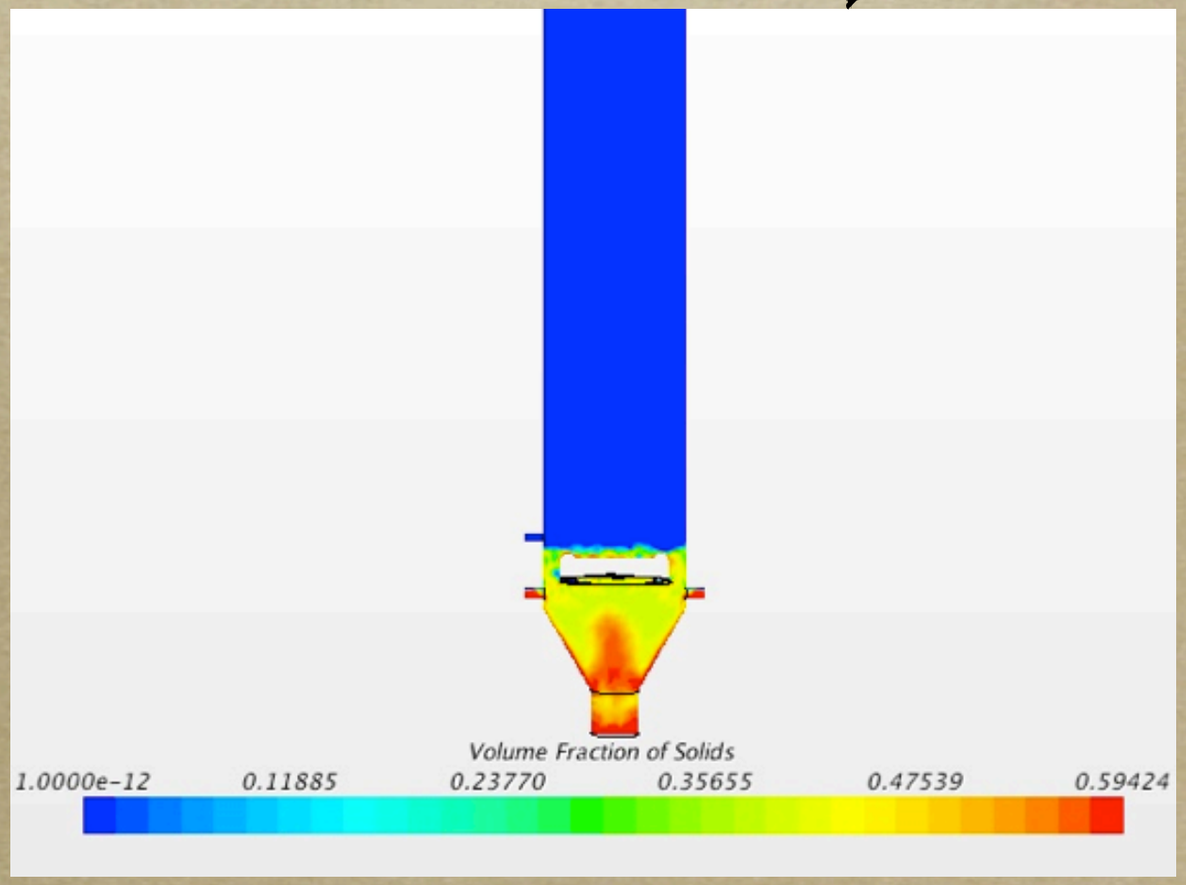

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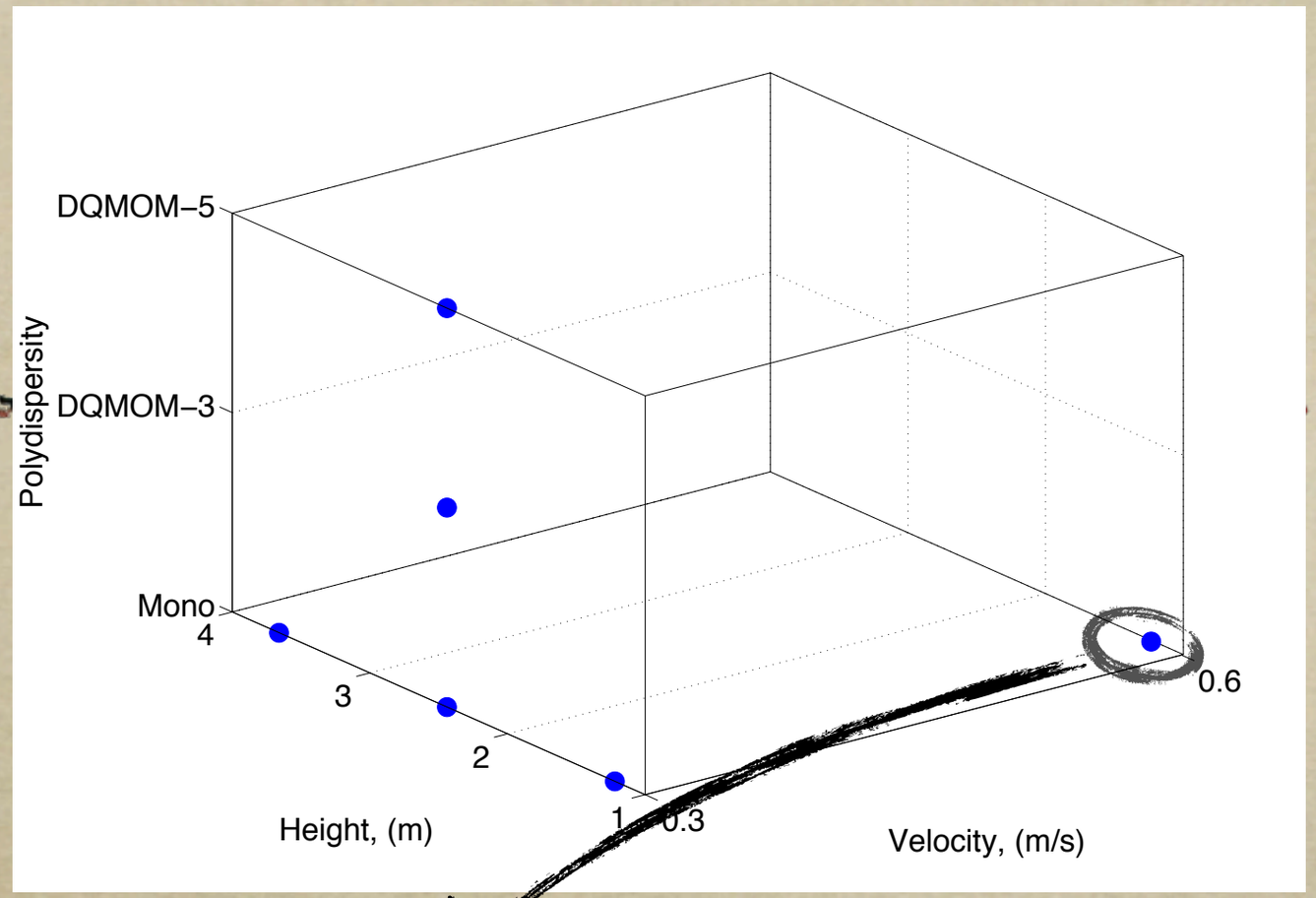

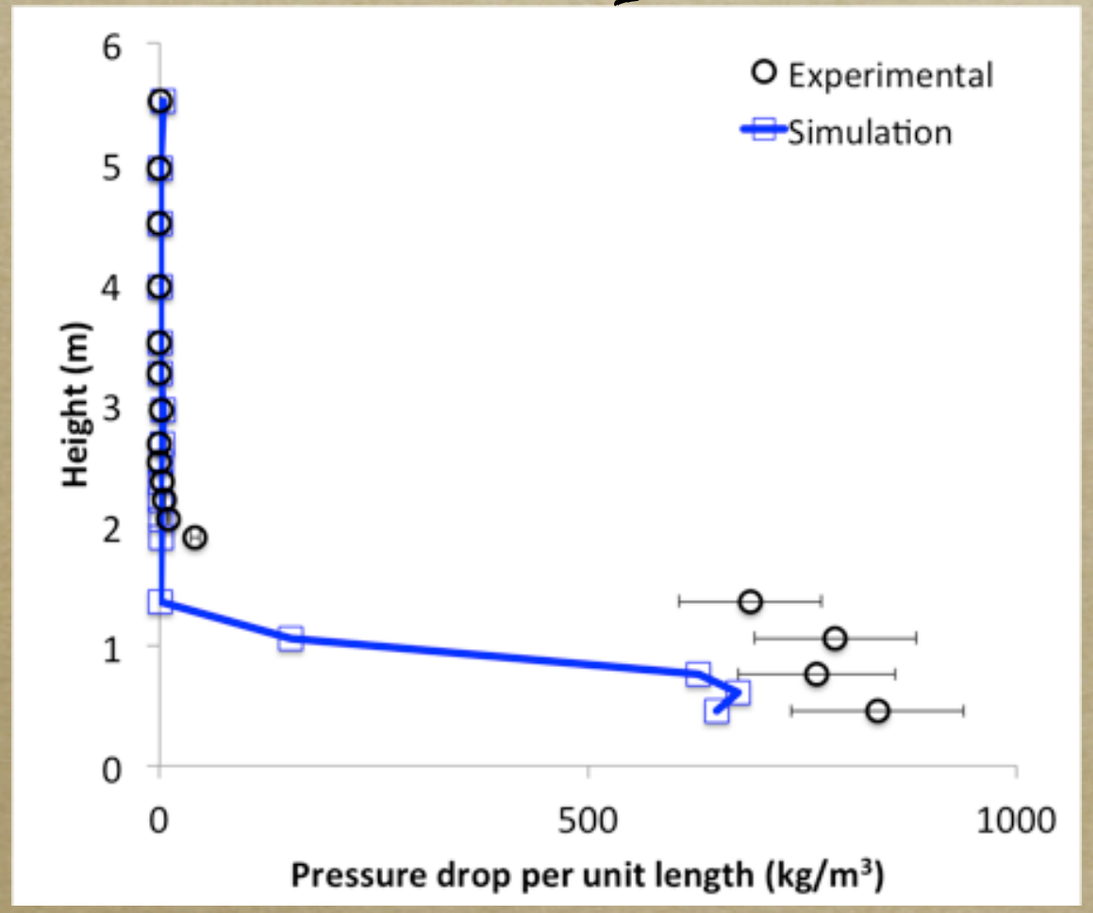

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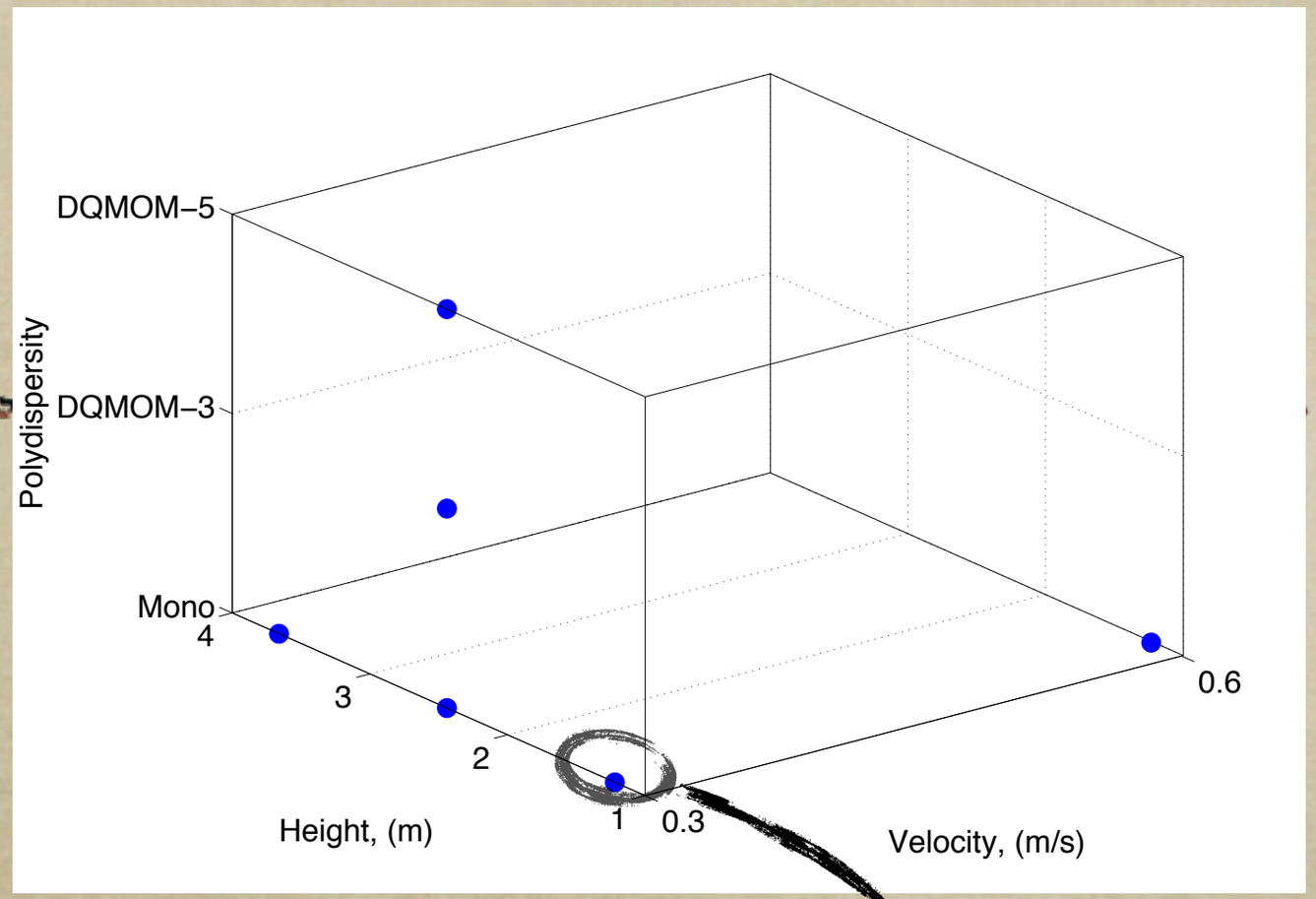
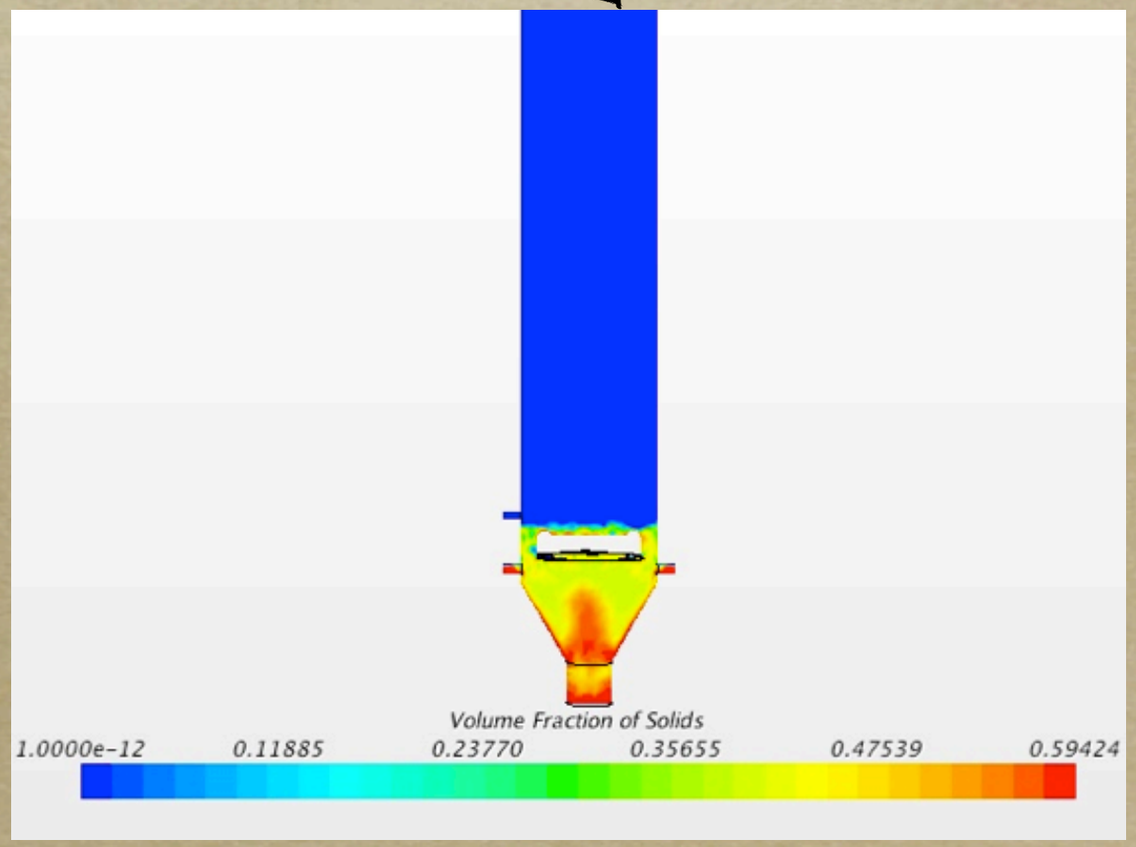


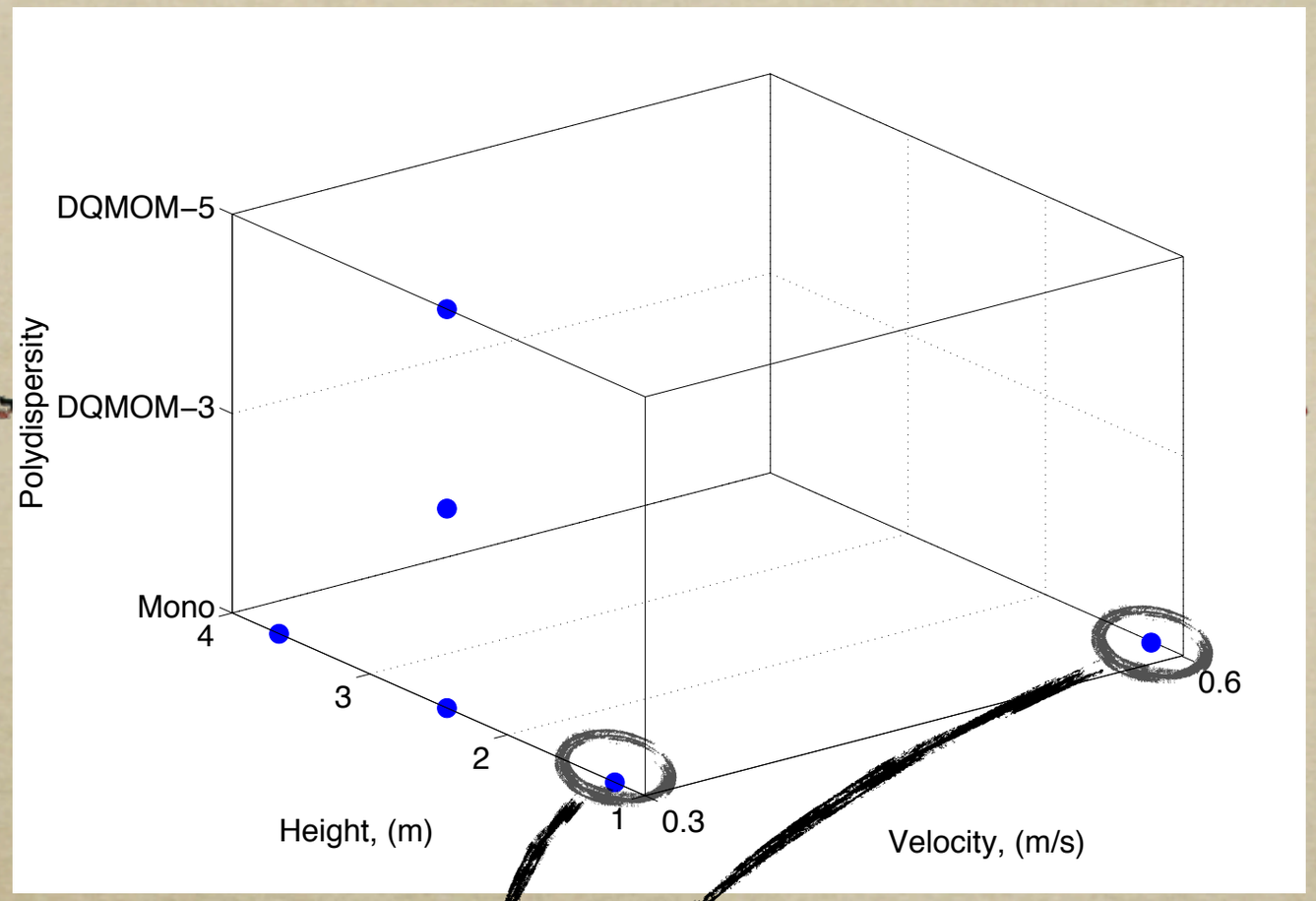


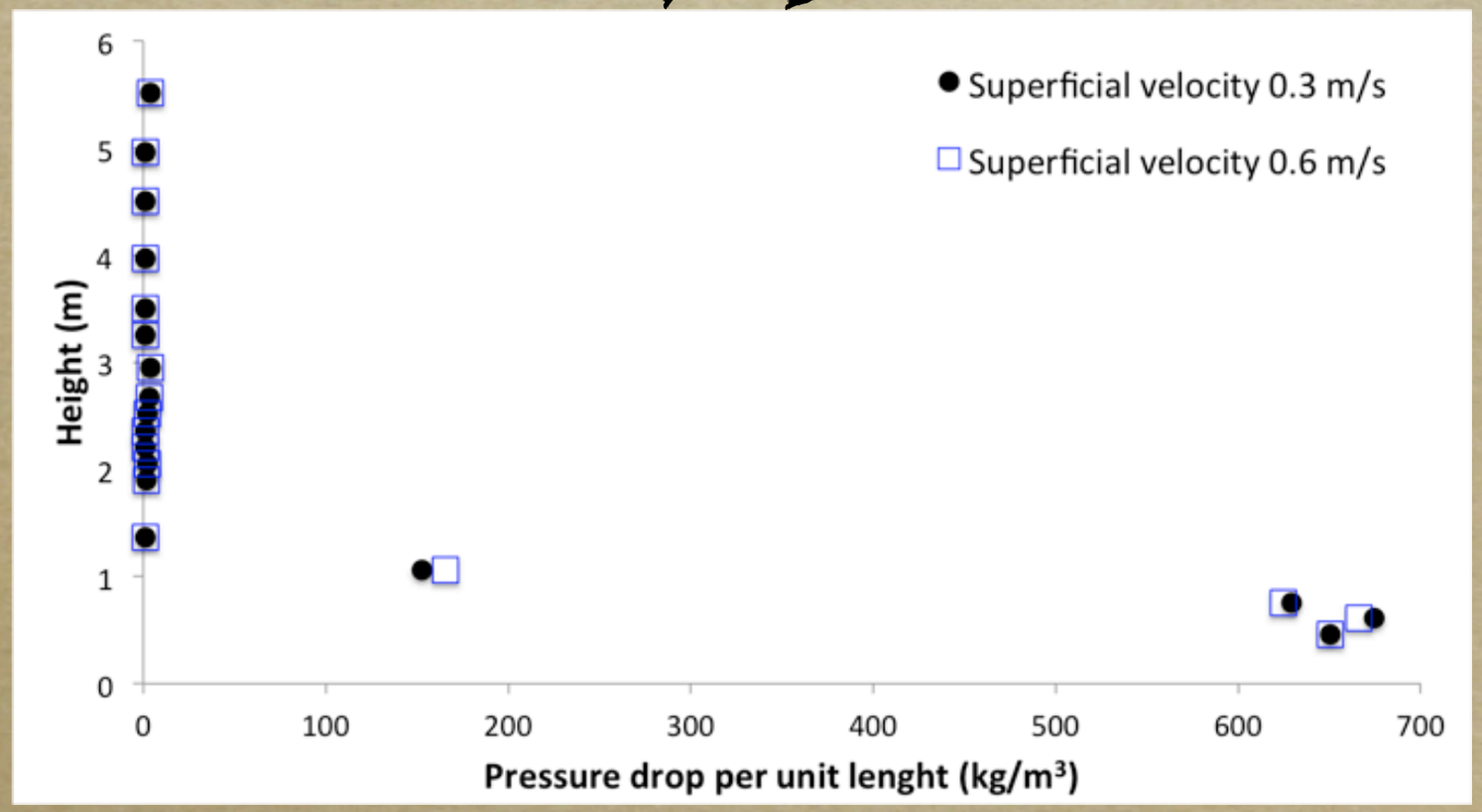
Simulation Task

modeling approaches

sensitivity analysis

comparison with experimental data and previous results





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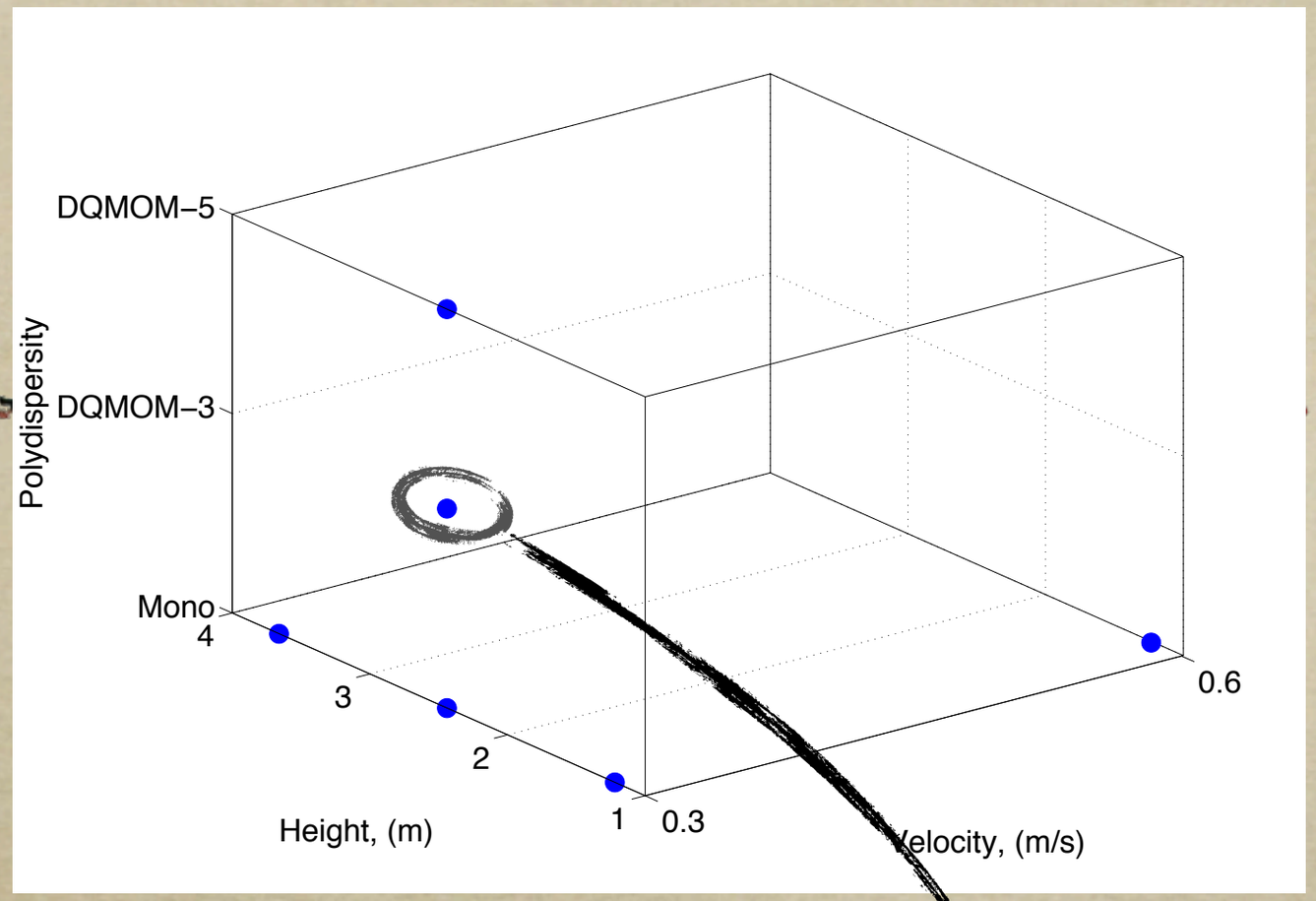

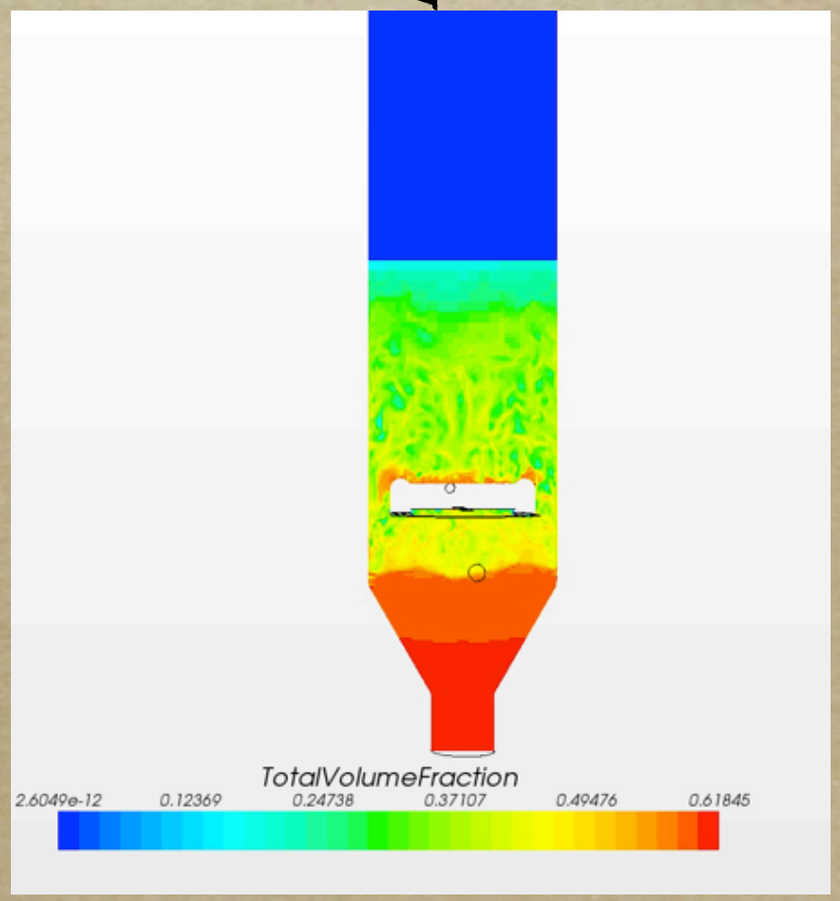

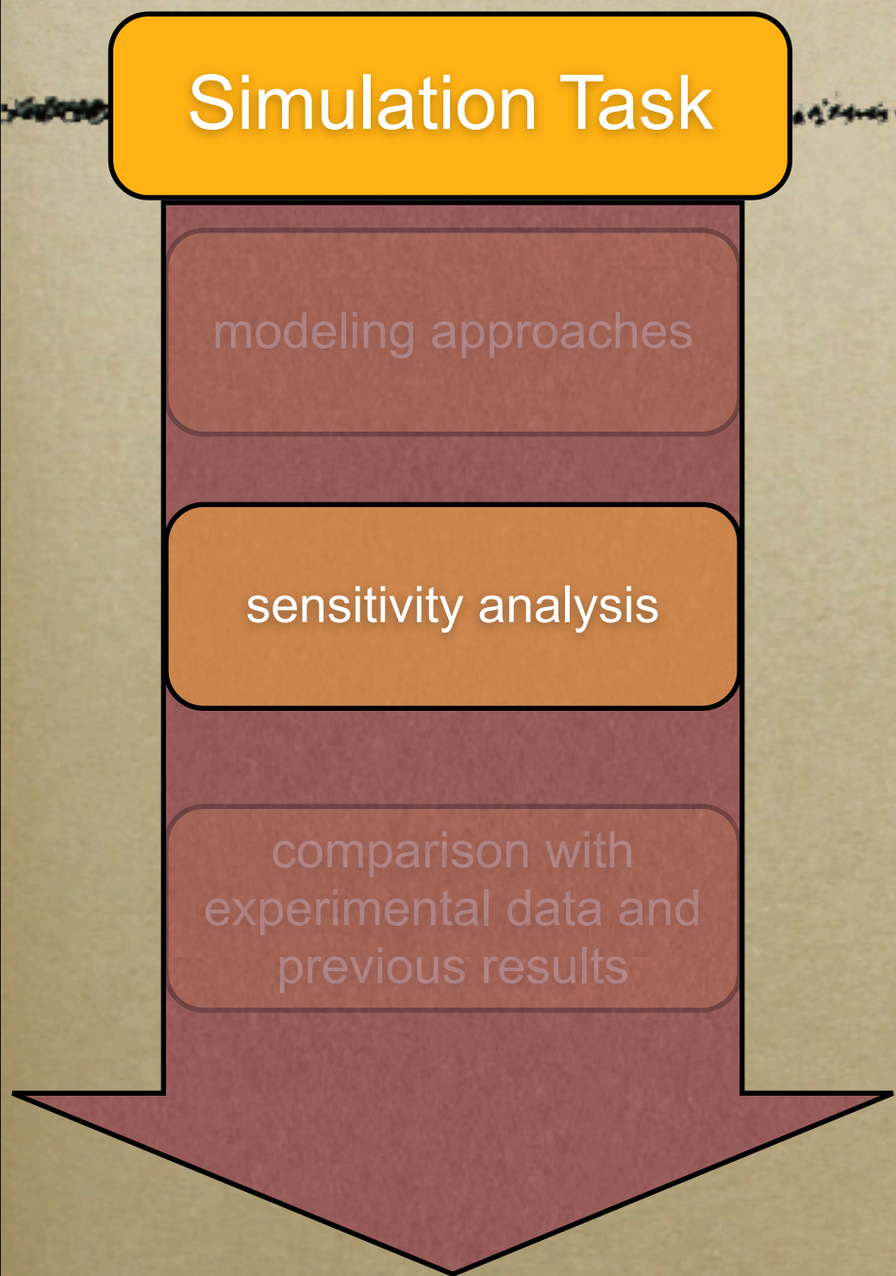
Simulation Task
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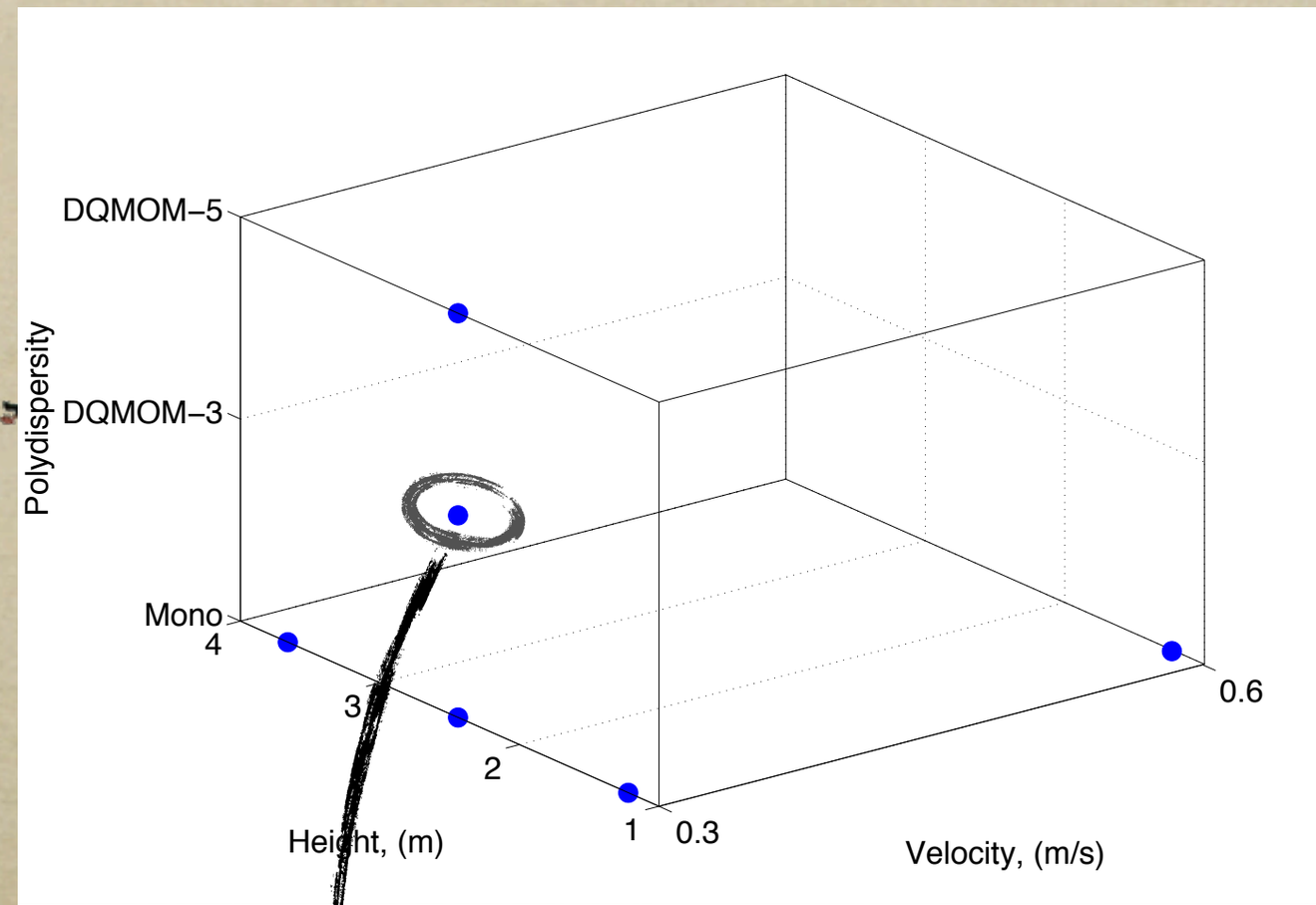
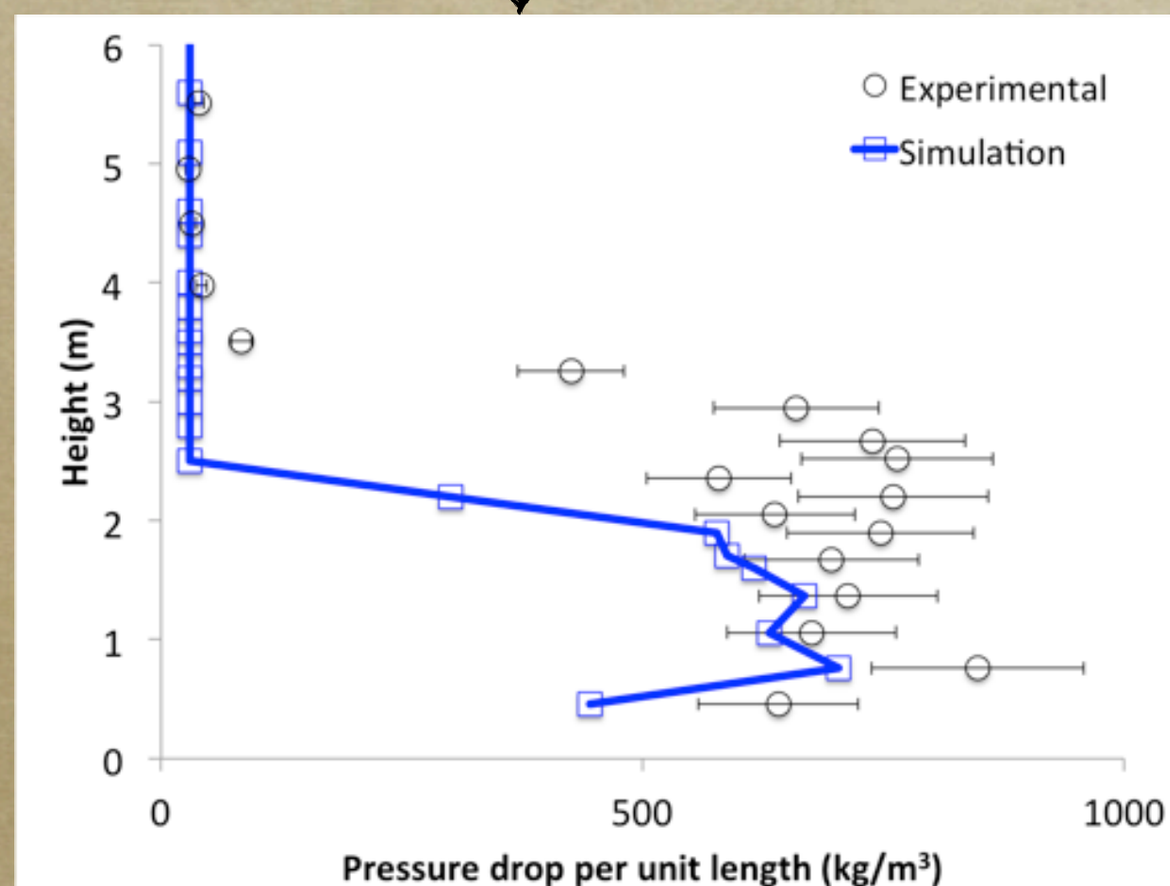

DQMOM−5
DQMOM−3
Mono
Polydispersity
4
3
2
1
Height, (m)
0.3
0.6
Velocity, (m/s)

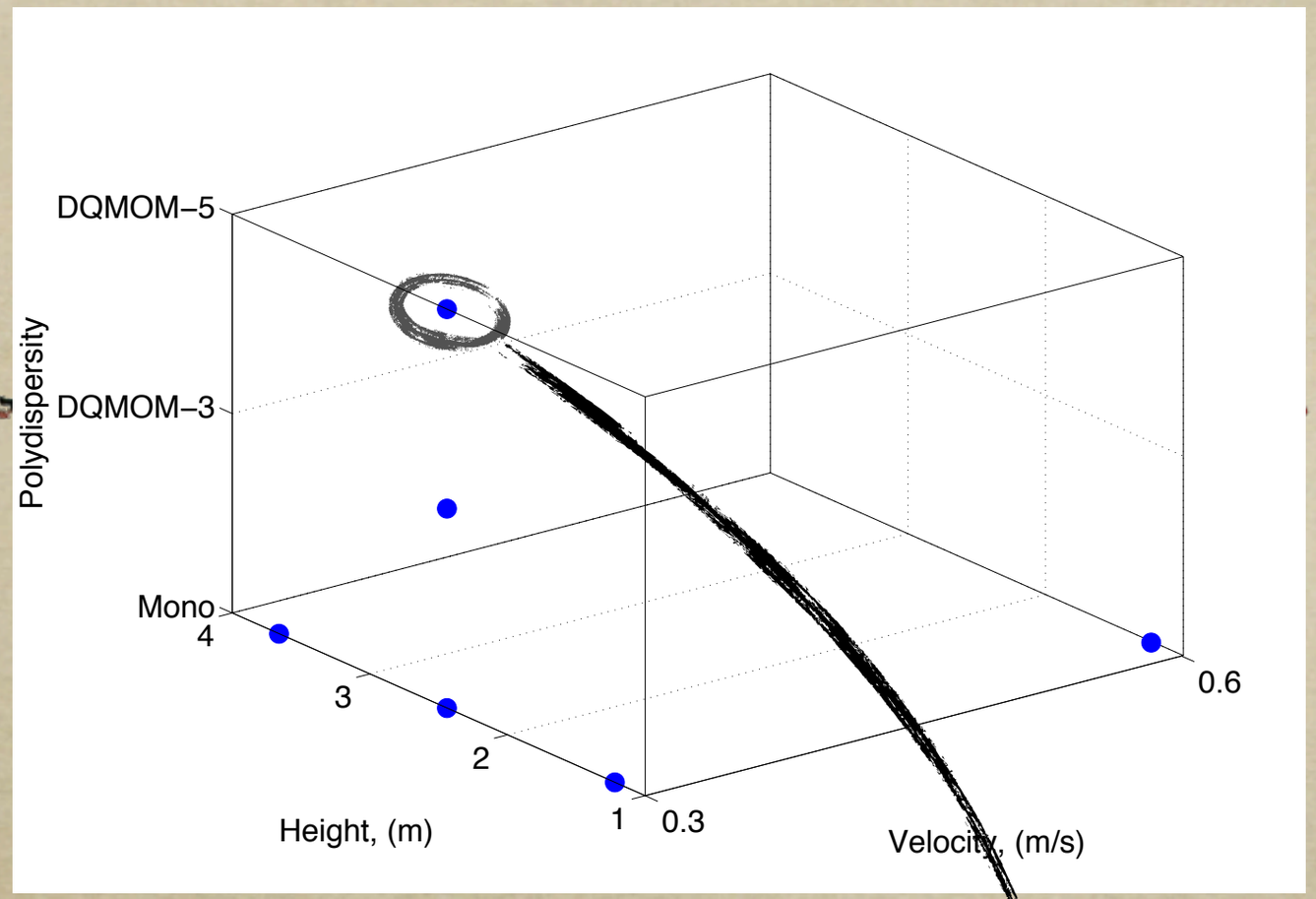

Experimental
Simulation
Height (m)
0
1
2
3
4
5
6
0
500
1000
Pressure drop per unit length (kg/m³)

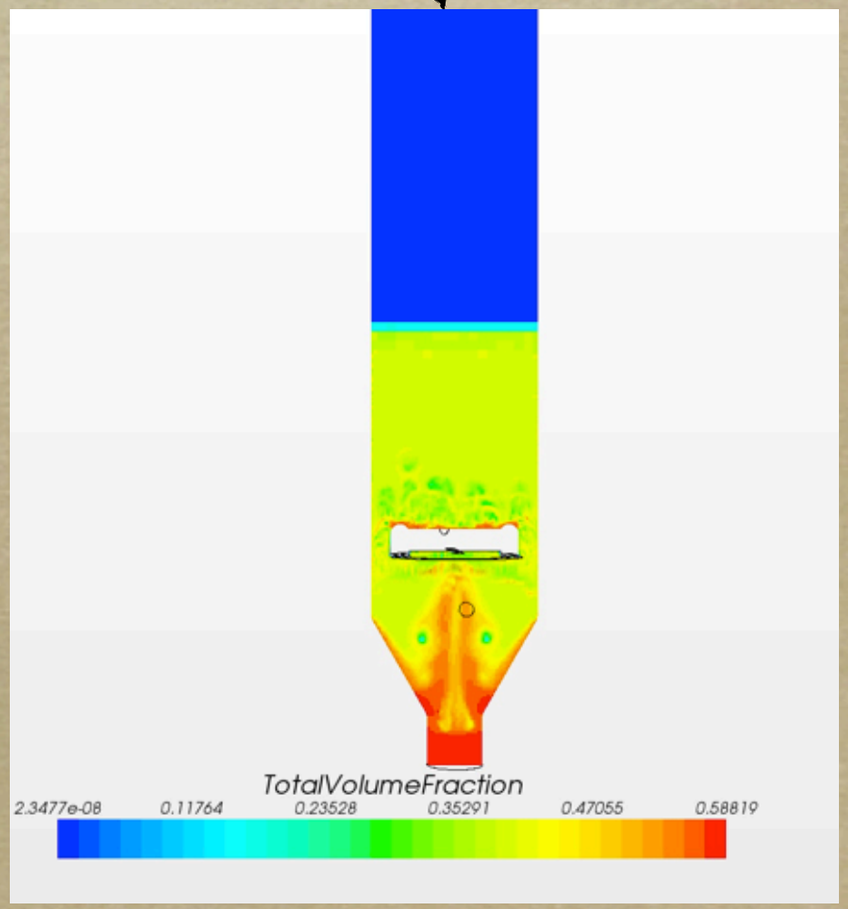
Simulation Task

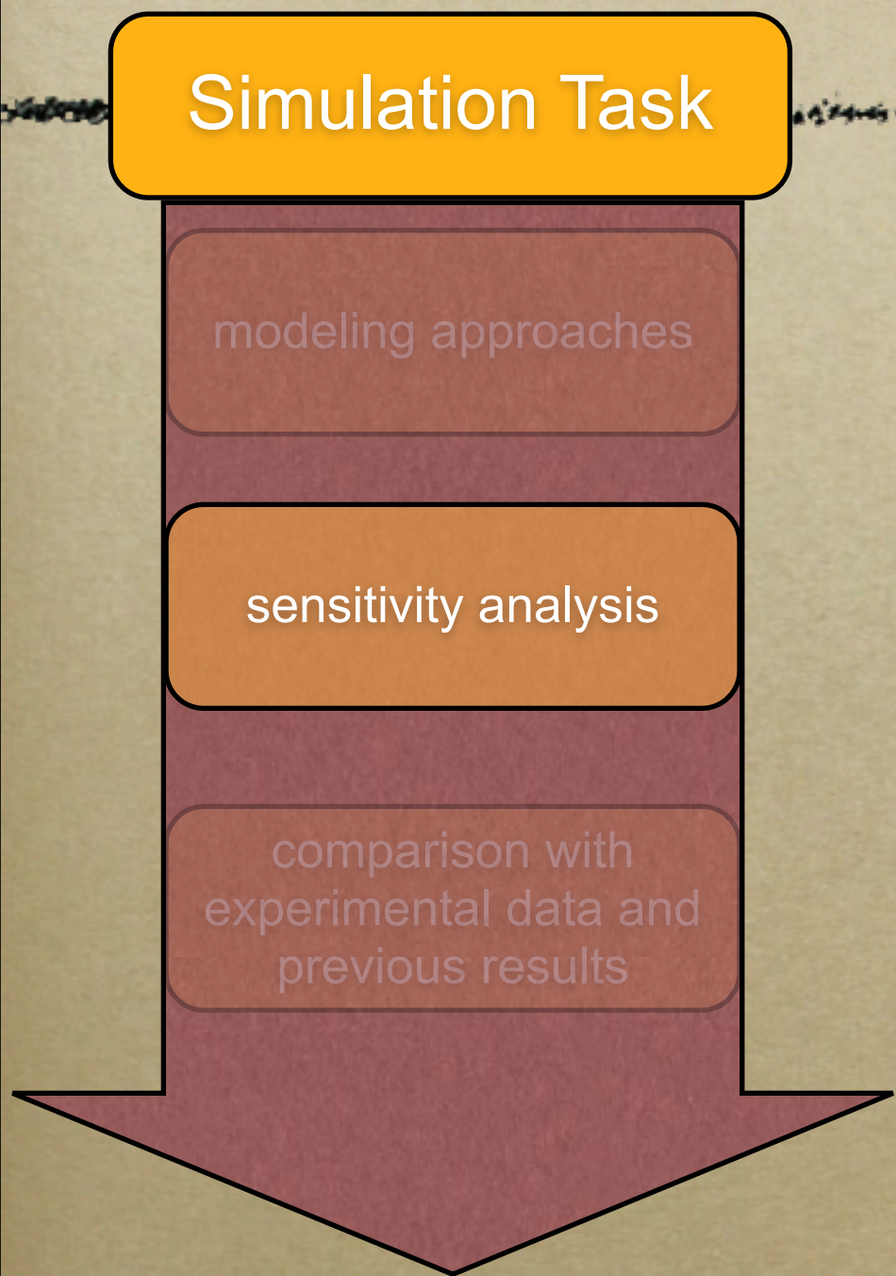
modeling approaches

sensitivity analysis

comparison with experimental data and previous results



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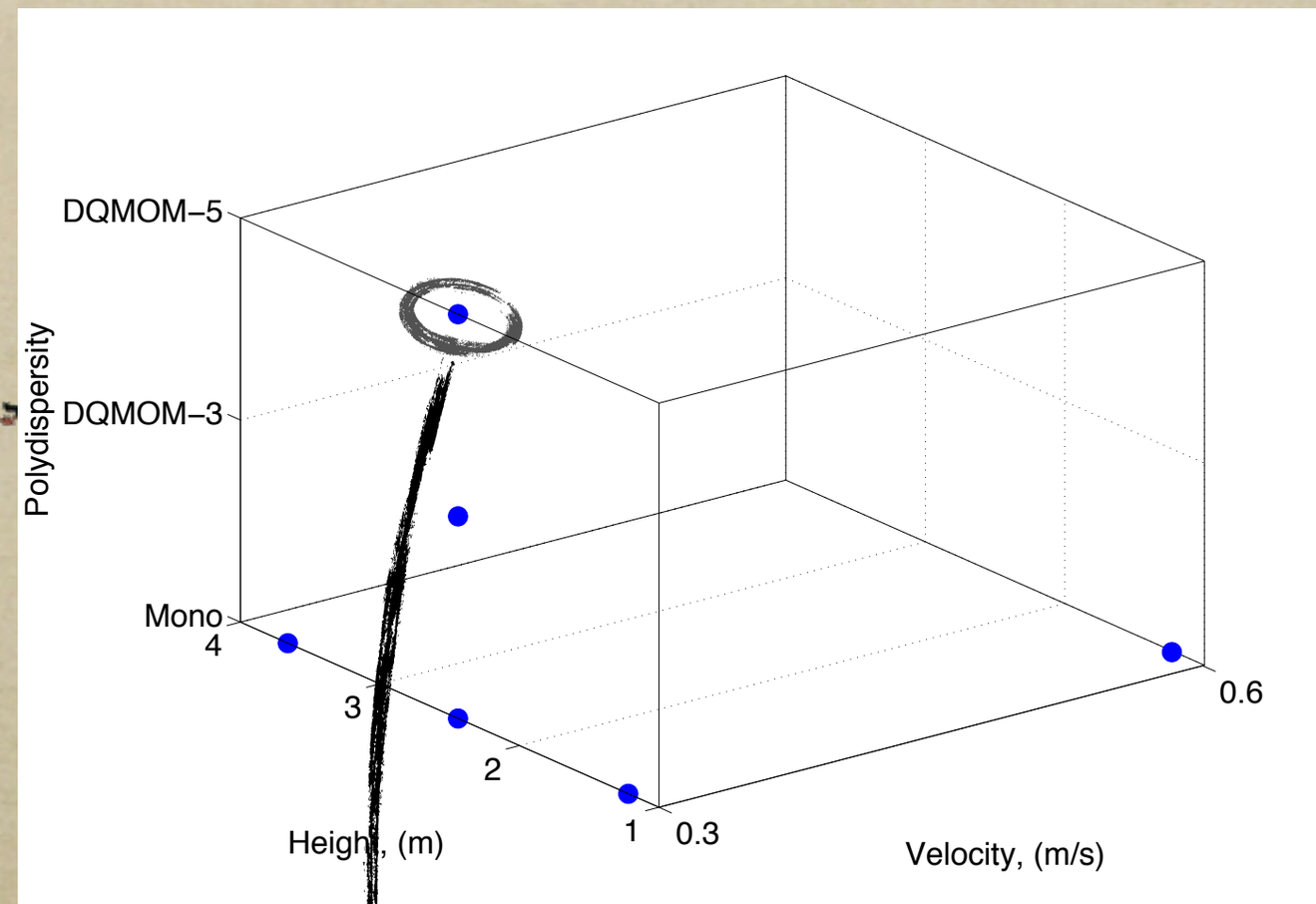
DQMOM−5
DQMOM−3
Mono
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4
3
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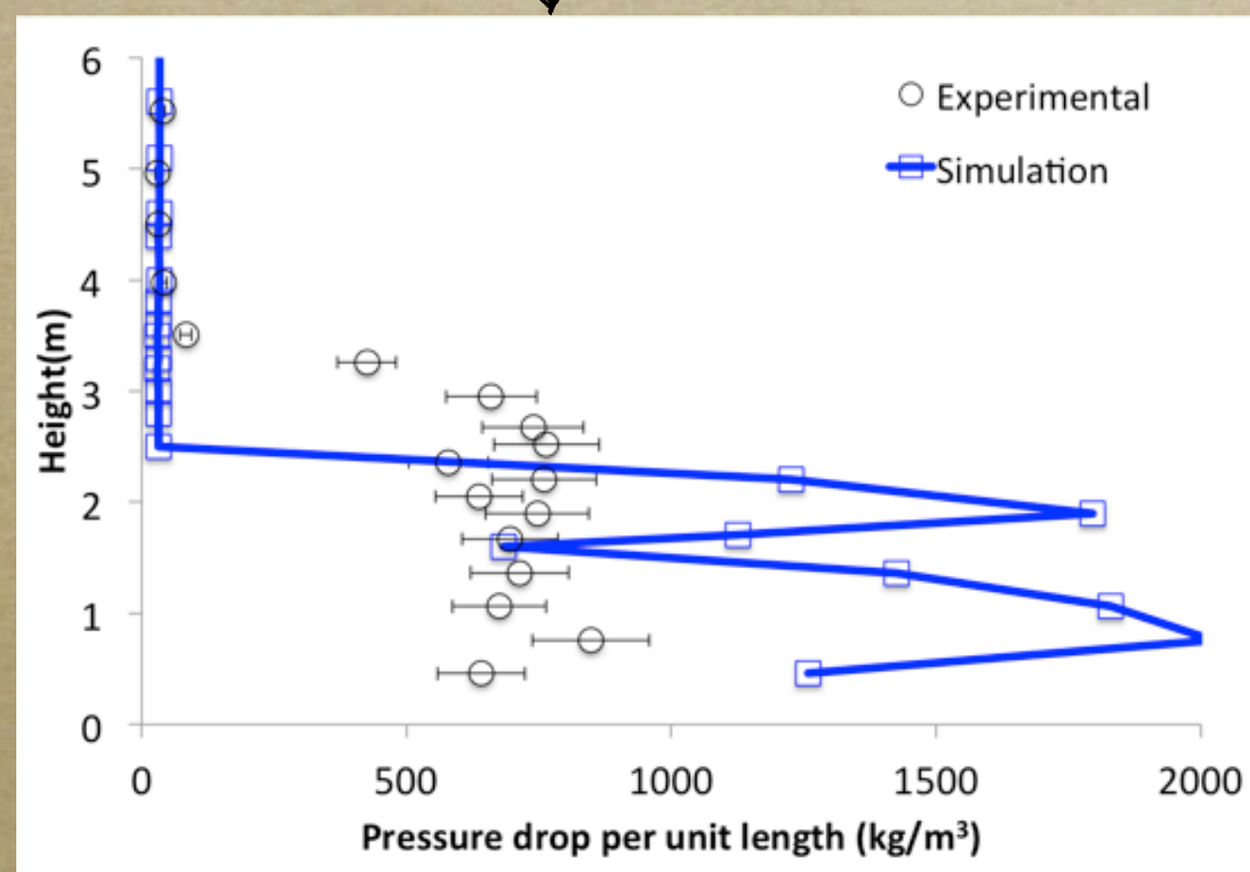
Height, (m)
0.3
0.6
Velocity, (m/s)

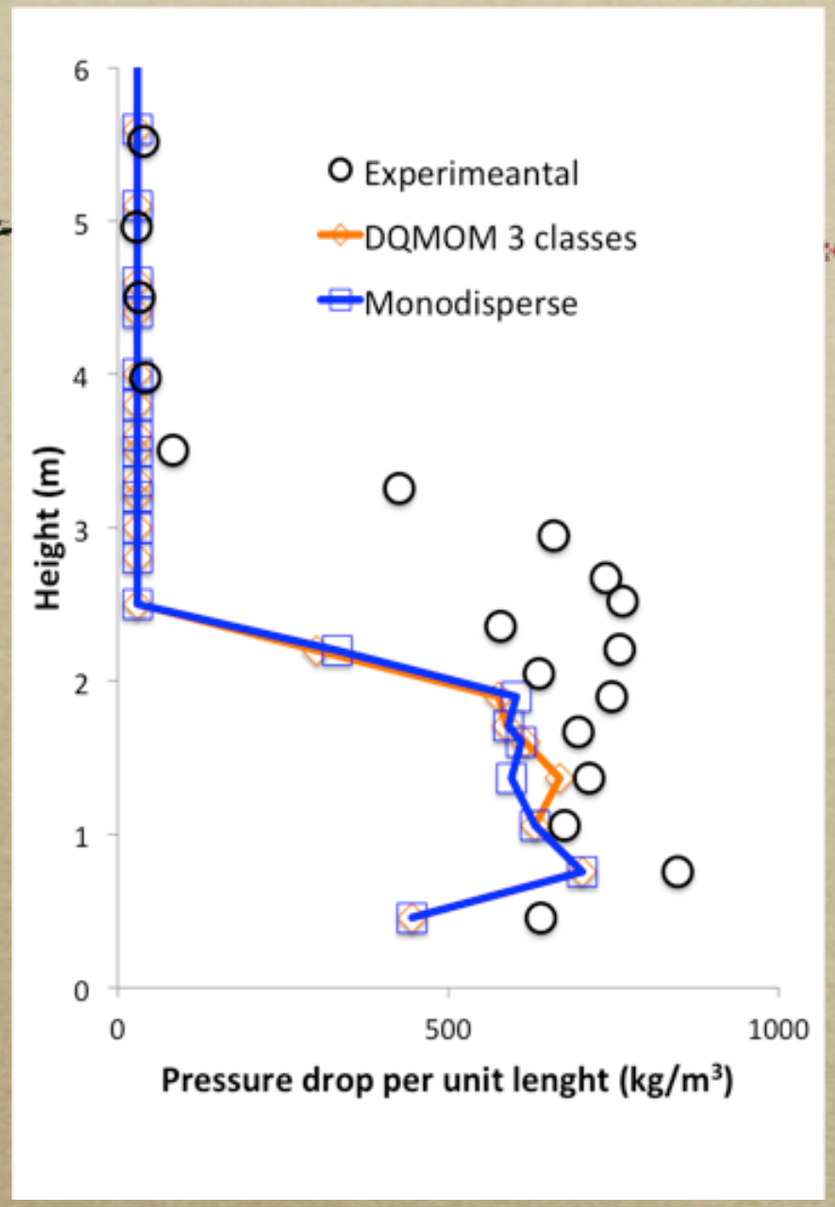

Experimental
Simulation
Height(m)
0
1
2
3
4
5
6
0
500
1000
1500
2000
Pressure drop per unit length (kg/m³)

Simulation Task

modeling approaches

sensitivity analysis

comparison with experimental data and previous results



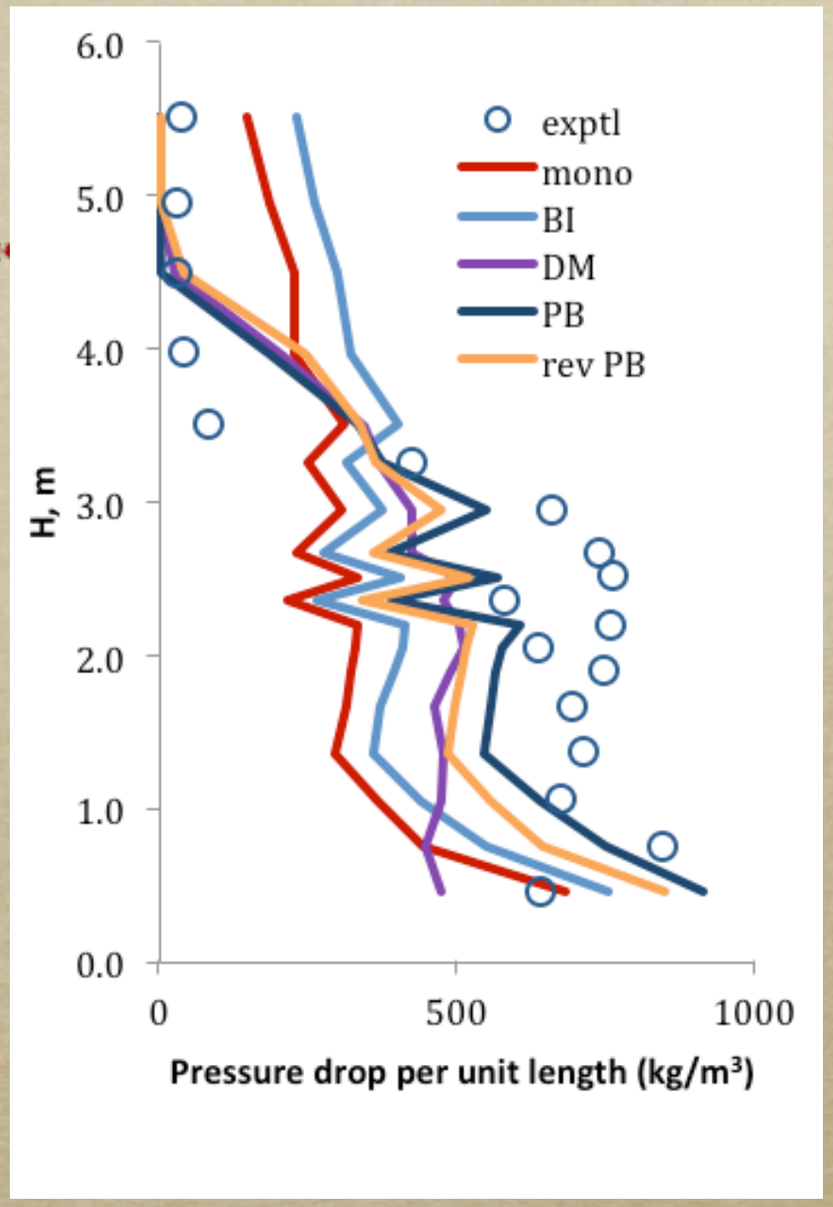


Figure from: Shadle, L., Shahnam, M., Cocco, R., Issangya, A., Guenther, C., Syamlal, M., et al. (2011, May 03). *Challenge Problem III. CFB X Workshop presentation* . Oregon: NETL-PSRI.

Simulation Task

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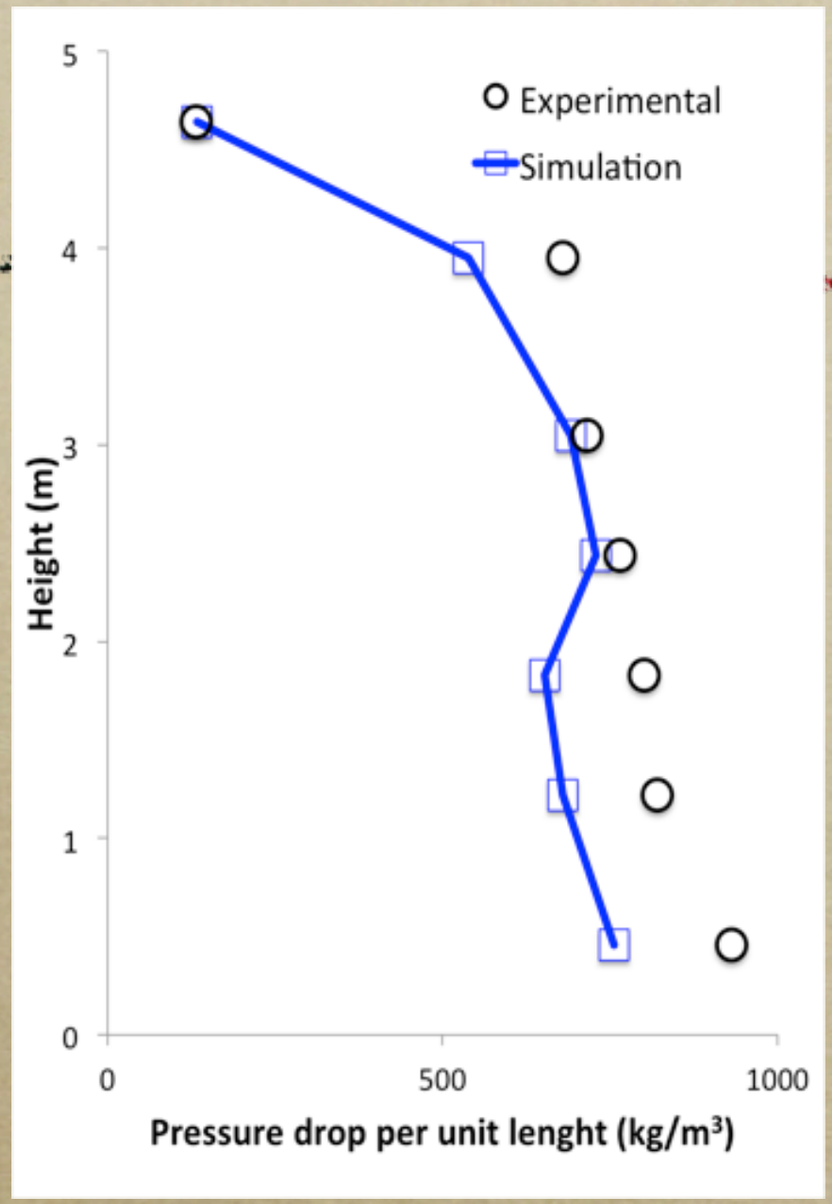
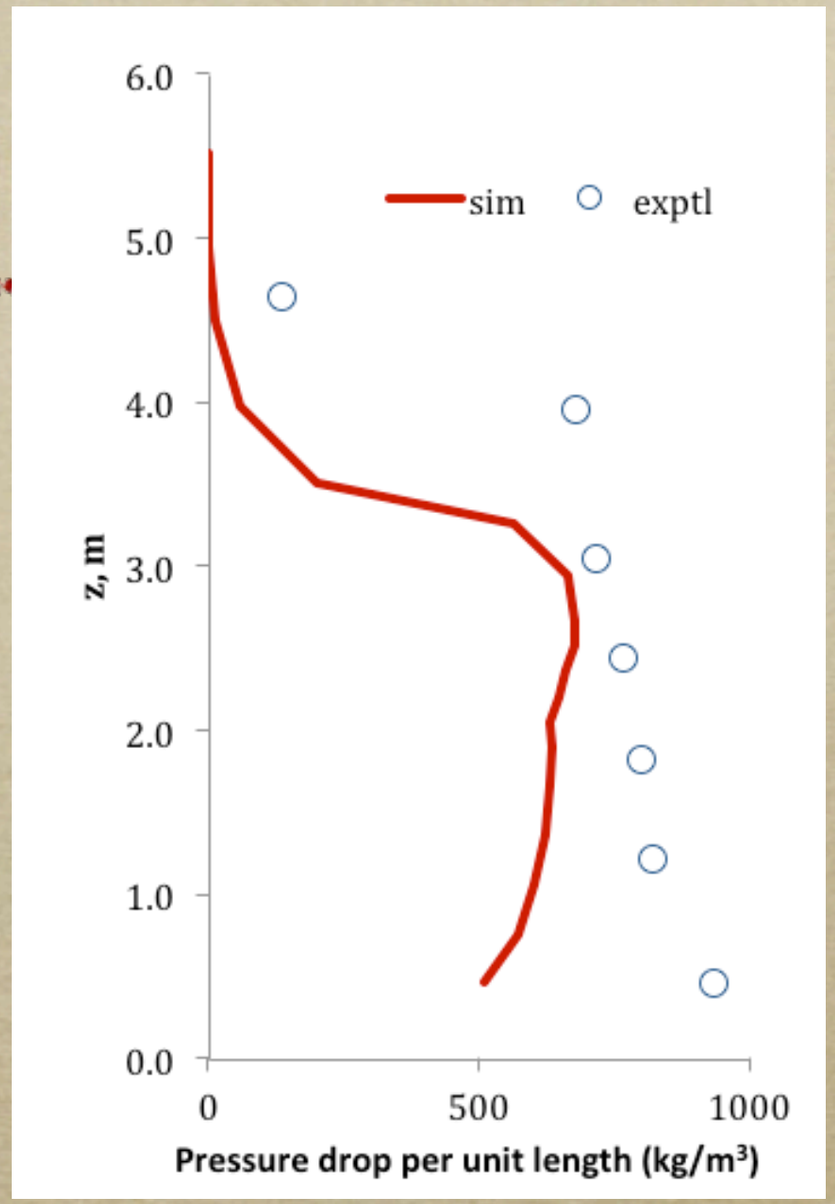
comparison with experimental data and previous results





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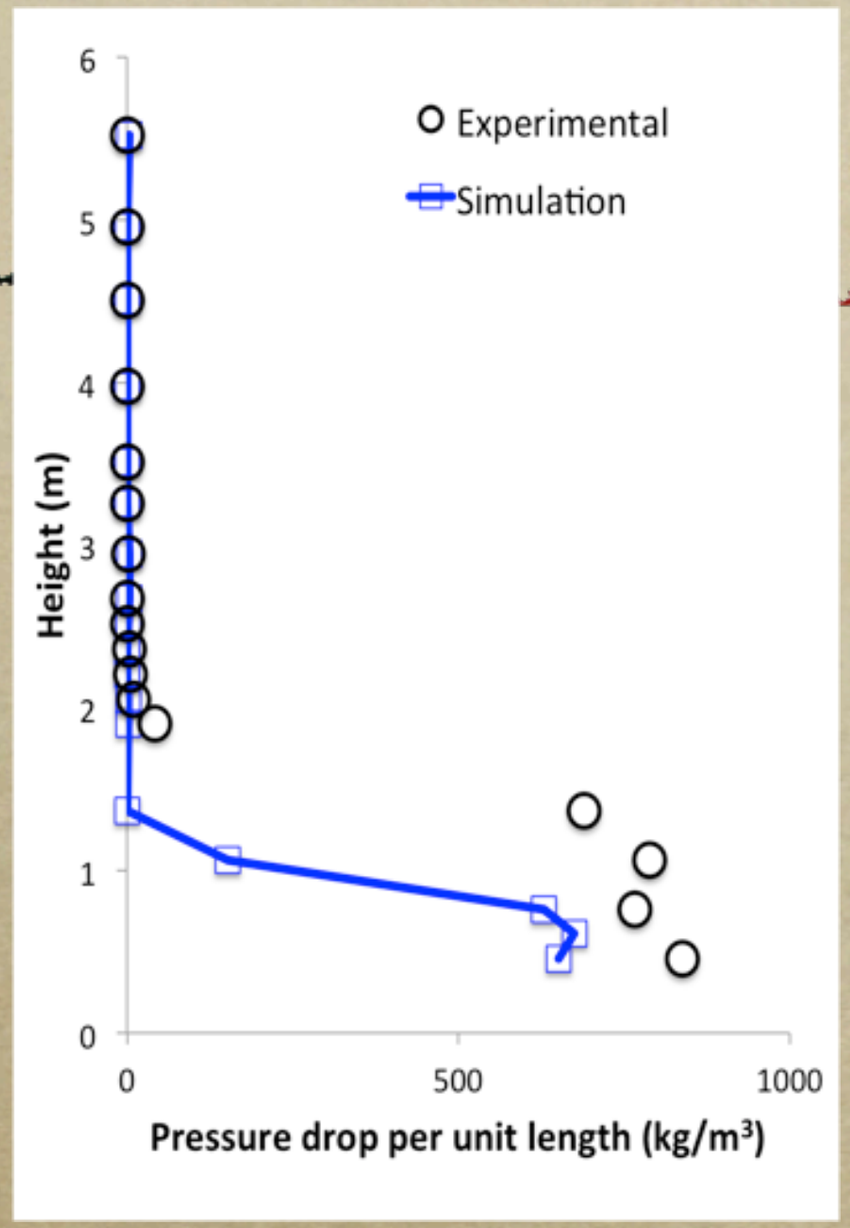

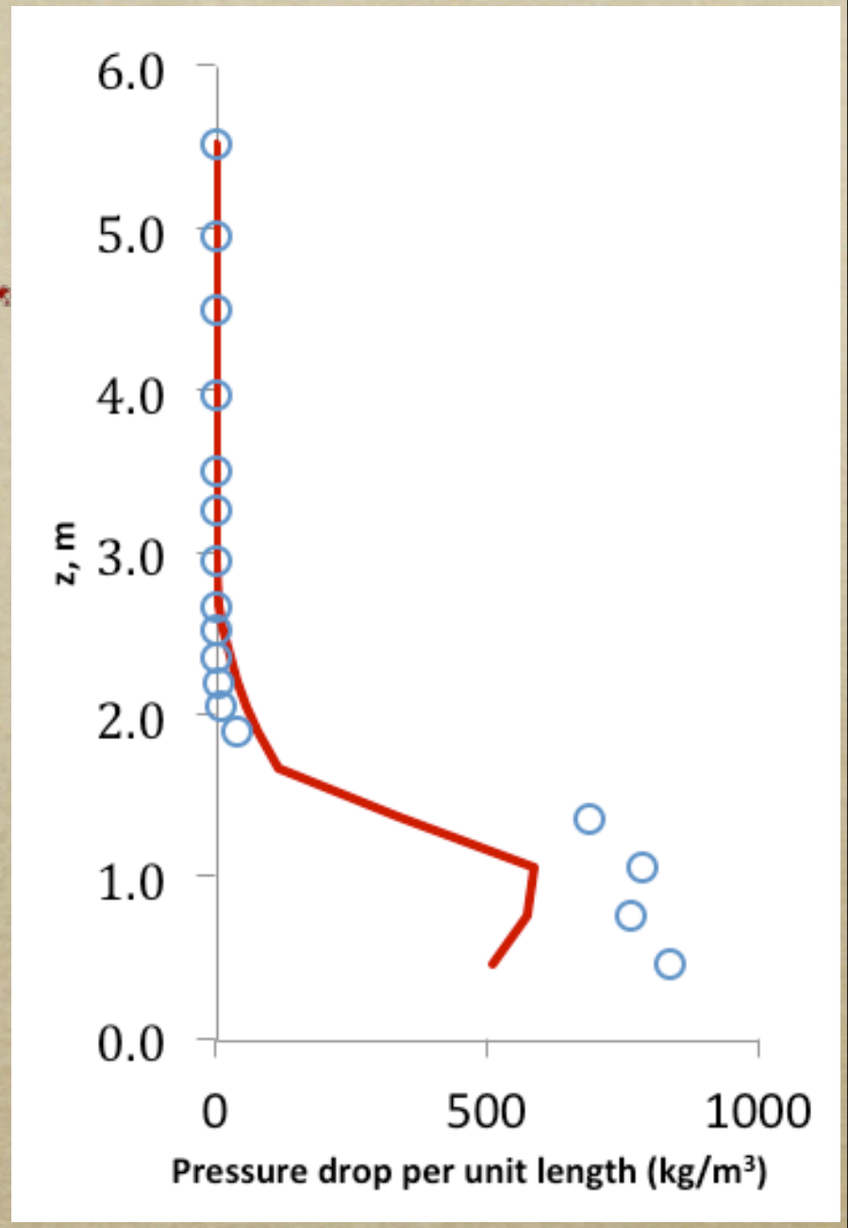

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Process Modeling

Lighty (and Sarofim)

INSTITUTE FOR
Clean and Secure Energy
THE UNIVERSITY OF UTAH

Process Modeling Approach

- **ASPEN Plus process models for CLOU and CLC have been developed to envision material and energy balance scenarios for a Process Development Unit (PDU) based on solid fuels**
- **Wyoming PRB is the targeted coal (North Antelope sub-bituminous)**

Proximate Analysis

Moisture	Volatile Matter	Ash
23.7	49.8	6.5

Ultimate Analysis

C(wt% d.a.f)	H(wt% d.a.f)	O(wt% d.a.f)	N(wt% d.a.f)	S(wt% d.a.f)	Cl(wt % d.a.f)	Heating Value (MJ/kg)
75.3	5.0	18.3	1.1	0.3	-	27.7(dry basis)

Design Considerations

- Circulating Fluidized Beds (CFB) are used for both air and fuel reactors
- Fluidization calculations have been performed using a thermal output of 3 MW/m^2 of bed area
- A superficial velocity to terminal velocity ratio of 2 has been used.
- The oxygen carriers used:

  CLC: 60% Fe_2O_3 supported on Al_2O_3

  CLOU : 40% CuO supported on ZrO_2

Design parameters for CLC with 60% Fe_2O_3 on Al_2O_3 oxygen carrier

Air Reactor (One module in ASPEN, RSTOICH):

- **4 minute residence time**
- **Conversion of Fe_3O_4 in air reactor = 80%**
  - $2Fe_3O_4\ (s) + 1/2\ O_2(g) \rightarrow 3Fe_2O_3\ (s)$

For simplicity, formation of $FeAl_2O_4$ has not been considered in the present calculation.

Design Parameters for CLC with 60% Fe_2O_3 on Al_2O_3 oxygen carrier

Fuel Reactor (Three Modules in ASPEN):

- Coal enters an RYIELD to yield a gas which enters the gasifier. The gasifier is modeled as an equilibrium reactor (RGIBBS) which produces syngas
- Reactions with syngas in RSTOICH
- Conversion of Fe_2O_3 to Fe_3O_4 is 99%

$$3Fe_2O_3\,(s) + CO\,(g) \rightarrow 2Fe_3O_4(s) + CO_2\,(g)$$

$$3Fe_2O_3\,(s) + H_2\,(g) \rightarrow 2Fe_3O_4\,(s) + H_2O\,(g)$$

- Assumption of 10 min residence time for coal conversion (limiting step)

CLOU with 40% CuO on ZrO_2 oxygen carrier: Design Parameters

- **Experimental data of Mattisson et al. (2009) and Sahir, et al. (2012) has been used to provide the copper reduction and oxidation kinetics**
- **Air Reactor (modeled with one module in ASPEN):**
  - **50% conversion of Cu_2O**
    - **$2Cu_2O + O_2 \rightarrow 4CuO$**
  - **Residence time is 42 s**

Mattisson, T. et al. (2009), International Journal of Greenhouse Gas Control, 3(1), pp. 11-19.
Sahir, A.H. et al. (2012), Energy and Fuels, 26(10), pp. 4395-4404.
Bartok W., Sarofim A.F., eds. (1991), Fossil Fuel Combustion A Source Book,,John Wiley & Sons.
Eyring, E.M. et al. (2011), Oil & Gas Science and Technology - Rev. IFP Energies nouvelles, 2011,66(2), pp. 209-221.

CLOU with 40% CuO on ZrO_2 oxygen carrier: Design Parameters

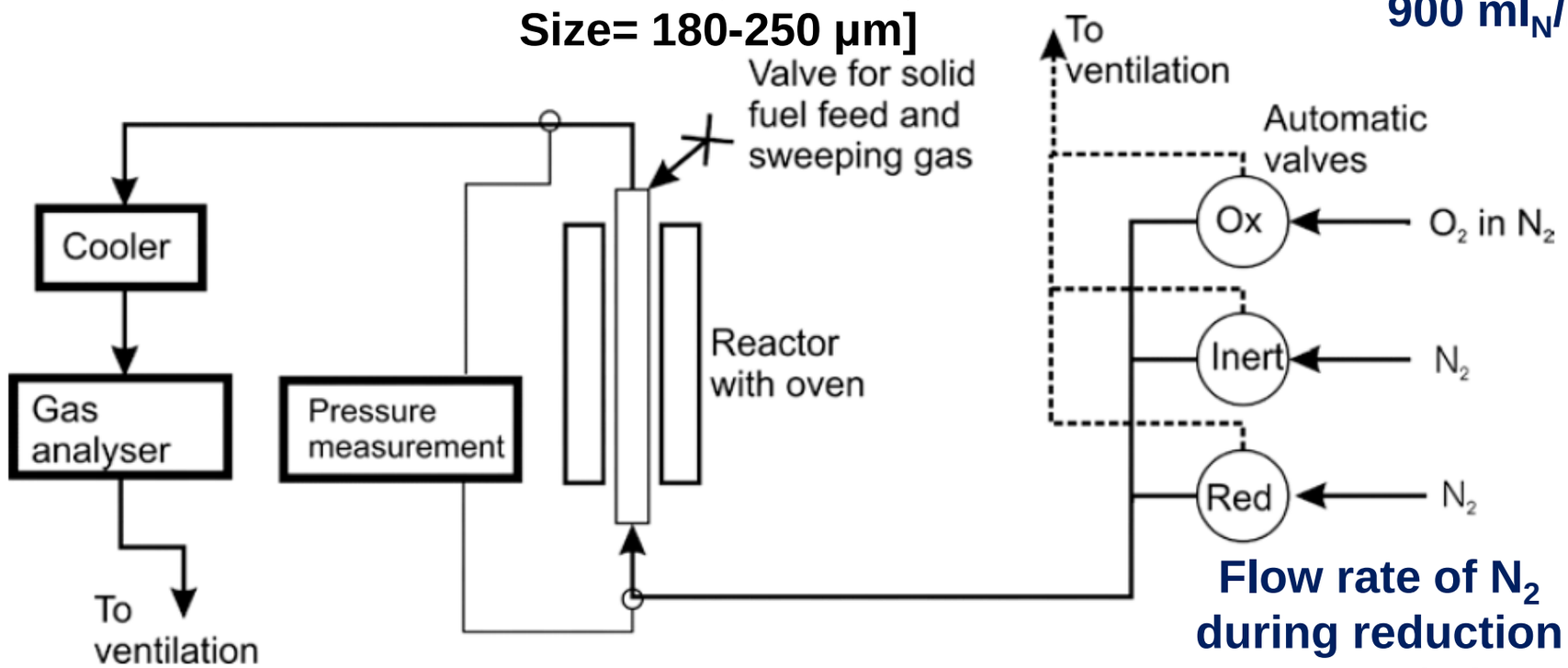
Fuel Reactor (Three Modules in ASPEN):

- Oxygen is generated from CuO in an RSTOICH
  - 54% conversion of CuO in the fuel reactor
    - ($4CuO \rightarrow 2Cu_2O + O_2$)
- Coal enters an RYIELD to yield a gas which enters the gasifier with the oxygen from above. The gasifier is modeled as an equilibrium reactor (RGIBBS)
  - Complete coal burnout
  - PRB coal combustion kinetics are from Bartok & Sarofim.
- Residence time is 35 secs based on CuO conversion

CLOU Combustion Experiment of Mexican Petcoke by Mattisson et al.(2009)

Fuel introduced:
0.1 g Mexican Petcoke particles
[88.8% C(by mass)
Size= 180-250 μm]

Flow rate of O_2-N_2 mixture during oxidation 900 ml_N/min



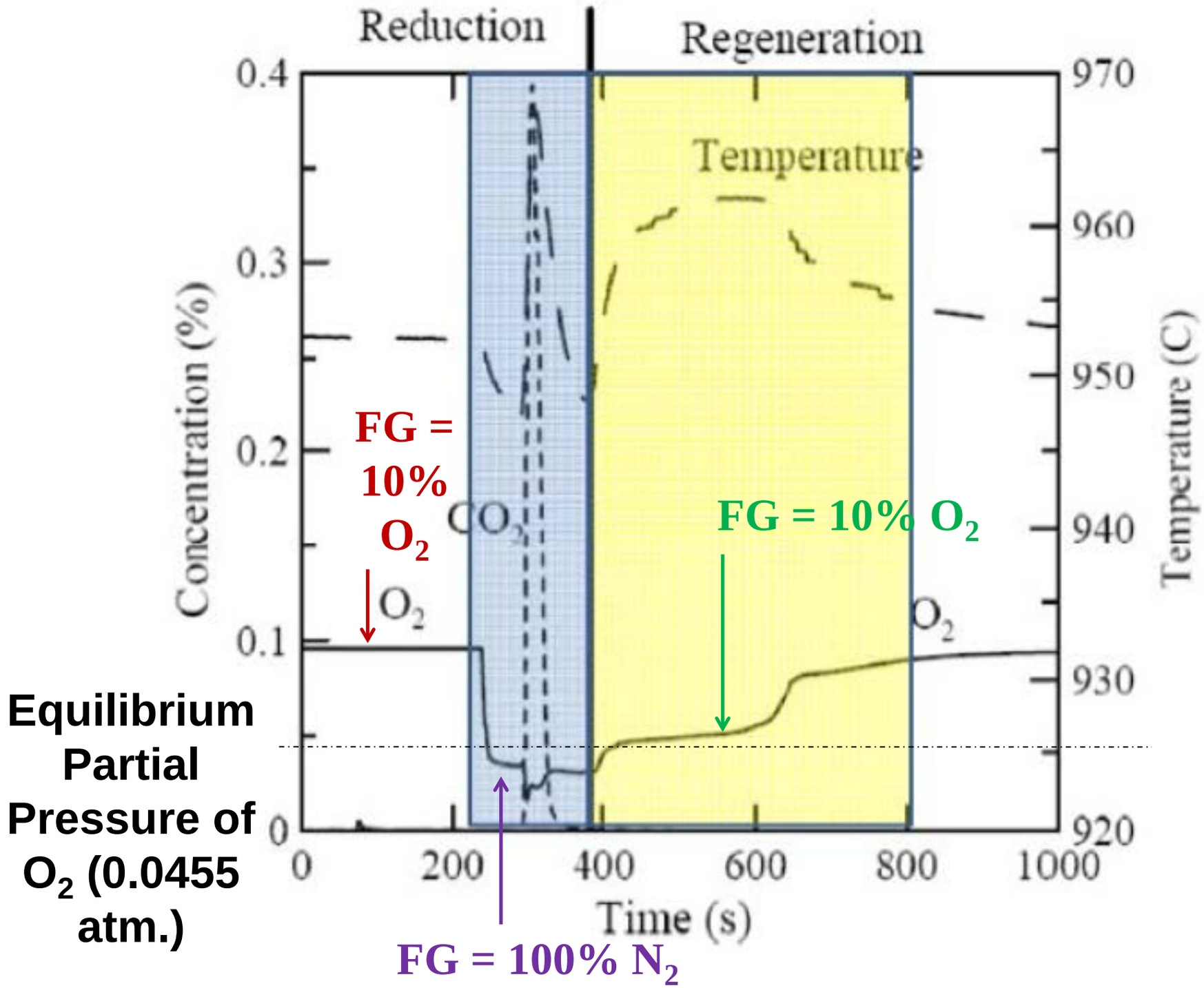
O_2 concentration
10% (for expt. at 950°C)
21% (for expt. at 985°C)

Flow rate of N_2 during reduction 900 ml_N/min

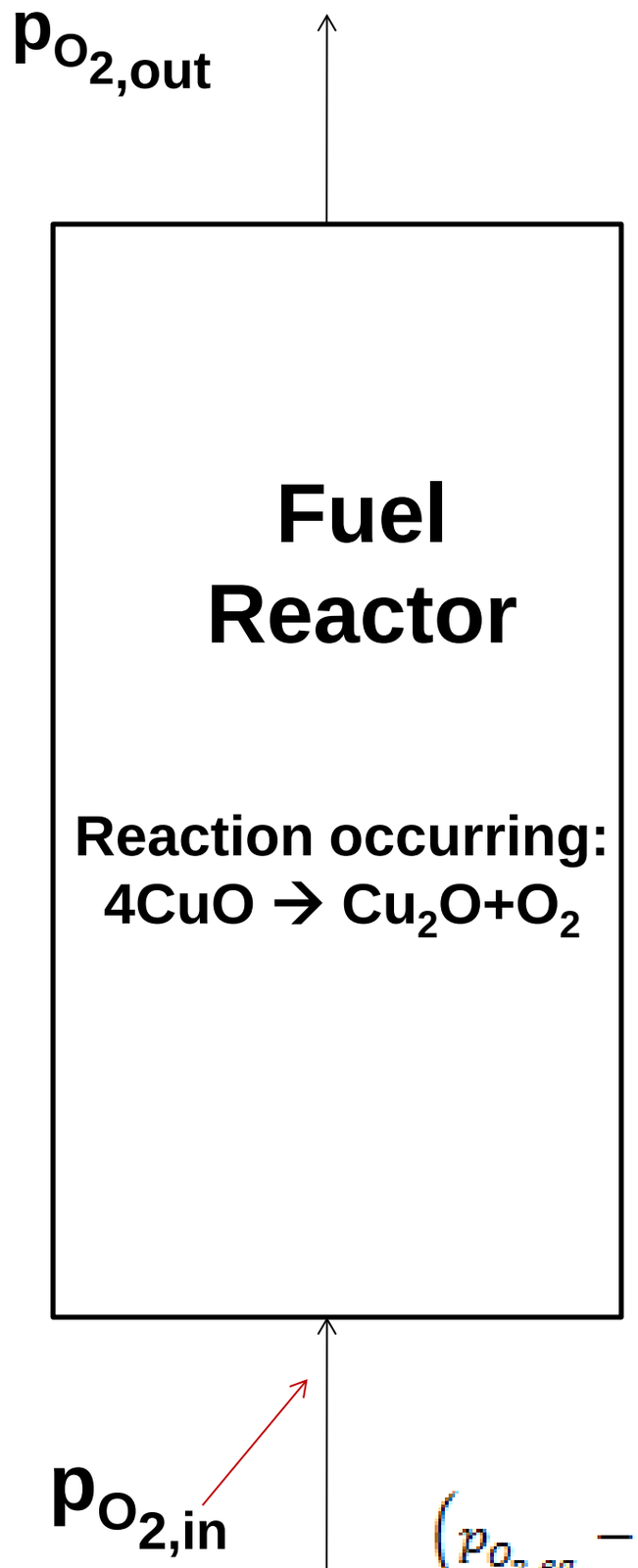
15 g of 40% CuO /60% ZrO_2 particles in the batch fluidized bed[Size= 125-180 μm]

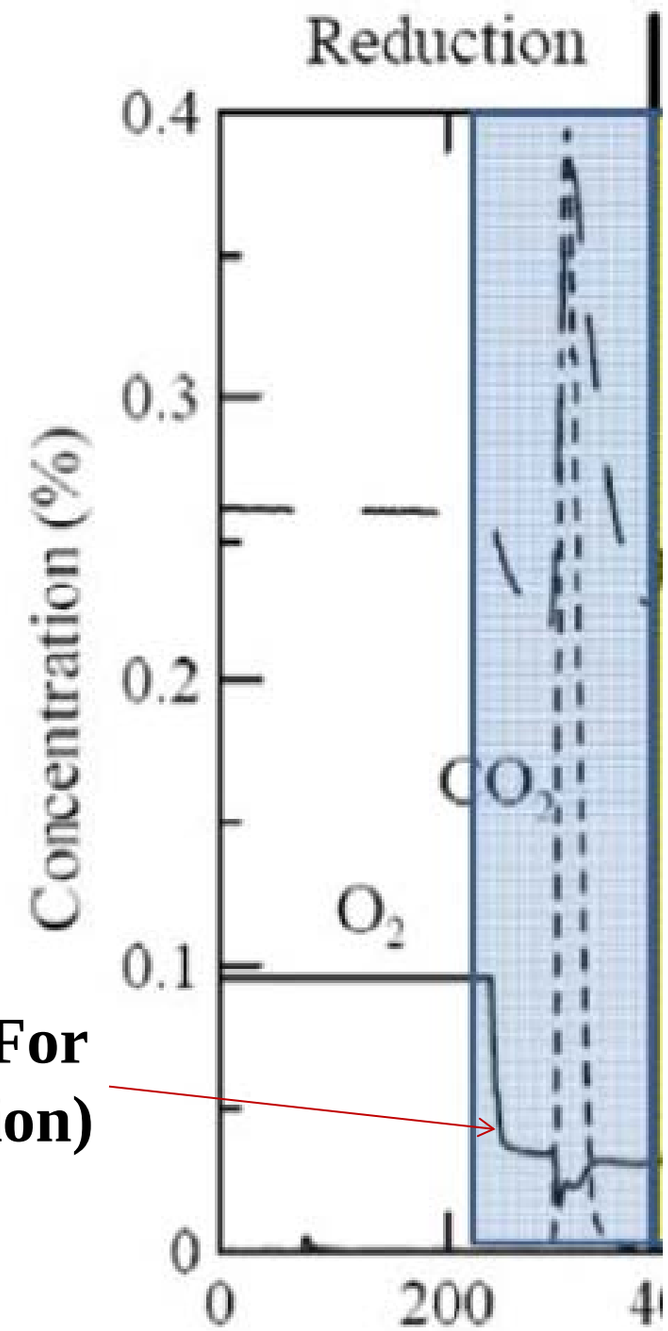
Mattisson T., Leion H., Lyngfelt A. (2009) Chemical-looping with oxygen uncoupling using CuO/ZrO_2 with petroleum coke, *Fuel* ***88, 683-690.***

Experimental Gaseous concentration profiles of CLOU Combustion of Mexican Petcoke at 955°C



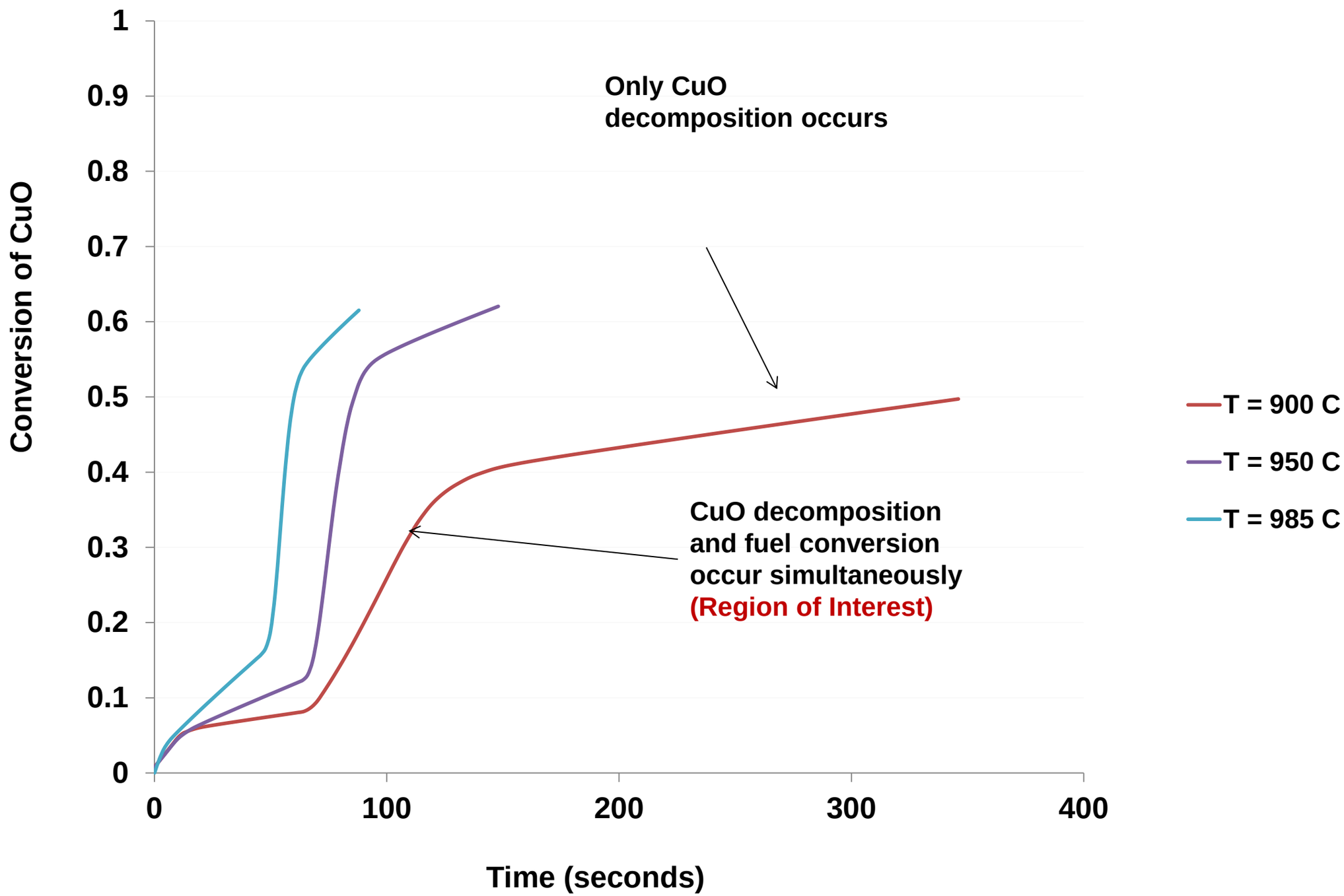
CuO Decomposition

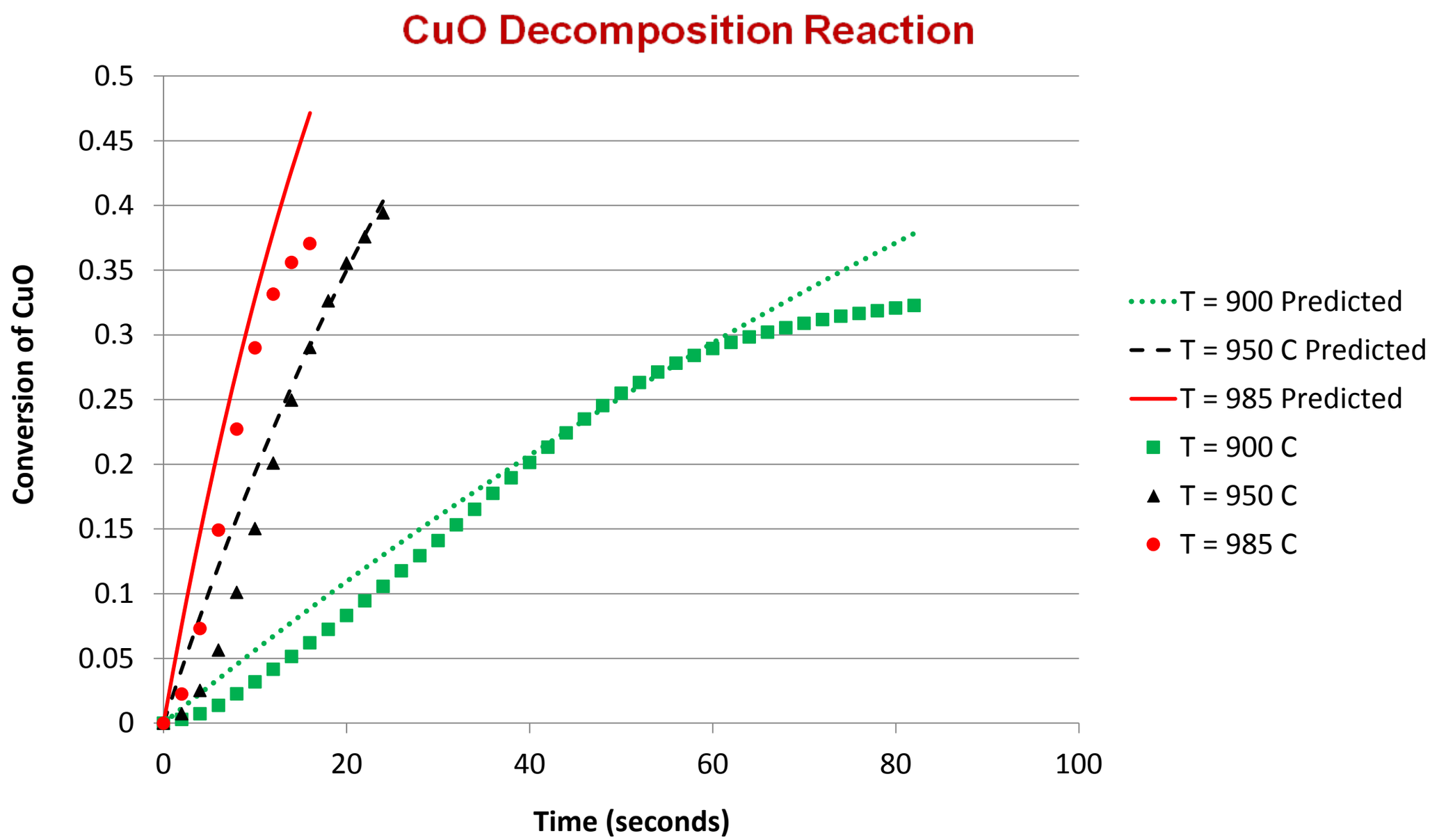




$$\left(p_{O_{2,eq}} - p_{O_2}\right)_{avg} = \frac{\left(p_{O_{2,eq}} - p_{O_{2,in}}\right) + \left(p_{O_{2,eq}} - p_{O_{2,out}}\right)}{2}$$

Analysis of CLOU Combustion of Mexican Petcoke: CuO conversion in "Fuel Reactor" Increase in rate of CuO decomposition with temperature



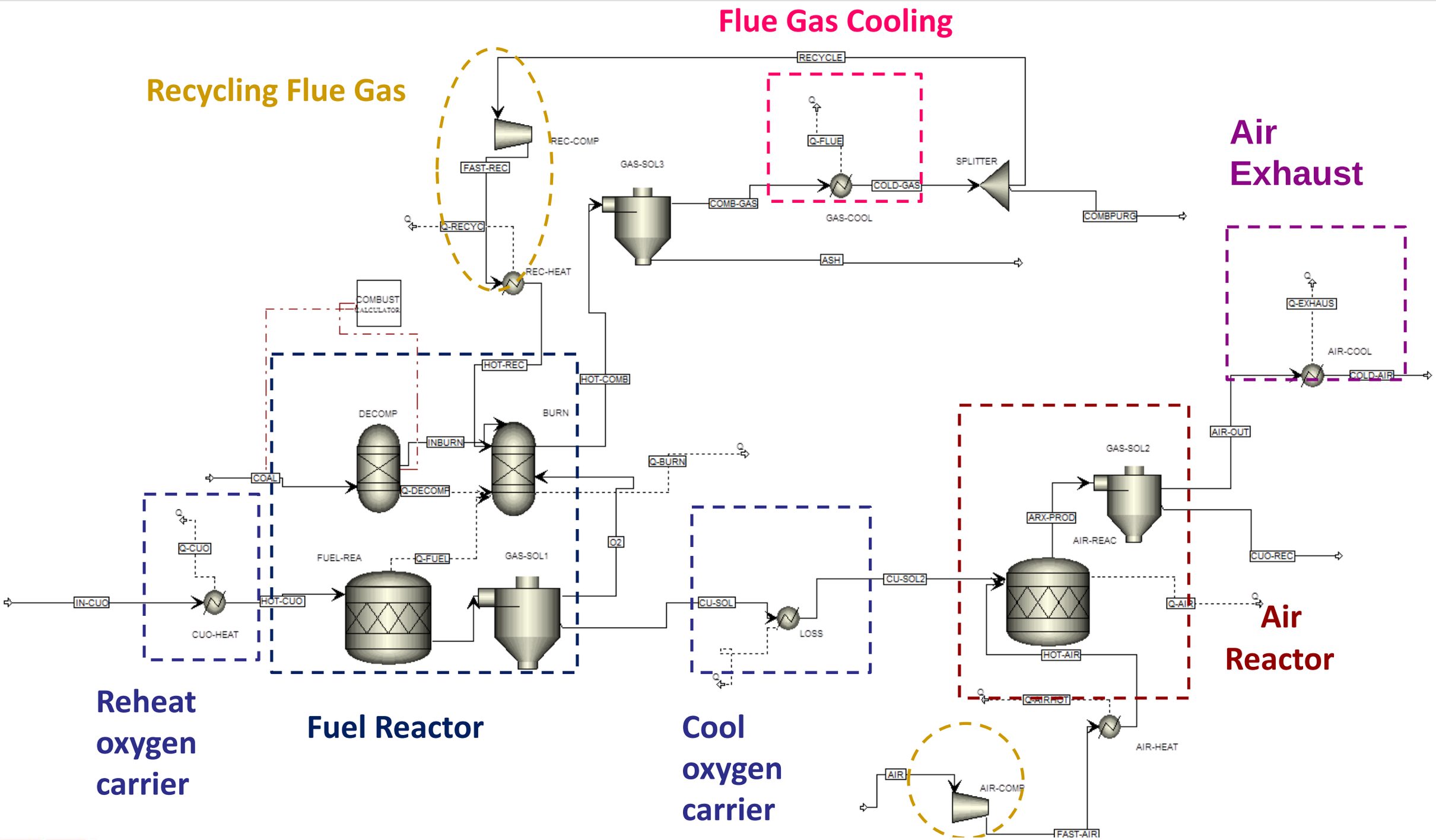


- **The activation energy from the first order rate constant k_{CuO} of the data for CuO/ZrO_2 particles was calculated to be 20 kJ/mol.**

- **The standard enthalpy of reaction at 1200 K (927°C) for the reaction $4CuO(s) \rightarrow 2Cu_2O(s) + O_2(g)$ is 261 kJ/mol.**

- **Value of 281 kJ/mol was close to reported literature data on CuO particles (322 kJ/mol-Chadda et al.; 327 kJ/mol – Eyring et al.)**

ASPEN PLUS Simulation for CLOU



Design Parameters for CLC with 60% Fe_2O_3 on Al_2O_3 oxygen carrier

Air Reactor (One module in ASPEN, RSTOICH):

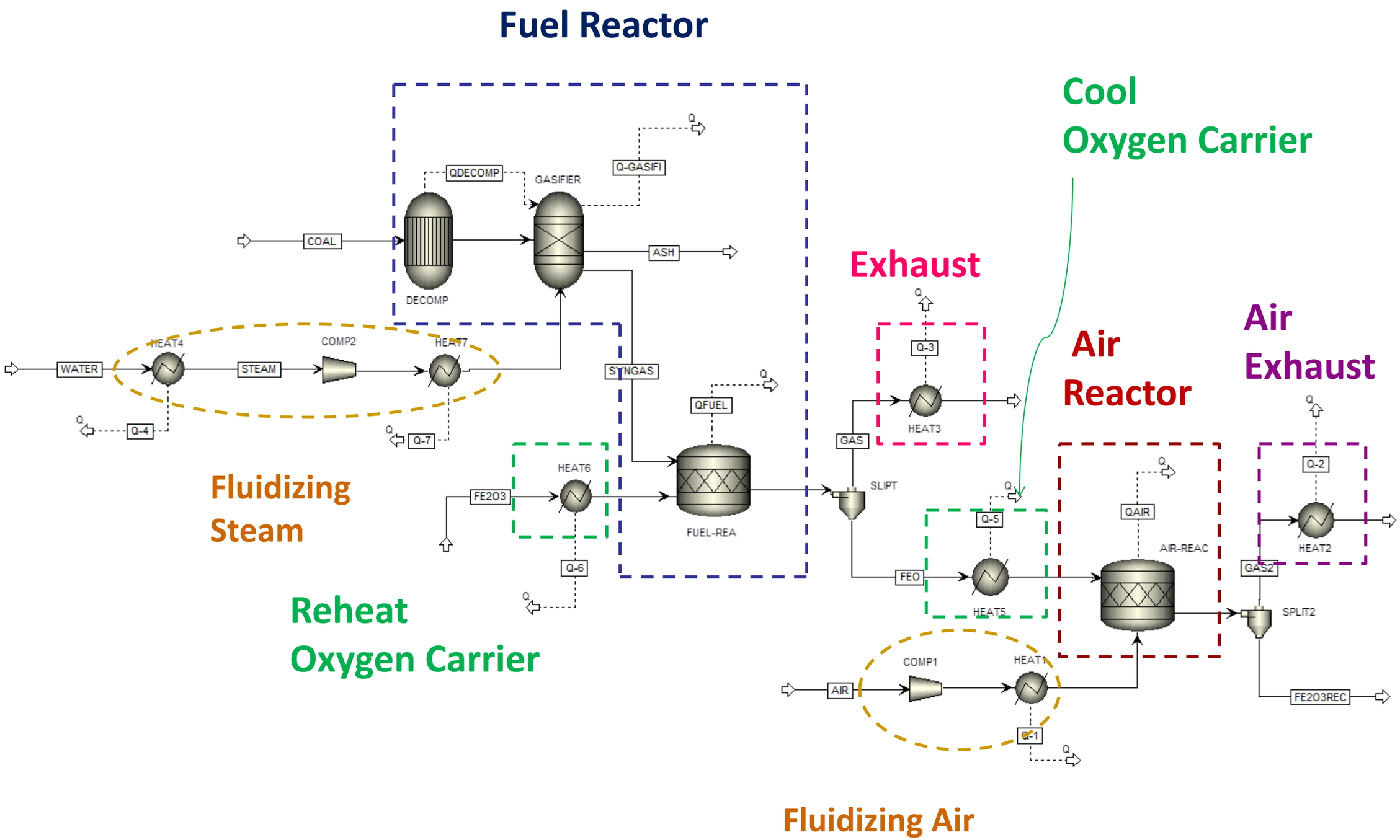
- **4 minute residence time**
  - **Conversion of Fe_3O_4 in air reactor = 80%**
  - **$2Fe_3O_4$ (s)+1/2 O_2(g)→ $3Fe_2O_3$ (s)**
- **For simplicity, formation of $FeAl_2O_4$ has not been considered in the present calculation.**

Design Parameters for CLC with 60% Fe_2O_3 on Al_2O_3 oxygen carrier

Fuel Reactor (Three Modules in ASPEN):

- Coal enters an RYIELD to yield a gas which enters the gasifier. The gasifier is modeled as an equilibrium reactor (RGIBBS) which produces syngas
- Reactions with syngas in RSTOICH
  - Conversion of Fe_2O_3 to Fe_3O_4 is 99%
  - $3Fe_2O_3\,(s) + CO\,(g) \rightarrow 2Fe_3O_4(s) + CO_2\,(g)$
  - $3Fe_2O_3\,(s) + H_2\,(g) \rightarrow 2Fe_3O_4\,(s) + H_2O\,(g)$
- Assumption of 10 min residence time for coal conversion (limiting step)

CLC ASPEN PLUS Simulation



CLC - Energy Recoveries/Utilization from System Components

	CLC, 950°C fuel, 935°C air		CLC, 970°C fuel, 1050°C air	
Fuel reactor	-160 kW_{th}	-202	-161 kW_{th}	51
Energy required/provided by oxygen carrier for fuel reactor	-42 kW_{th}		212 kW_{th}	
Heat steam from 150°C to fuel reactor temperature	-96 kW_{th}		-97 kW_{th}	
Air reactor	663 kW_{th}	516	658 kW_{th}	238
Energy required/provided by OC for air reactor operation	41 kW_{th}		-205 kW_{th}	
Heat air from 25°C to air reactor temperature	-188 kW_{th}		-215 kW_{th}	
Cool air reactor exhaust to 25°C	137 kW_{th}		158 kW_{th}	
Cool flue gas to 150°C	117 kW_{th}		121 kW_{th}	
TOTAL (including 43 kW of compressor/pump work)	429 kW_{th}		428 kW_{th}	

Energy Recoveries/Utilization from System Components

	CLOU, 950°C fuel, 935°C air
Fuel Reactor	109
Energy required/provided by oxygen carrier for fuel reactor	-35 kW
Heat recycled gas from 150°C to fuel rxt temp	-185 kW
Air reactor	394 kW
Energy required/provided by OC for air reactor operation	33 kW
Heat air from 25°C to air rxt temp	-265 kW
Cool air reactor exhaust to 25°C	196 kW
Cool flue gas to 150°C	271 kW
TOTAL (including 5 kW of compressor/pump work)	513 kW

74

Process Conditions Based on an ASPEN PLUS process model for a 100 kg/h coal feed rate(~0.5 MW_{th})

	CLOU	CLC
Fuel reactor temperature	950°C	970°C
Air reactor temperature	935°C	1050°C
Energy contributions from fuel reactor operation and oxygen carrier transfer(heating for CLOU/cooling for CLC) -kW_{th}	74	51
Energy contributions from air reactor operation , oxygen carrier transfer (cooling for CLOU/heating for CLC) and air heating requirements (kW_{th})	162	238
Energy required for heating recycled CO_2 (kW_{th})	(185)	-
Energy required for heating steam (kW_{th})	-	(97)
Energy recovered from cooling exhaust gases from fuel and air reactors (kW_{th})	467	279
Energy required for compression(kW_{th})	(5)	(43)
Total energy (kW_{th})	513	428

Economic Analysis

Capital costs:

Compressor Work, W(in kW)	$W = \frac{n}{(n-1)} \frac{p_{inlet} v_{inlet} \dot{m}_{inlet}}{\eta_{fan}} \left[\left[\frac{p_{inlet} + \Delta p}{p_{inlet}} \right]^{(n-1)/n} - 1 \right]$
Capital Cost of Centrifugal Compressor	580000+(20000*$W^{0.6}$)
Capital Cost of Cyclone	0.05*(Capital Cost of the reactors)
Capital Cost of Reactor in US$ million (2000) per process train	$16.15 \left(\frac{V_R}{180\ m^3} \right)^{0.6}$

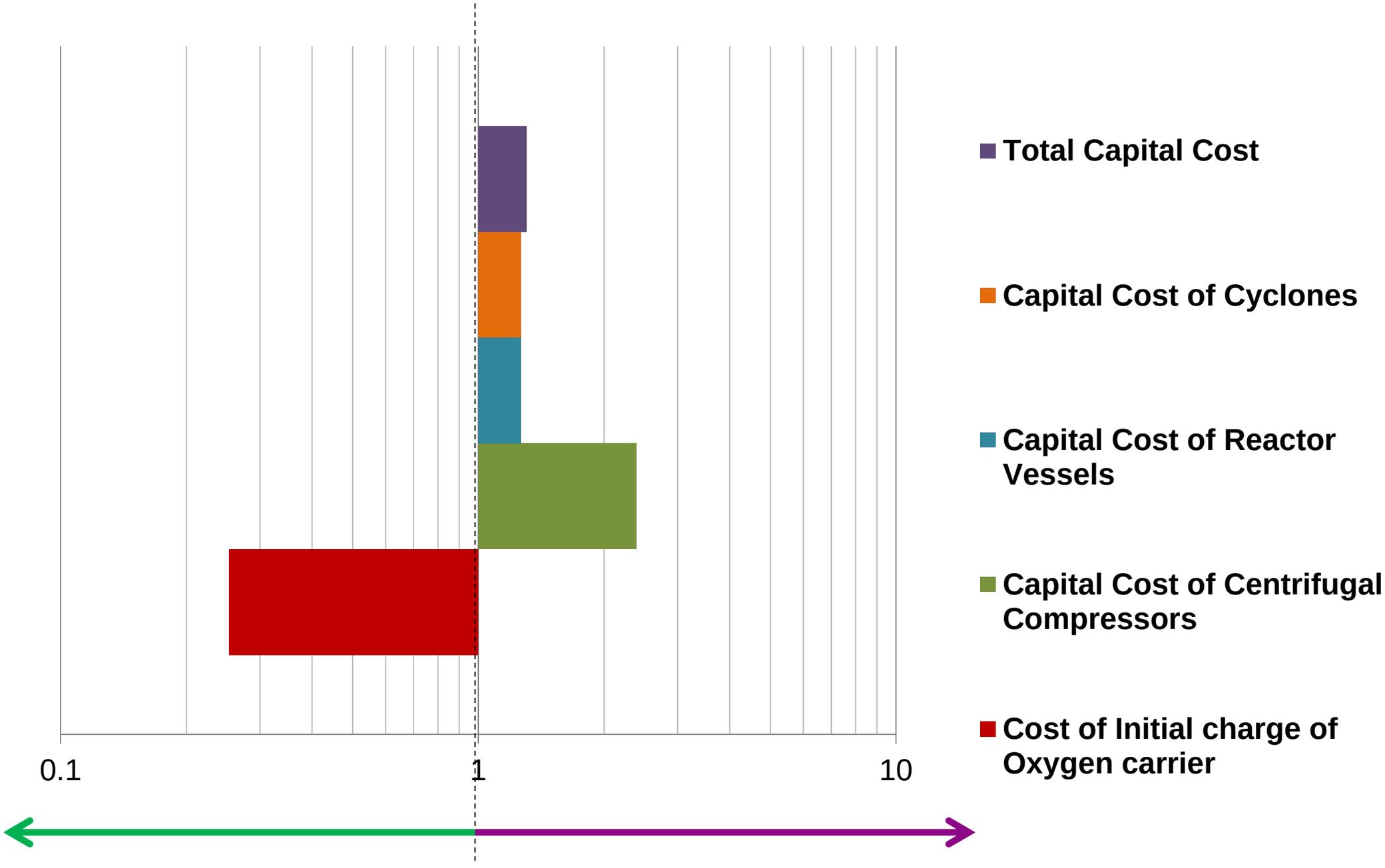
Oxygen carrier and operating costs:

Cost of Cu based oxygen carrier for CLOU	US$6600 per metric ton
Cost of Fe based oxygen carrier for CLC	US$200 per metric ton
Attrition Rate of Carrier	0.05% per hour
Cost of electricity	US$0.06 per kWh

**The cost of compression required for CO_2 sequestration has <u>not</u> been incorporated in this study.

Relative Capital Costs

It was identified that only one air reactor was required for CLOU at the 100 MW_{th} scale, versus 2 for CLC. Two fuel reactors where required for both cases.

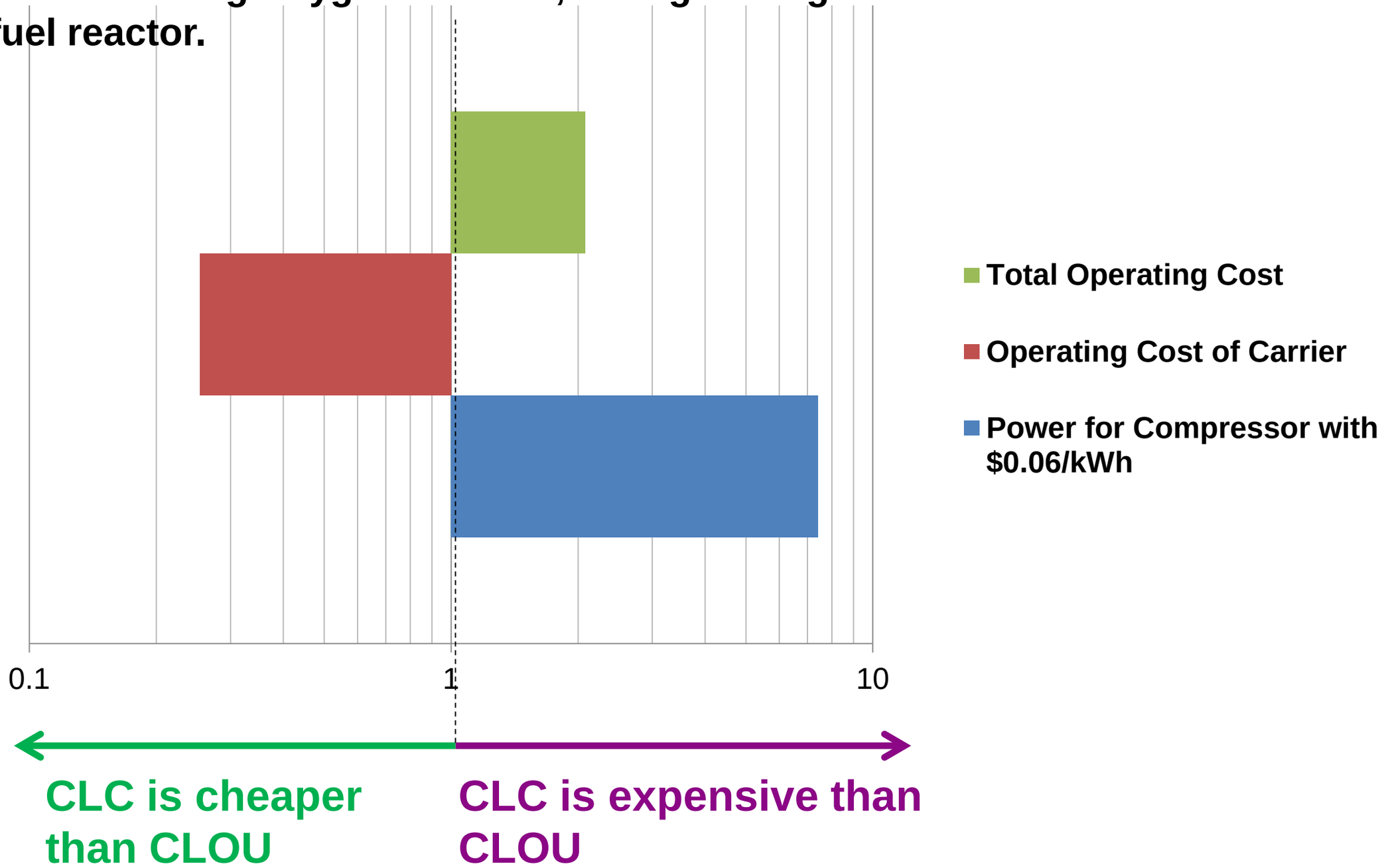


CLC is cheaper than CLOU

CLC is more expensive than CLOU

Relative Operating Costs

Higher operating cost is attributed to the energy requirements associated with fluidizing oxygen carriers, owing to large residence times in the CLC fuel reactor.



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CONCLUSIONS

Conclusions (1)

CLC Kinetics

- **Various supported copper materials were developed and kinetic data were obtained**
  - **The preparation of CuO/SiC materials using the rotary evaporation method showed improved kinetics**
  - **Higher surface area bSiC was made more stable by a coat and bake method of preparation. These materials performed well.**

Laboratory-scale studies

- **Oxidation and decomposition (O_2 release) depend on the so-called "driving force" associated with the difference between the O_2 partial pressure in the reactor environment and the equilibrium O_2 partial pressure.**
- **For oxidation:**
  - **This explains the decrease in oxidation kinetic rate with temperature beyond roughly 850°C.**
  - **There are two regimes, a low temperature regime in which the rate at high conversion slows due to pore blocking and a high temperature regime (>700°C) which is best modeled by considering grain nucleation and growth**
  - **The reaction order in oxygen driving force was concluded to be 1.3**

Conclusions (2)

Laboratory-scale studies (Continued)

- **For decomposition:**
  - **The observed activation energy for CuO reduction was roughly 274 kJ/mol**
  - **Reaction was first order in oxygen driving force**
  - **Small particle were converted more rapidly, due to limited mass transfer limitations**
- **Robust carriers displayed an attrition rate of approximately 0.0008% per hour.**
  - **Materials manufactured by combining ultrafine powers rapidly wore down and experienced significant bed loss over short periods.**

Simulation of fluidized beds

- **Simulations developed captured the BFB behavior and compare well with experimental results**
- **Results using DQMOM models either matched or under-performed the behavior captured by monodisperse models**
  - **DQMOM models were more computationally intensive**
  - **However, these models enabled a distribution of particle sizes**

Conclusions (3)

Process and economic models.

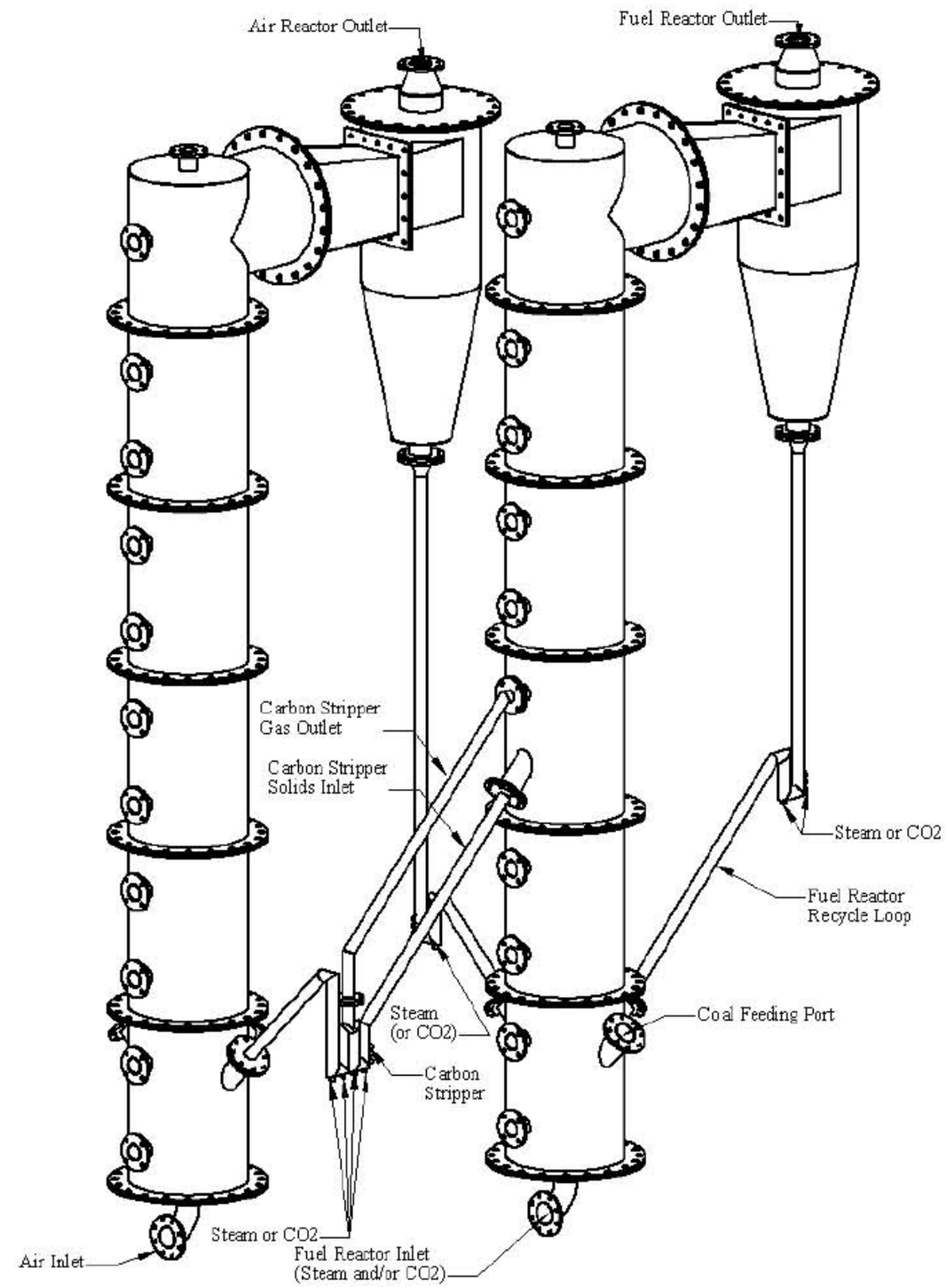
- **The CLOU process has the potential to reduce reactor size and oxygen carrier inventory.**
- **The lifetime of the oxygen carrier is the key factor for developing CLOU technology.**
  - **Although oxygen availability/reactivity is important, carrier strength and stability are at least as important**
- **It is vital to investigate strategies to reduce the residence time in the fuel reactor for the CLC process**
  - **Affects oxygen carrier inventory, cyclone and reactor size, and fluidization costs.**
- **CLOU and CLC differ in energy extraction methodology, which impacts process design**
  - **In CLOU it is possible to extract energy from the air and fuel reactors.**
  - **In CLC the air reactor must be operated at a higher temperature than the fuel reactor.**
- **The effective utilization of steam for gasification and fluidization of oxygen carriers needs future analysis**

▪155 South 1452 East Room 380 ▪Salt Lake City, Utah 84112 ▪1-801-585-1233

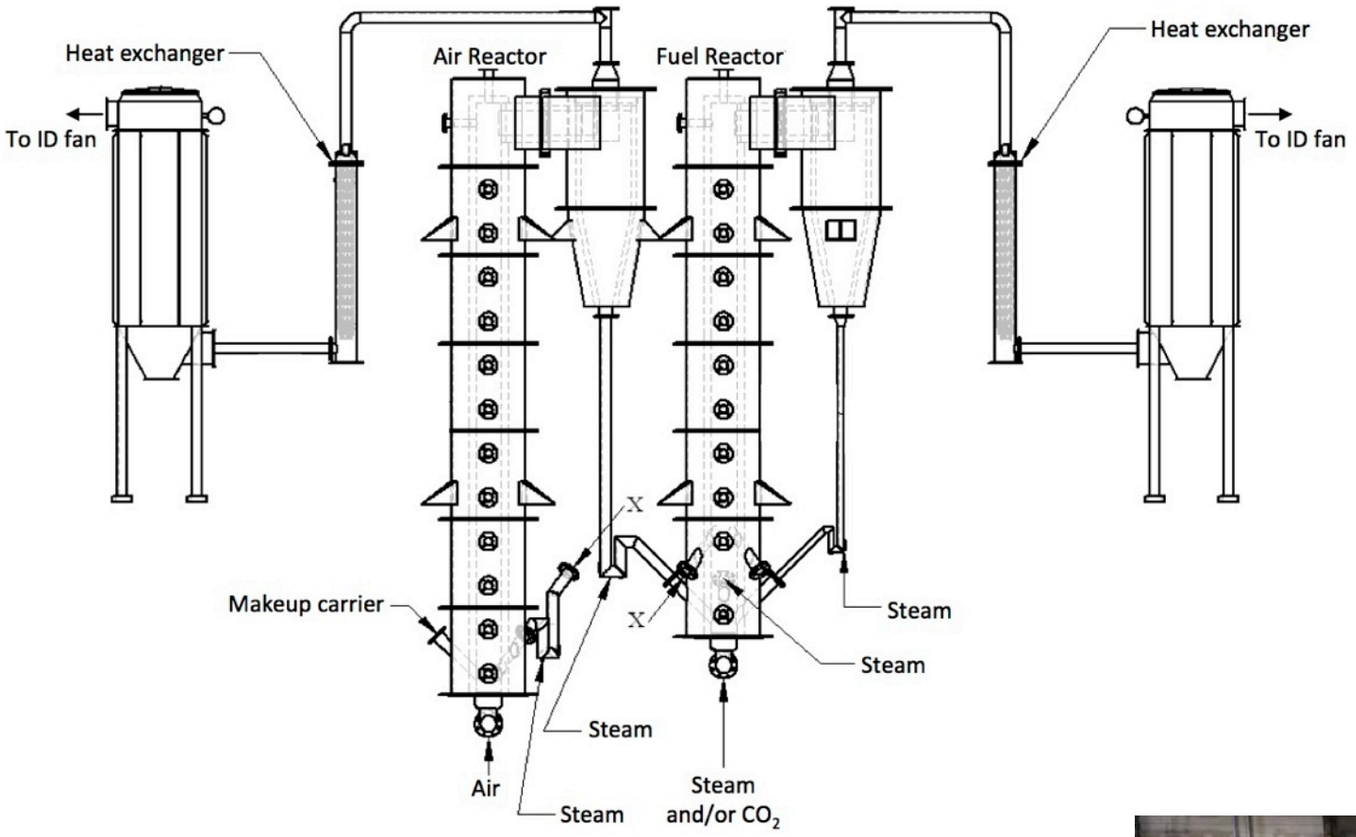
Future Work

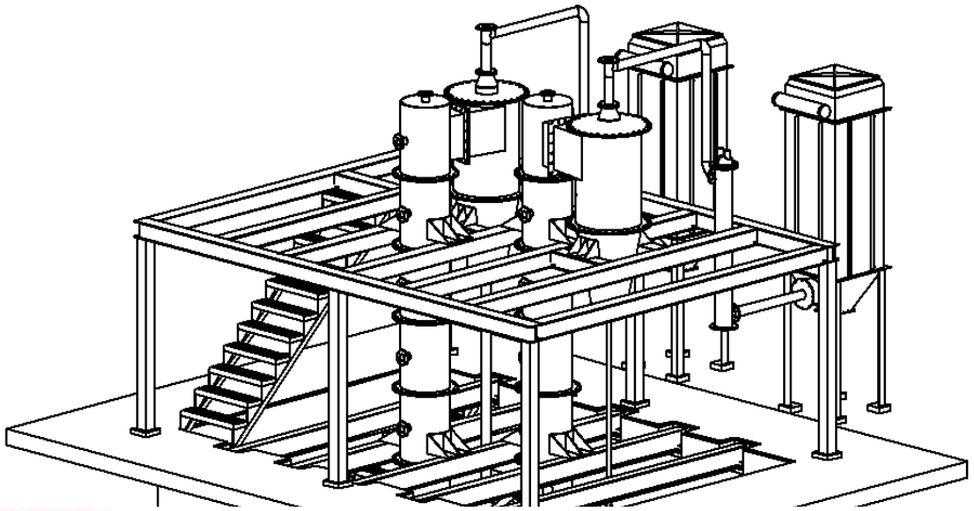
University of Utah
Chemical Looping Research Facility

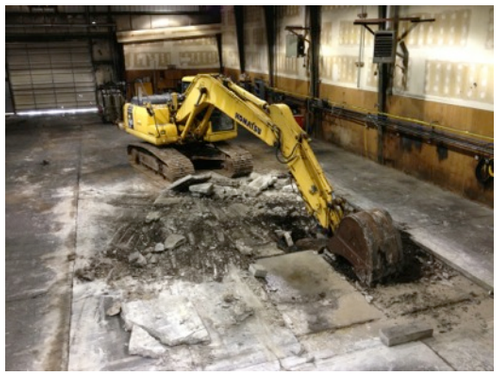
- Similar to proven design for UofU's circulating fluidized bed combustor
- Approx. 20 ft (6 m) tall overall
- Distinct reactors offers flexibility in terms of interconnecting piping, circulation, etc.
- Designed for operation to 220 kW_{th}
- High temperature gas pre-heat for both reactors
- Designed for CLOU with solid fuels, but can operate as conventional CLC or as twin-bed gasifier

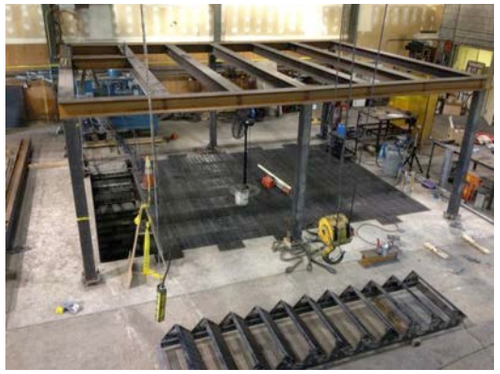


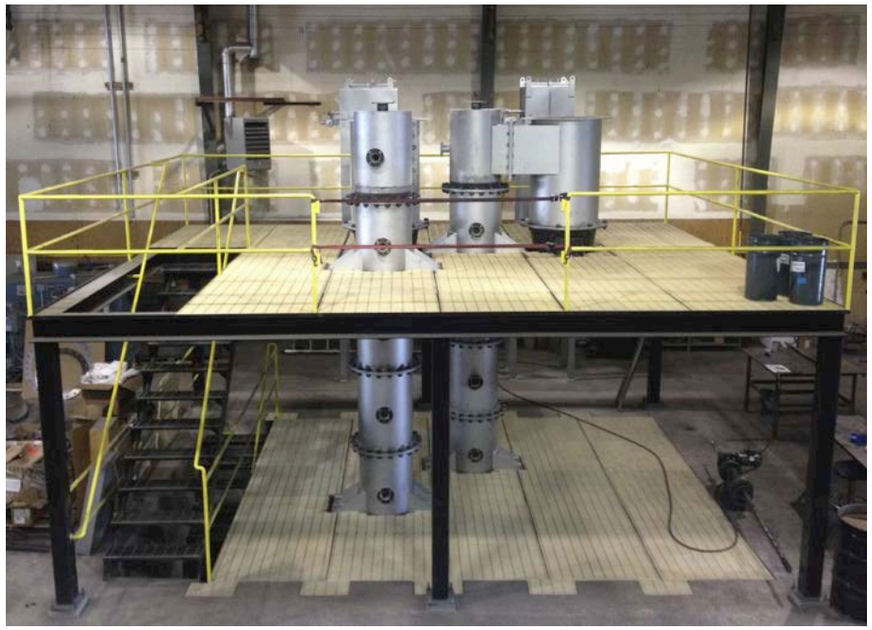
Chemical Looping Research Facility Design and Construction



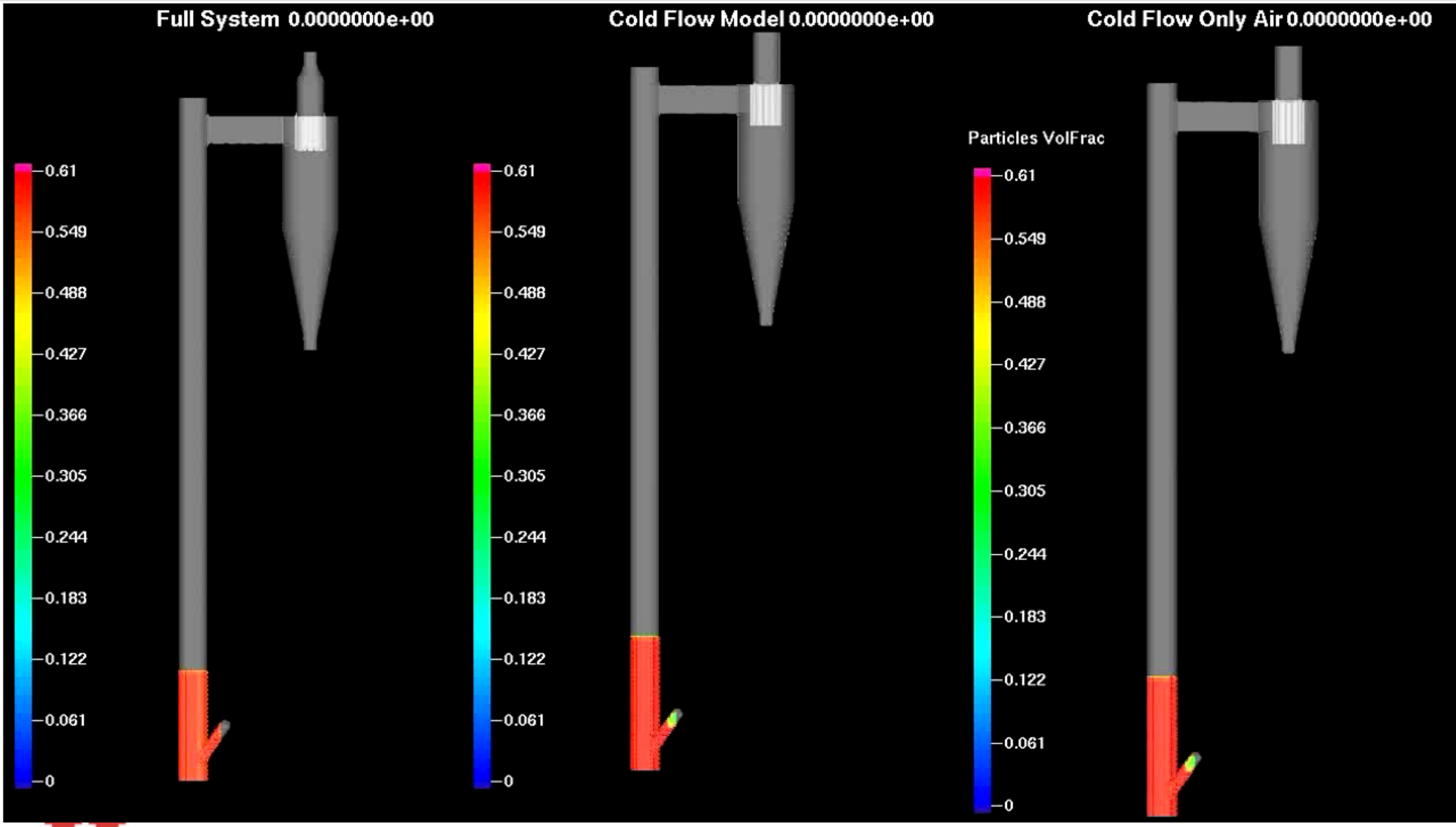








Barracuda Simulation: Air Reactor PDU & Cold Flow Unit



Peer Reviewed Publications

- Clayton, C.K., Sohn, H.Y., Whitty, K.J., "Oxidation Kinetics of Cu_2O in Oxygen Carriers for Chemical Looping with Oxygen Uncoupling," *Industrial & Engineering Chemistry Research,* 2014, in press.
- Clayton, C.K.; Whitty, K.J. Measurement and Modeling of Decomposition Kinetics for Copper-Based Chemical Looping with Oxygen Uncoupling, *Applied Energy*, 2013, in press.
- Clayton, C.K.; Eyring, E.M.; Konya, G.; Lewis, R.J.; Peterson, S.B.; Whitty, K.J.; Wilde, B.R. Characteristics and CLOU Performance of a Novel SiO_2-Supported Oxygen Carrier Prepared from CuO and β-SiC, *Energy & Fuels*, submitted for publication.
- E. M. Eyring, G. Konya, J. S. Lighty, A. H. Sahir, A. F. Sarofim, Kevin Whitty, "Chemical Looping with Copper Oxide as Carrier and Coal as Fuel," *Oil and Gas Science Technology*, Vol. 66, No. 2, 209-221, (2011). http://dx.doi.org/10.2516/ogst/2010028
- Peterson, S.B.; Konya, G.; Clayton, C.K.; Lewis, R.J.; Eyring, Wilde, B.R.; Eyring, E.M.; Whitty, K.J. Characteristics and CLOU Performance of a Novel SiO_2-Supported Oxygen Carrier Prepared from CuO and β-SiC, *Energy & Fuels,* 2013, 27,10, pp. 6040-6047.
- Sahir, A.H.; Dansie, J.K.; Cadore, A.L.; Lighty, J.S. A Comparative Process Study of Chemical-Looping Combustion (CLC) and Chemical-Looping with Oxygen Uncoupling (CLOU) for Solid Fuels, *International Journal of Greenhouse Gas Control*, 2014, 22, pp. 237-243.
- Sahir, A.; Sohn, H.Y.; Leion, H.; Lighty, J.S.; Lighty, J.S. Rate Analysis of Chemical-Looping with Oxygen Uncoupling (CLOU) for Solid Fuels, *Energy & Fuels,* 2012, 26, pp. 4395-4404.
- Sahir, A.; Lighty, J.S.; Sohn, H.Y. Kinetics of Copper Oxidation in the Air Reactor of a Chemical Looping Combustion System using the Law of Additive Reaction Times, *Industrial & Eng Chem Research*, 2011, 50 (23), pp. 13330–13339.