Chemical Looping with Oxygen Uncoupling with Coal

University of Utah
Departments of Chemical Engineering and Chemistry
Institute for Clean and Secure Energy

Project Team PIs:
JoAnn Lighty, Kevin Whitty, Philip Smith, Ted Eyring

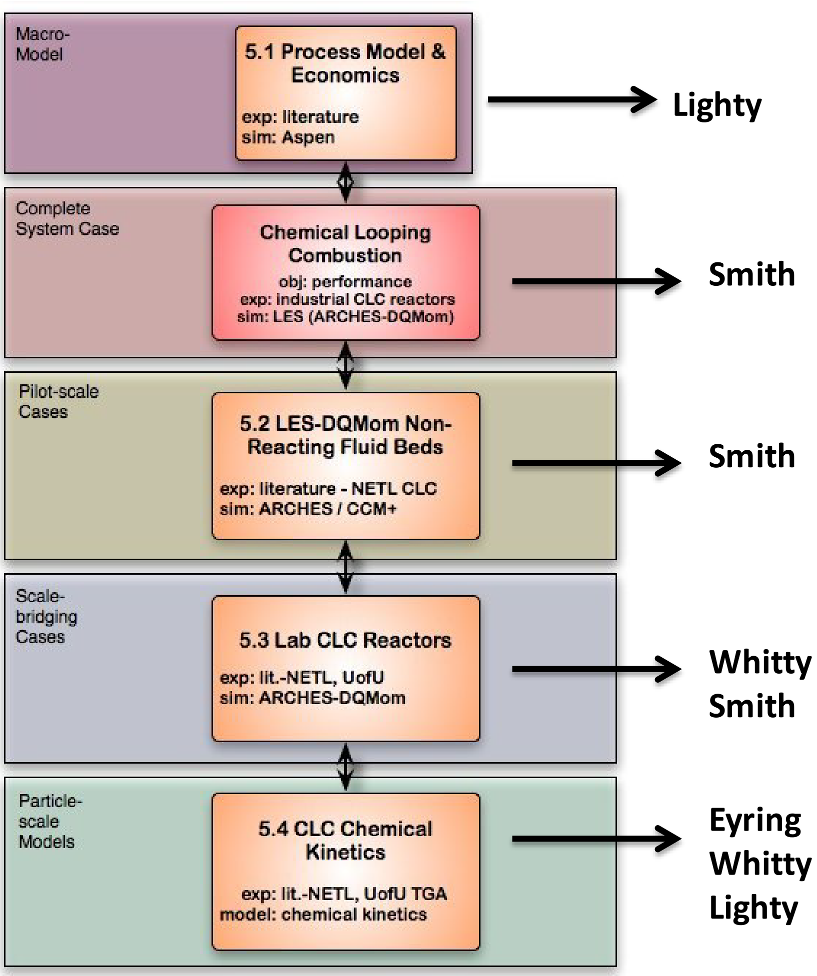
Funding & Participants

- Funding Period
  - 10/2009 to 8/2013
- Participants
  - Edward Eyring, Gabor Konya, Robert Lewis, Sean Peterson
  - 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 373,452
    - Cost Share 93,363
  - Kevin Whitty
    - DOE 227,528
    - Cost Share 56,882
  - JoAnn Lighty
    - DOE 254,378
    - Cost Share 63,594
  - Philip Smith
    - DOE 268,174
    - Cost Share 67,044

Overall Project Objectives

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



Macro-Model

5.1 Process Model & Economics
exp: literature
sim: Aspen

→ Lighty

Complete System Case

Chemical Looping Combustion
obj: performance
exp: industrial CLC reactors
sim: LES (ARCHES-DQMom)

→ Smith

Pilot-scale Cases

5.2 LES-DQMom Non-Reacting Fluid Beds
exp: literature - NETL CLC
sim: ARCHES / CCM+

→ Smith

Scale-bridging Cases

5.3 Lab CLC Reactors
exp: lit.-NETL, UofU
sim: ARCHES-DQMom

→ Whitty
Smith

Particle-scale Models

5.4 CLC Chemical Kinetics
exp: lit.-NETL, UofU TGA
model: chemical kinetics

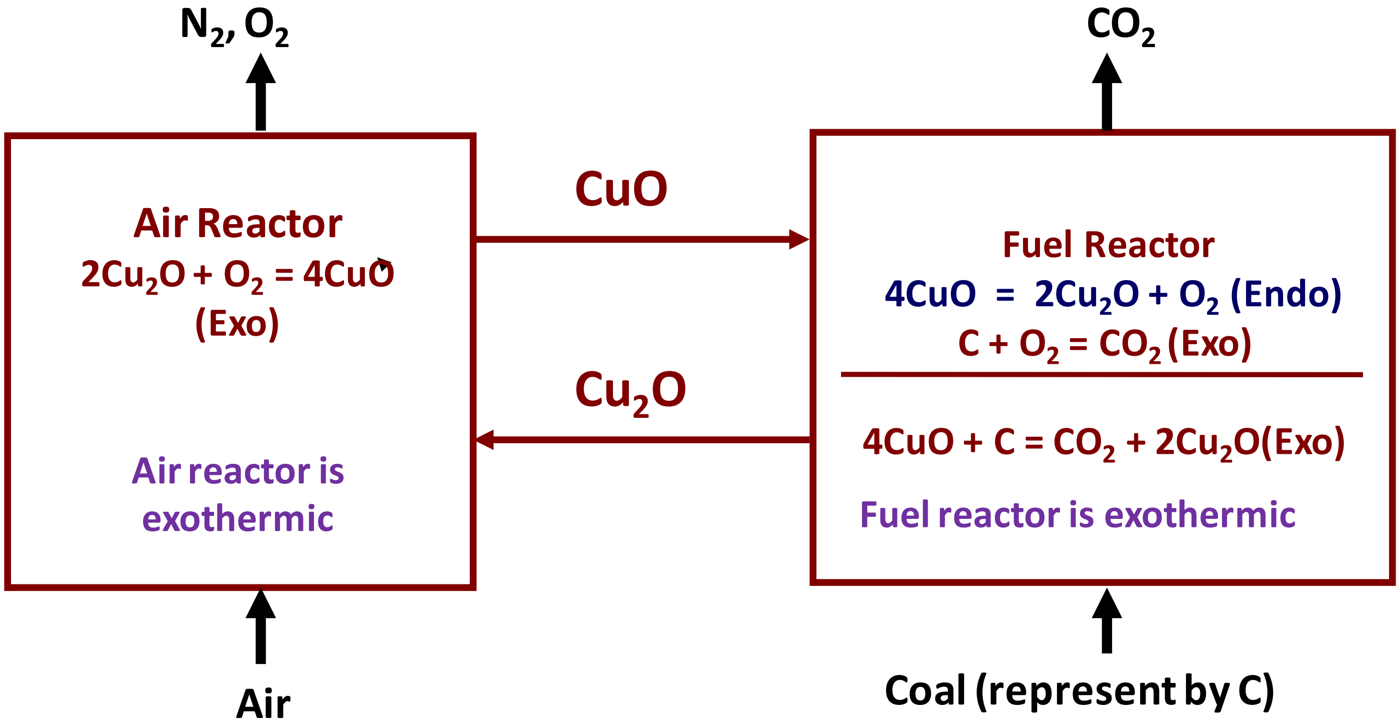
→ Eyring
Whitty
Lighty

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

Chemical Looping Combustion with Oxygen Uncoupling (CLOU)

Key Difference : The oxygen carrier dissociates at high temperature to yield oxygen for combustion reactions



Air Reactor

$2Cu_2O + O_2 = 4CuO$

(Exo)

Air reactor is exothermic

Fuel Reactor

$4CuO = 2Cu_2O + O_2$ (Endo)

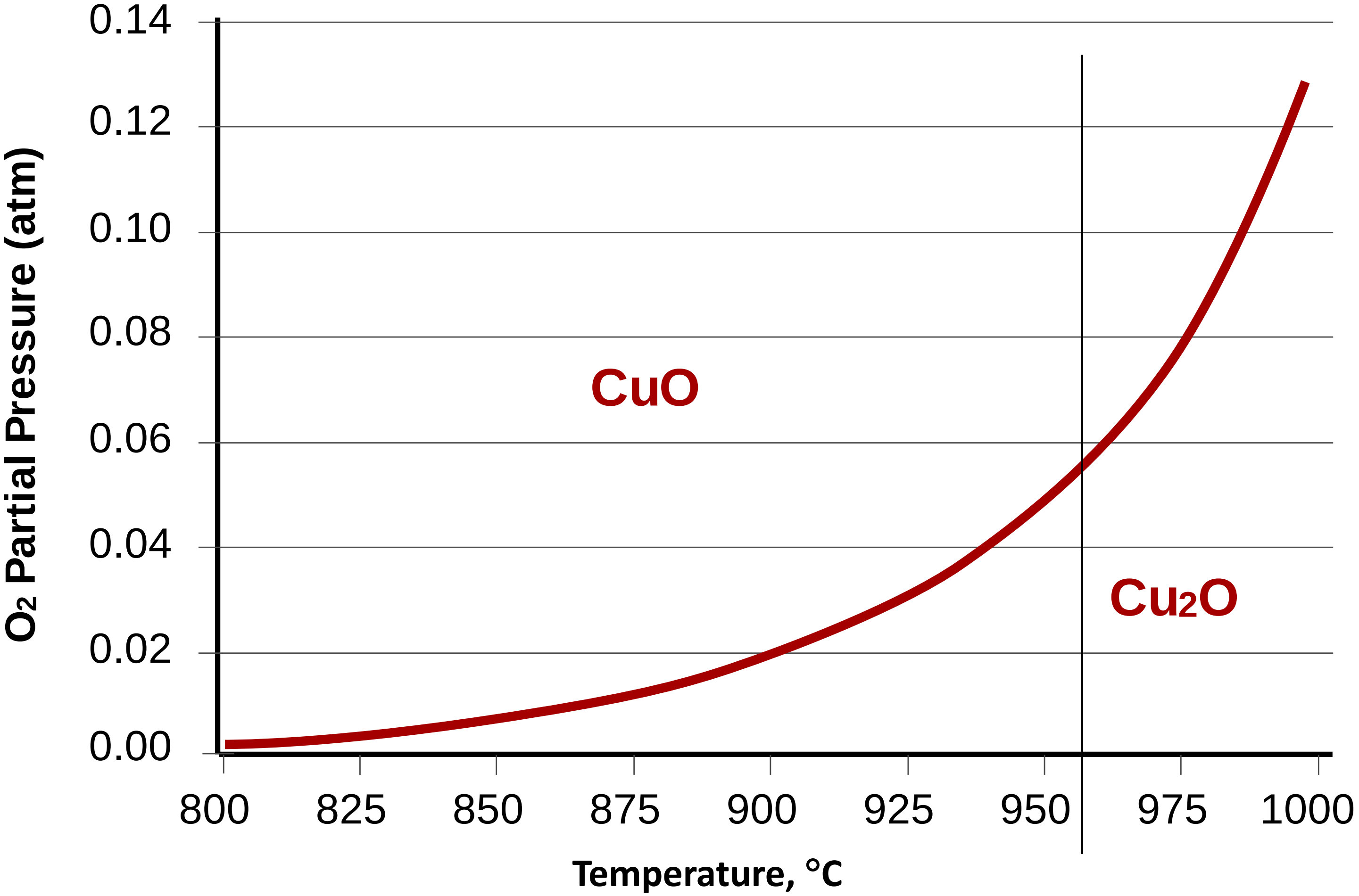
$C + O_2 = CO_2$ (Exo)

$4CuO + C = CO_2 + 2Cu_2O$(Exo)

Fuel reactor is exothermic

Equilibrium of the Reaction

$Cu_2O + \frac{1}{2} O_2 \longleftrightarrow 2\,CuO$



No need for an ASU; saves energy and reduced costs

Challenges

- Oxygen Carrier: amount, availability, cost, operation (sintering, attrition)
- Energy utilization: exothermic reaction in fuel reactor
- Unit design: ash/OC separation, char carry-over, size

Project Schedule and Milestones

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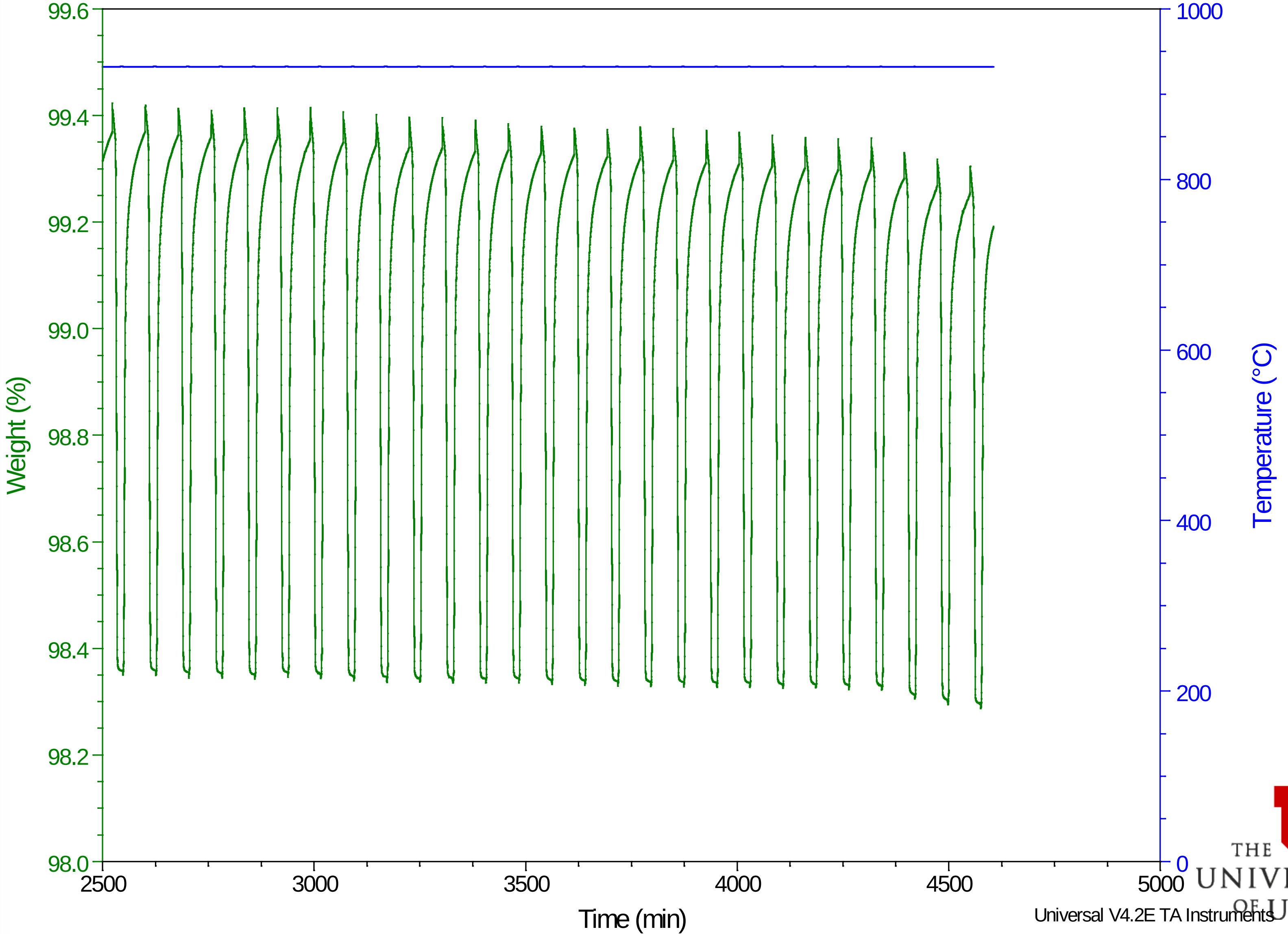
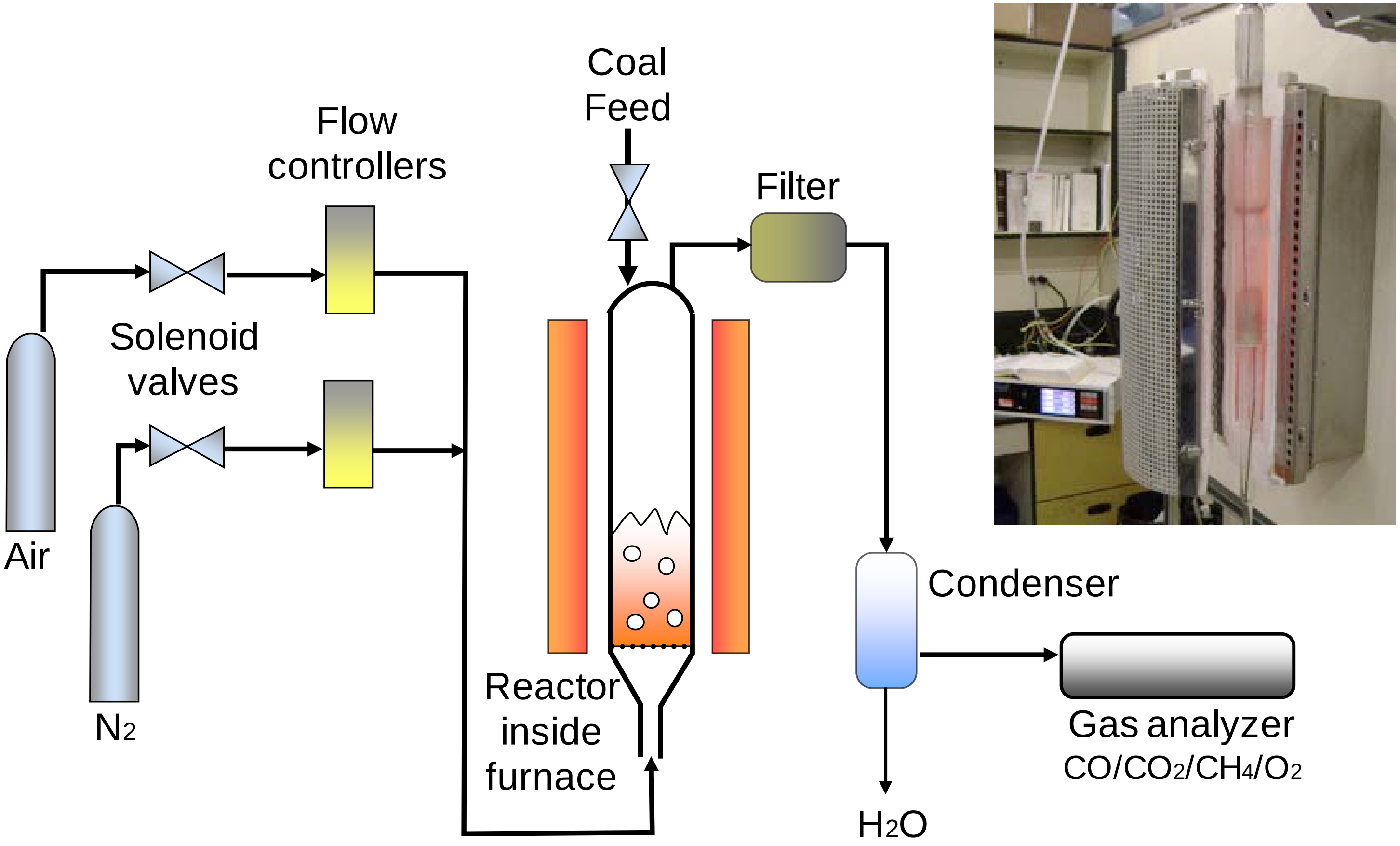
Carrier Development and Characterization

TGA & FBC Studies

TGA : β-SiC with 20%CuO



Lab-scale FBC



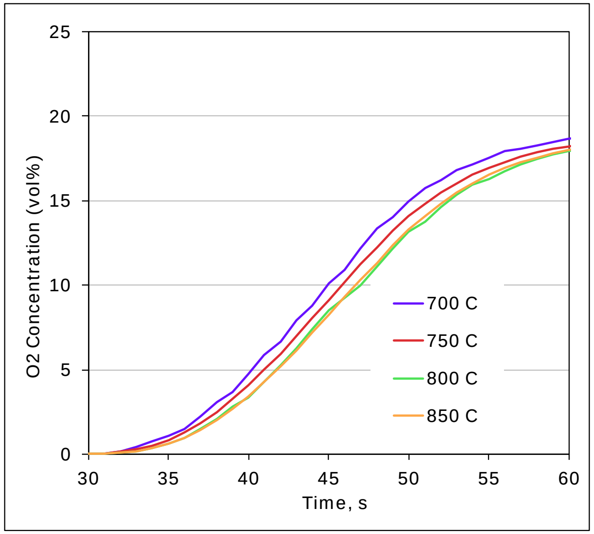
5 cm diameter quartz reactor

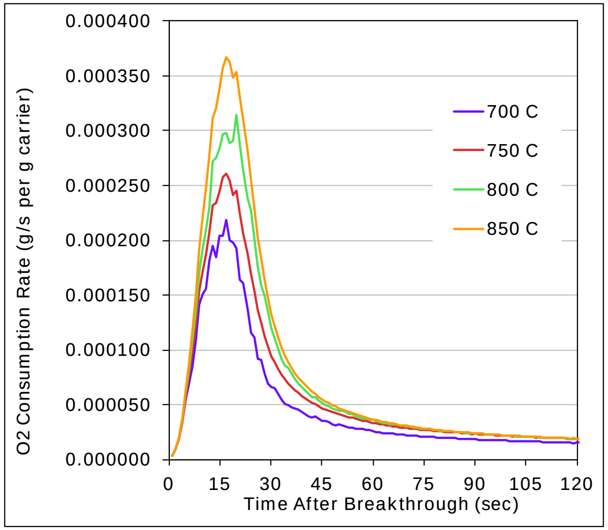
Max T = 1200 C

Automated gas supply switching

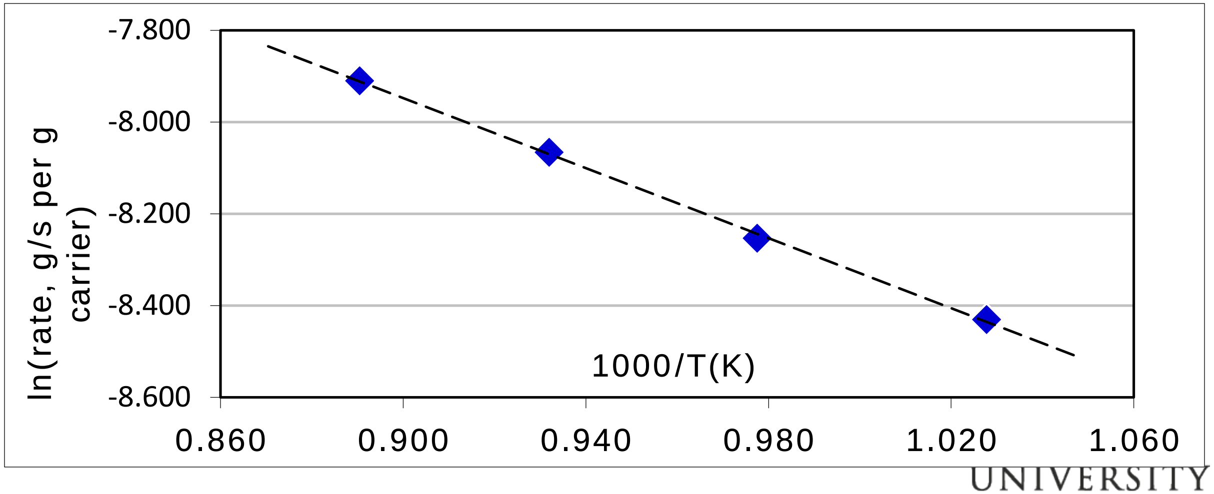
Online analyzer with data logging

Oxidation - Ilmenite

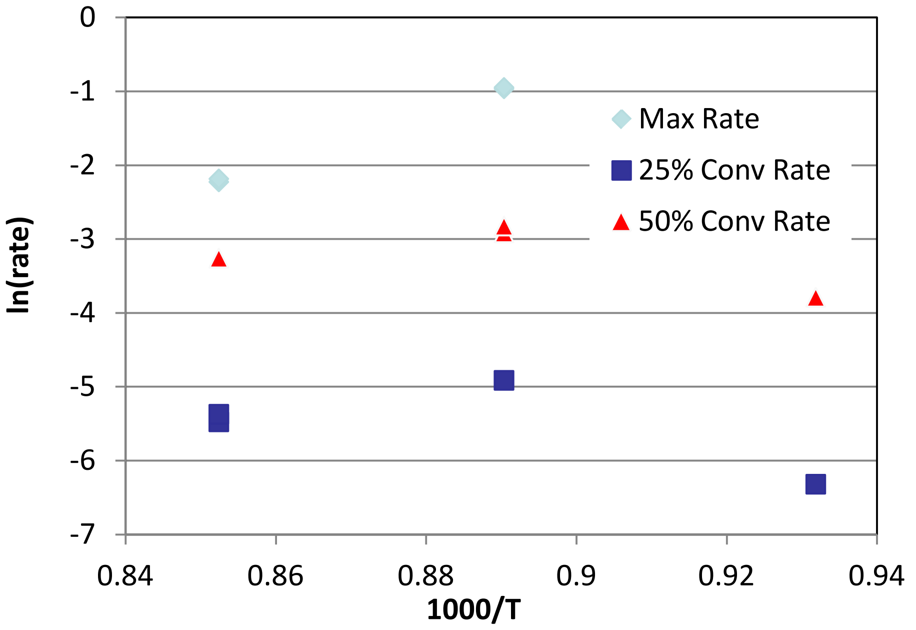




Ea = 32 kJ/mole



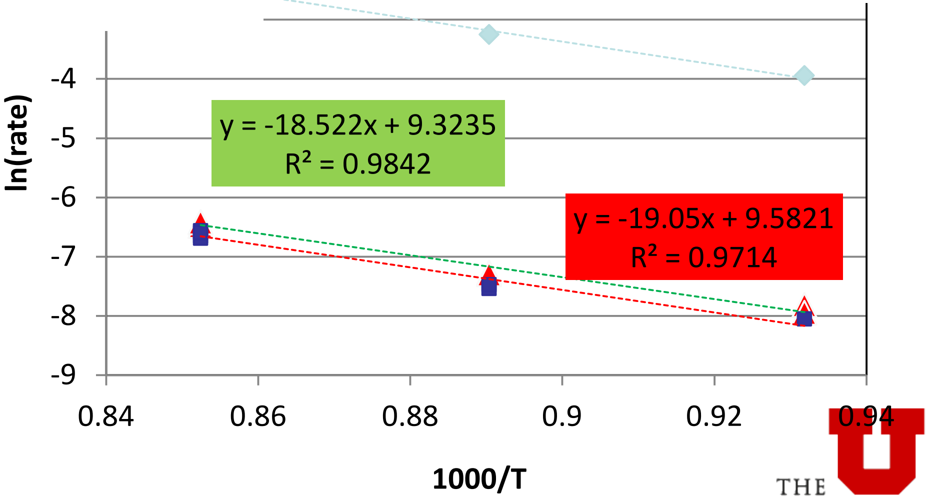
50 wt% CuO on zirconia



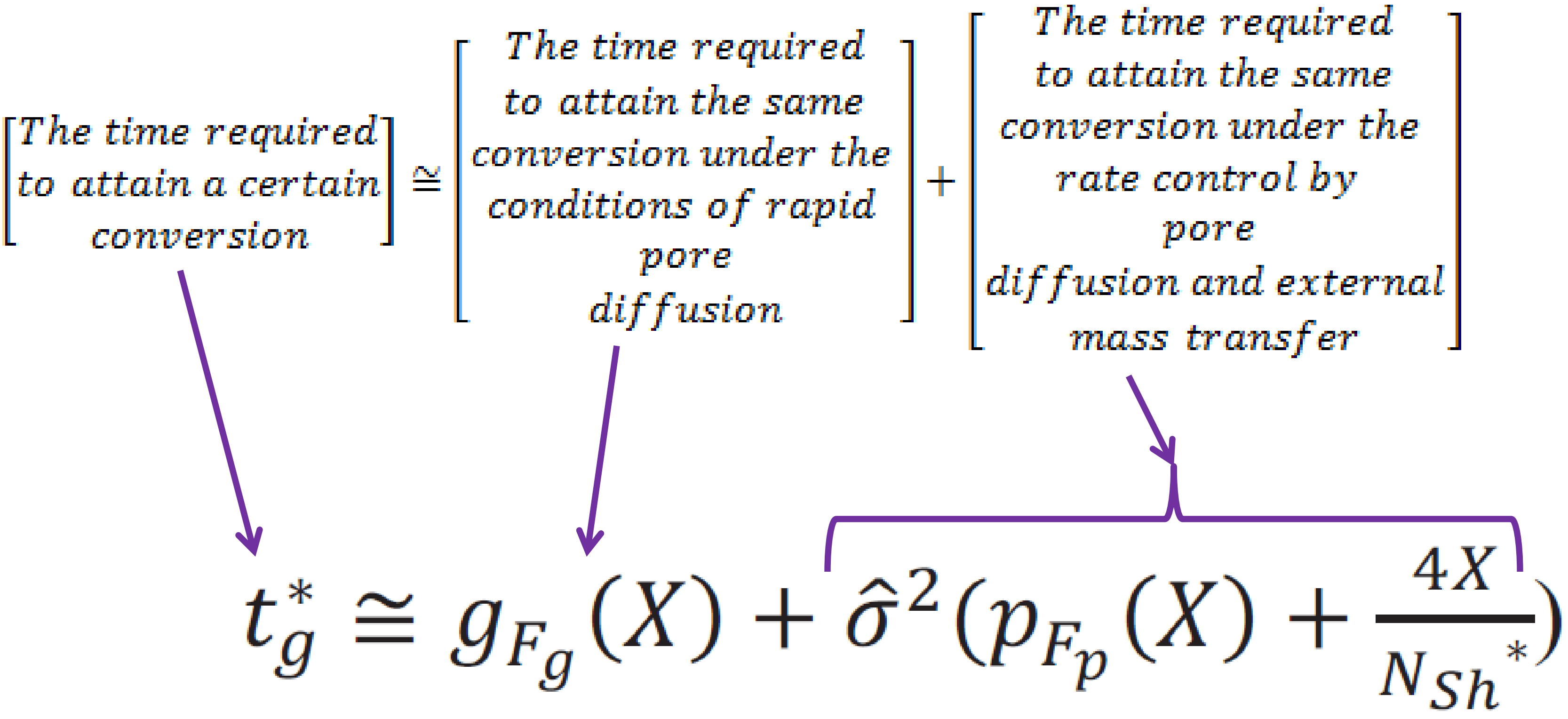
Oxidation

Reduction

Ea = 158 kJ/mole



"The Law of Additive Reaction Times is a closed-form equation for the relationship between the conversion of solid reactant and time. The law is applicable for isothermal reactions in which the effective diffusivity of the solid remains constant during the reaction."



$$\left[\begin{array}{c}\text{The time required}\\ \text{to attain a certain}\\ \text{conversion}\end{array}\right] \cong \left[\begin{array}{c}\text{The time required}\\ \text{to attain the same}\\ \text{conversion under the}\\ \text{conditions of rapid}\\ \text{pore}\\ \text{diffusion}\end{array}\right] + \left[\begin{array}{c}\text{The time required}\\ \text{to attain the same}\\ \text{conversion under the}\\ \text{rate control by}\\ \text{pore}\\ \text{diffusion and external}\\ \text{mass transfer}\end{array}\right]$$

$$t_g^* \cong g_{F_g}(X) + \overbrace{\hat{\sigma}^2\left(p_{F_p}(X) + \frac{4X}{{N_{Sh}}^*}\right)}$$

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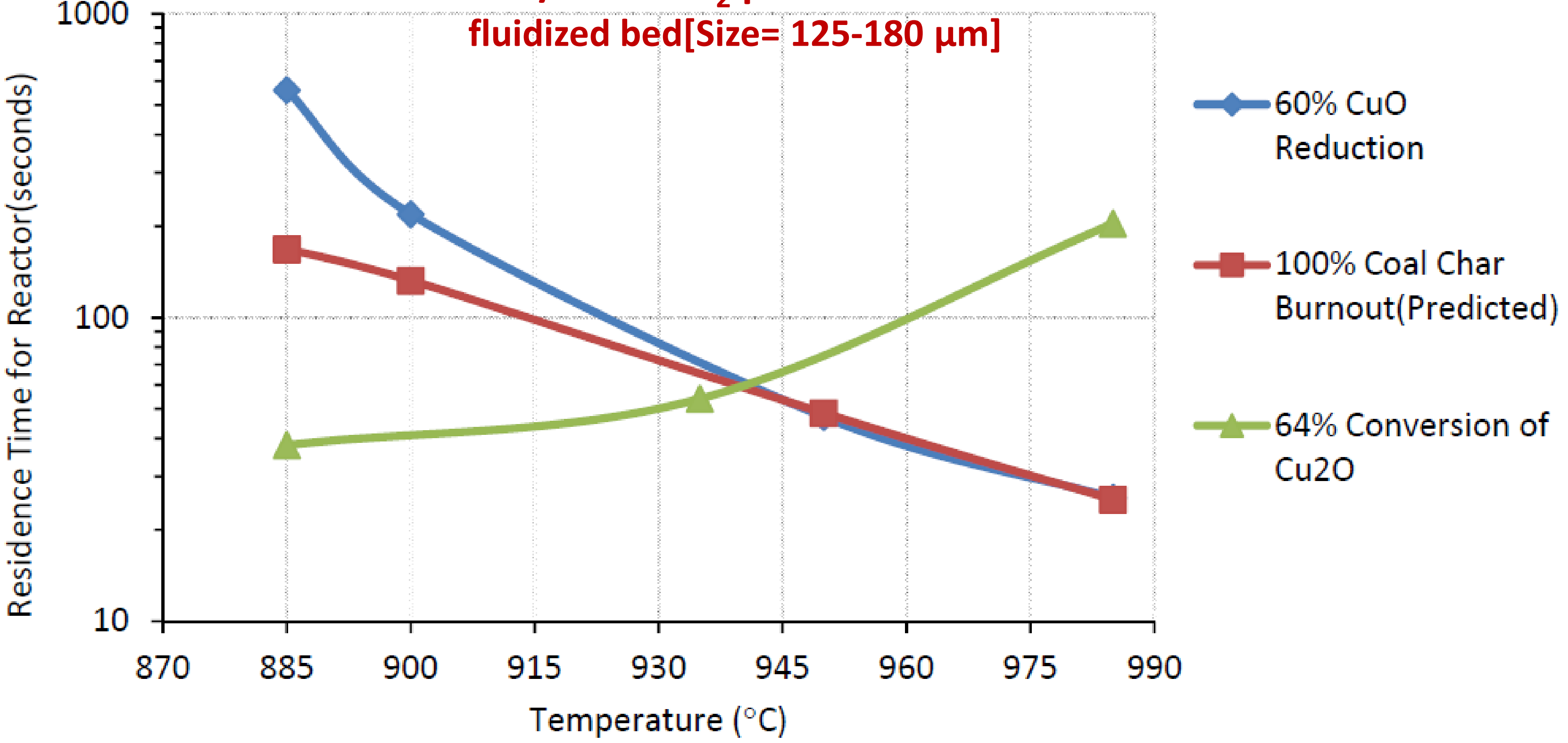
Process Modeling

Kinetics

Residence time vs. temperature; range of 885-985 C

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

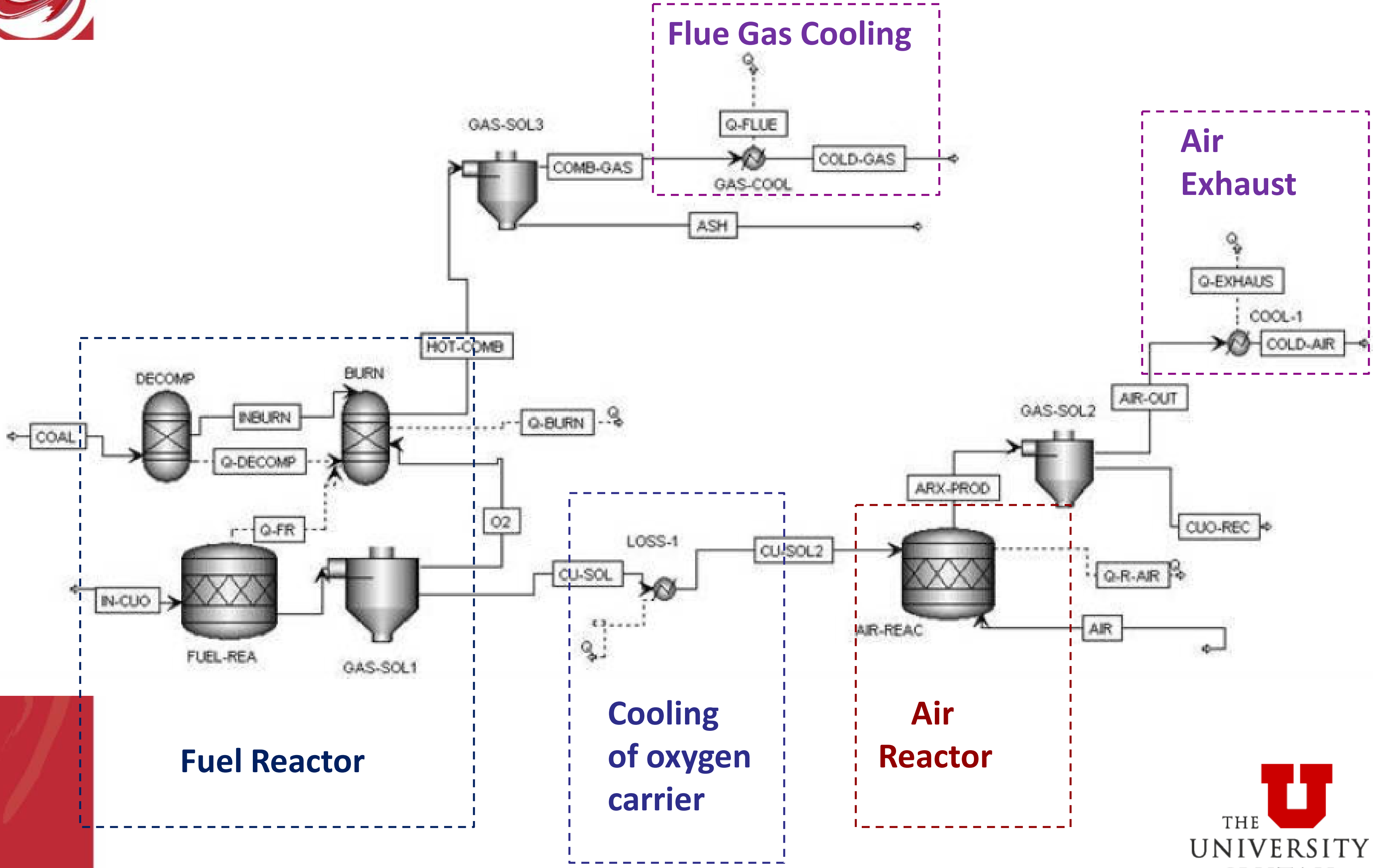
40% CuO /60% ZrO_2 particles in the batch fluidized bed[Size= 125-180 µm]



Fuel Reactor : CuO reduction and coal char oxidation (higher T, lower residence time)

Air Reactor : Cu_2O oxidation (higher T, higher residence time)

ASPEN PLUS Simulation



Flue Gas Cooling

Air Exhaust

Fuel Reactor

Cooling of oxygen carrier

Air Reactor

ASPEN Simulation Blocks

Process Unit in CLOU	ASPEN Simulation Block(s)
Fuel Reactor	RYIELD and RGIBBS combust the coal. Oxygen is provided by the decomposition of CuO to Cu_2O, modeled by a RSTOIC block with a specified conversion
Air Reactor	RSTOIC with a specified conversion of Cu_2O to CuO
Treatment of Coal/Carbonaceous Feedstock	An EXCEL Spreadsheet interface is used to allow for various C,H,N,O,S properties of carbonaceous feedstock and appropriately evaluate oxygen requirements and thus oxygen carrier circulation.

ASPEN PLUS Simulation Parameters

Ultimate Analysis for fuels used for comparison

Coal	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)	Heating Value (MJ/kg)
Mexican Petcoke	88.8	3.1	0.5	1.0	6.6	30.9(as recd.)
North Antelope PRB	75.3	5.0	18.3	1.1	0.3	27.7(dry basis)

*Note: Aspen simulation done with PRB ultimate analysis

Major ASPEN PLUS Simulation Parameters

Coal Feed Rate	100 kg/h
Air Flow Rate	794 kg/h
Temperature Range of Fuel Reactor investigated in simulation	885°C - 985°C
Temperature Range of Air Reactor investigated in simulation	885°C - 985°C
Amount of Cu circulating in the system*, 15% excess O_2	3262 kg/h
Amount of ZrO_2 circulating in the system	4579 kg/h

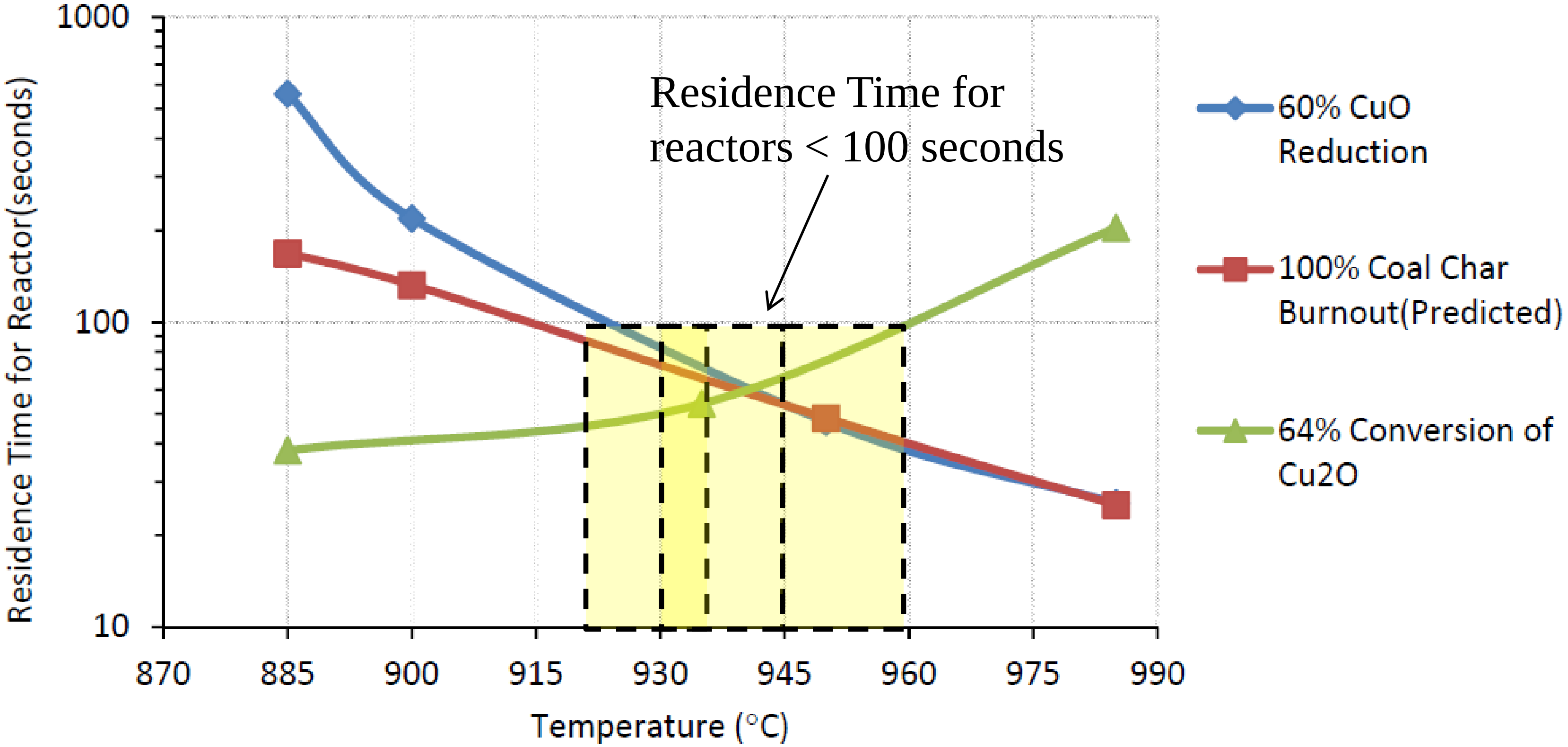
*Note: represents 40% CuO on ZrO_2

Energy Analysis from Sources

Fuel Reactor Temp. (°C)	Air Reactor Temp. (°C)	ΔT between Fuel and Air Reactor	Heat Duty for Air Reactor (kW)	Heat Duty for Fuel Reactor (kW)	Energy Associated with Flue Gas(kW)	Energy Associated with Loss(kW)	Energy Associated with exhaust from air reactor (kW)	Total (kW)
885	885	0	189	110	76	0	139	514
985	985	0	159	109	89	0	160	517
950	935	15	174	86	84	-22	150	472
935	885	50	189	32	82	-73	139	369
985	935	50	174	30	89	-73	150	370
950	885	65	189	8	84	-95	139	325
985	885	100	189	-47	88	-146	139	223

Kinetics

Residence time vs. temperature; range of 885-985 C



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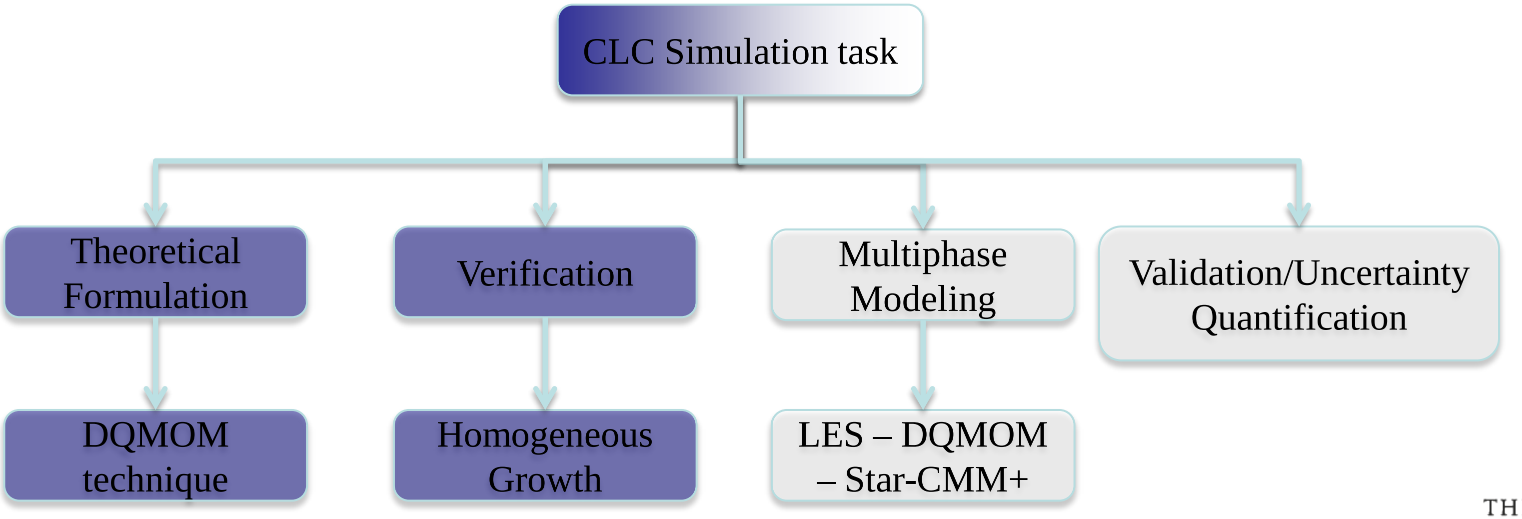
Simulation

CLC Simulation Task Overview

Fluidized Beds

Fixed/Moving Beds

Implementing Direct Quadrature Method of Moments (DQMOM) technique in a commercial software (Star-CCM+). DQMOM provides a robust and accurate description of multiphase flows. Coupling this technique with available Large Eddy Simulation (LES) CFD models in Star-CCM+ allows us to produce a better description of both the fluid and dispersed phases.



CLC Simulation task

Theoretical Formulation

Verification

Multiphase Modeling

Validation/Uncertainty Quantification

DQMOM technique

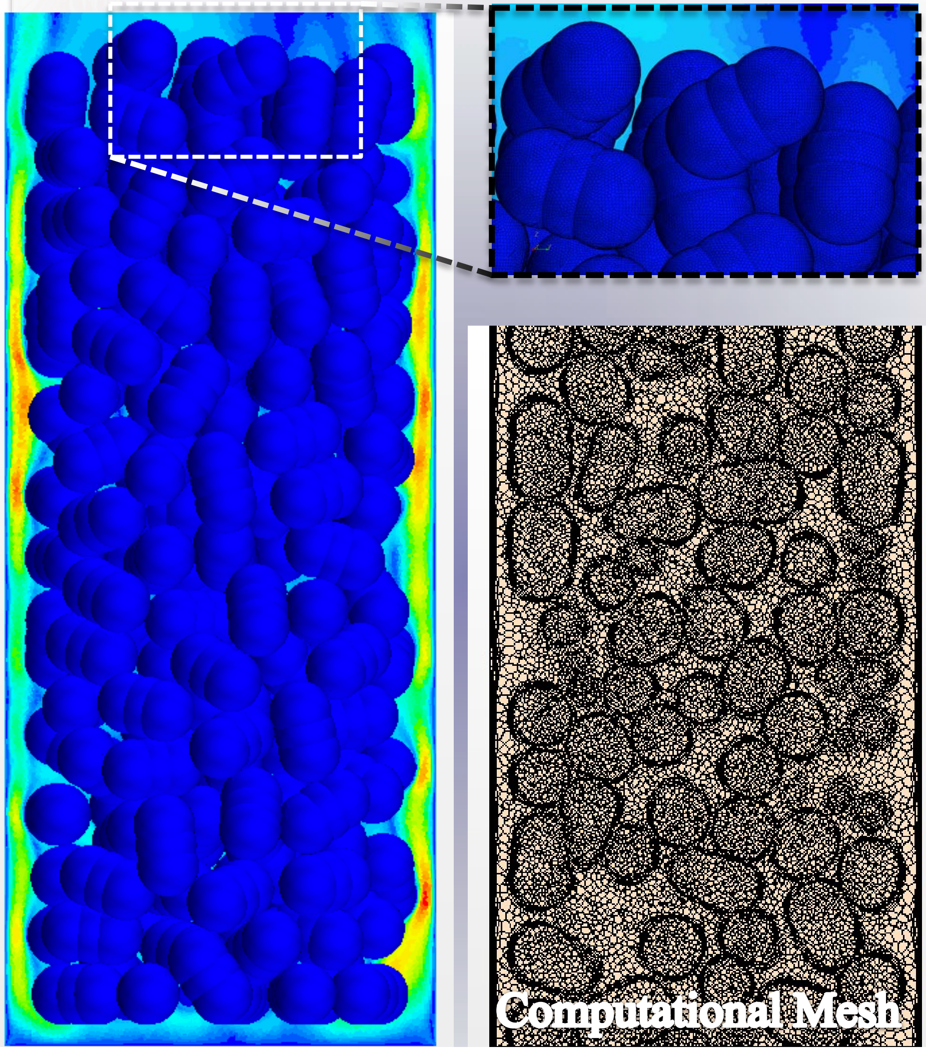
Homogeneous Growth

LES – DQMOM – Star-CMM+

Completed

In progress

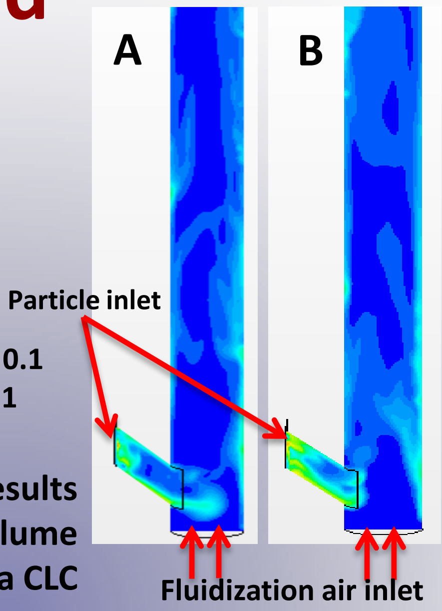
Fixed Bed



This figure depicts air passing through a bed of solid particles. Complex meshing schemes and cells on the order of millions are typically required to simulate such phenomena. This figure shows a meshing scheme for a CLC fixed bed system.

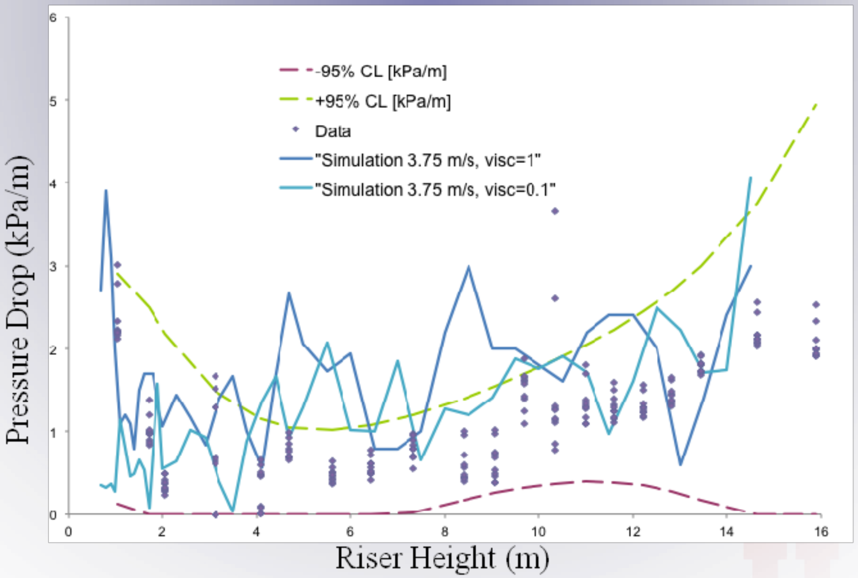
Fluidized Bed

Verification with CLC to assess the Star-CCM+ software capabilities in representing multiphase phenomena.



A: Solid viscosity = 0.1
B: Solid viscosity = 1

Simulation results representing volume fraction of solid in a CLC



Comparison of experimental pressure drop (NETL) with simulated results for a CLC riser.

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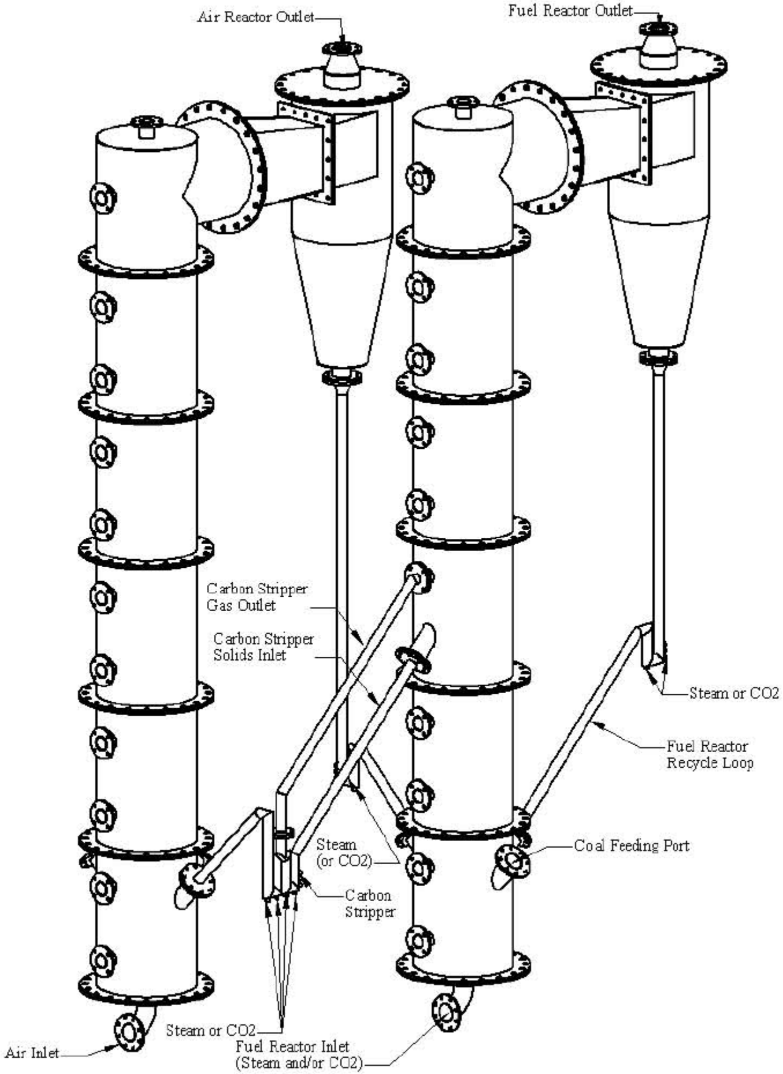
Future Development

- **Continue to test materials in lab-scale FBC**
  - Obtain kinetics of OC reduction/oxidation
  - Test different coals
  - Gather information on attrition
- **Continue Process Modeling and Evaluations**
  - Comparisons with CLC
  - Develop scenarios for energy utilization
  - Refine process model based on studies above

Future Development

- **Newly-funded system to focus on CLOU-based CLC for coal**
  - **Funded by Univ. Wyoming**
  - **Focus initially on PRB coal**
- **Target approx. 200 kW_{th}**
- **Designed flexibly to operate as conventional (non-CLOU) CLC with solid or gaseous fuels**
- **Approx. 20 ft (6 m) tall overall**
- **Construction complete early 2013**



Progress and Plans

- **Initial trials with conventional CLC**
  - Ilmenite as carrier, natural gas as fuel
  - Ilmenite as carrier, coal as fuel
- **Transition to CuO-based carrier, coal as fuel**
  - Also consider petroleum coke as fuel (low volatiles release
- **Use process modeling and simulation to scale up and explore operation**

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QUESTIONS?