NATIONAL ENERGY TECHNOLOGY LABORATORY

Chemical Looping:
Reactor Experiments, Modeling and Simulation

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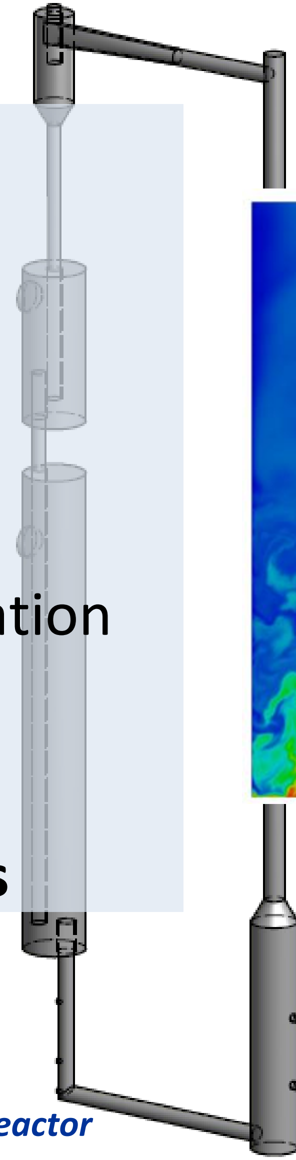
U.S. DEPARTMENT OF ENERGY

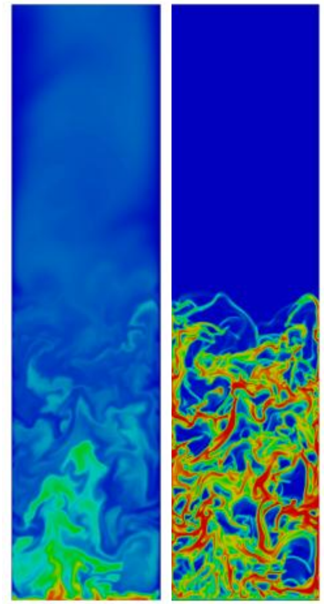
Outline

- **Overview**
- **Selected Results**
  - Solid Separation
  - Particle Modeling
  - Fuel Reactor Simulation
- **Future Work & Experimental Facilities**

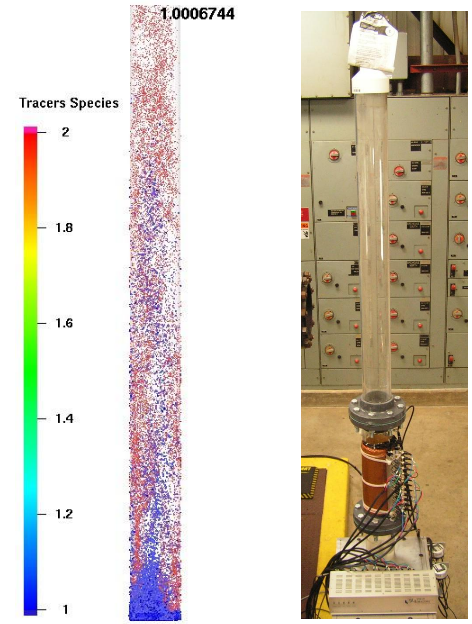


25 kW CL Reactor

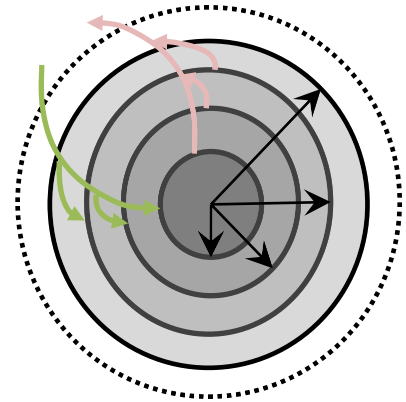
FR Simulation



Solid Separation



Particle Modeling

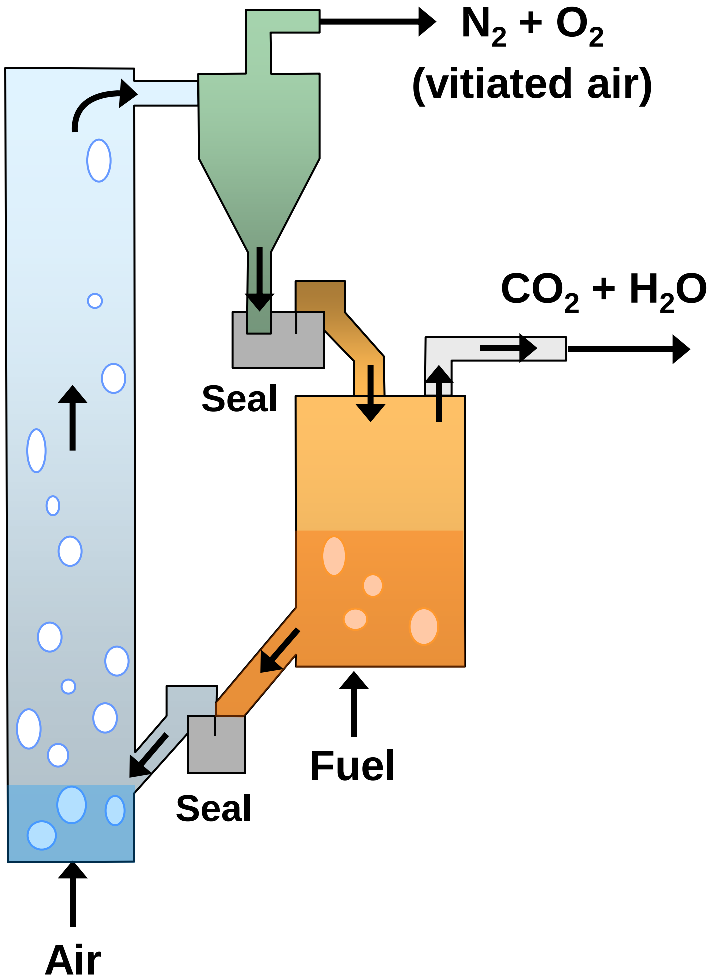


Overview

- **Objectives**
  - accelerate commercial deployment of Chemical Looping Technology *(if determined to be viable)*
  - Natural Gas and Coal
  - Power (Electricity) as well as other applications

- **Approach**
  - Integrated Program of Experiments, Modeling and Simulation

Chemical Looping



Air reactor

- carrier is oxidized by air
- heat is released

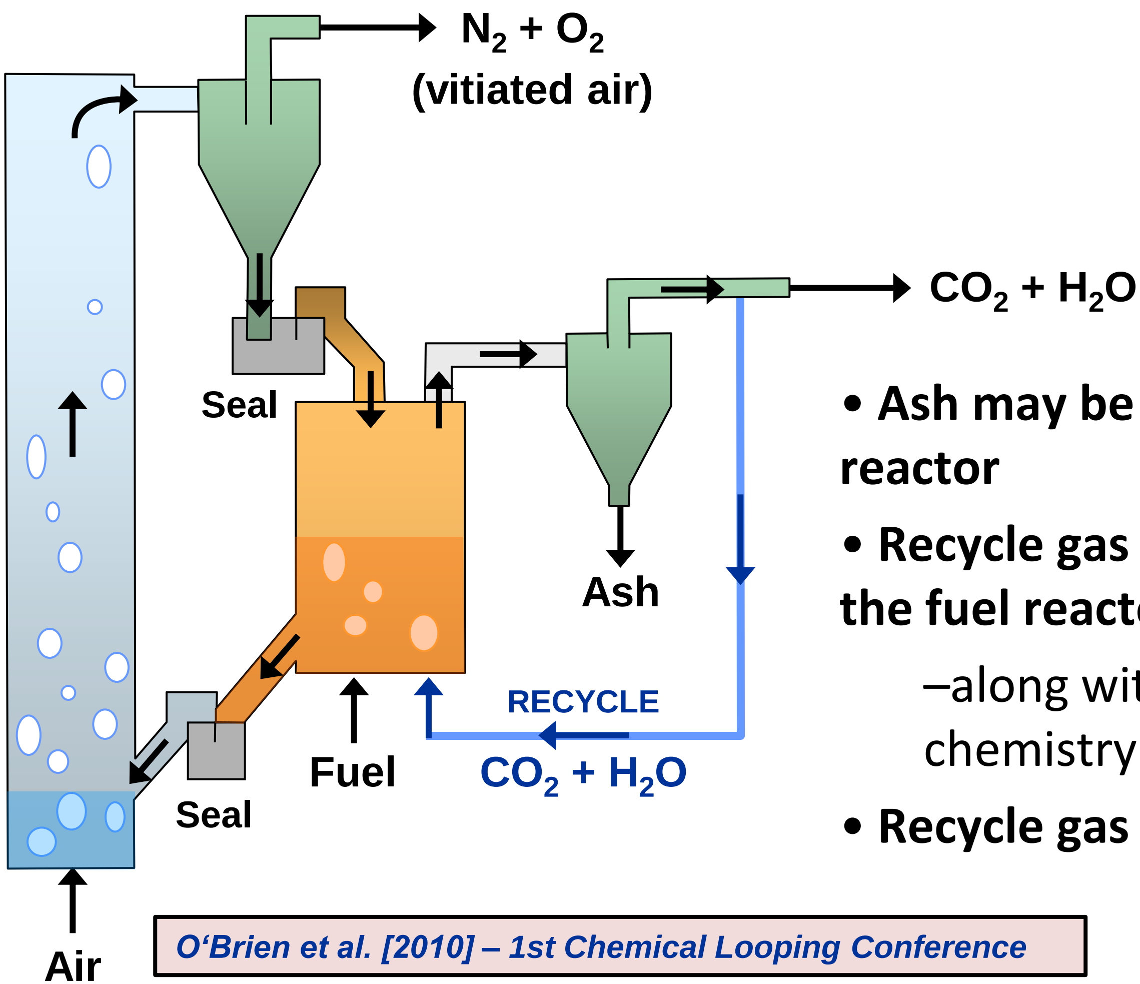
Cyclone

- hot oxidized carrier separated from vitiated air
- hot vitiated air is used for power generation

Fuel reactor

- carrier oxidizes fuel
- form CO_2 and H_2O (usually $\Delta H_r < 0$)
- carrier returned to the air reactor

Chemical Looping Combustion (with *in situ* gasefication of solid fuel)



- **Ash may be elutriated from the fuel reactor**
- **Recycle gas must be used to fluidized the fuel reactor**
  - –along with self fluidization due to chemistry
- **Recycle gas must "burn out" the char**

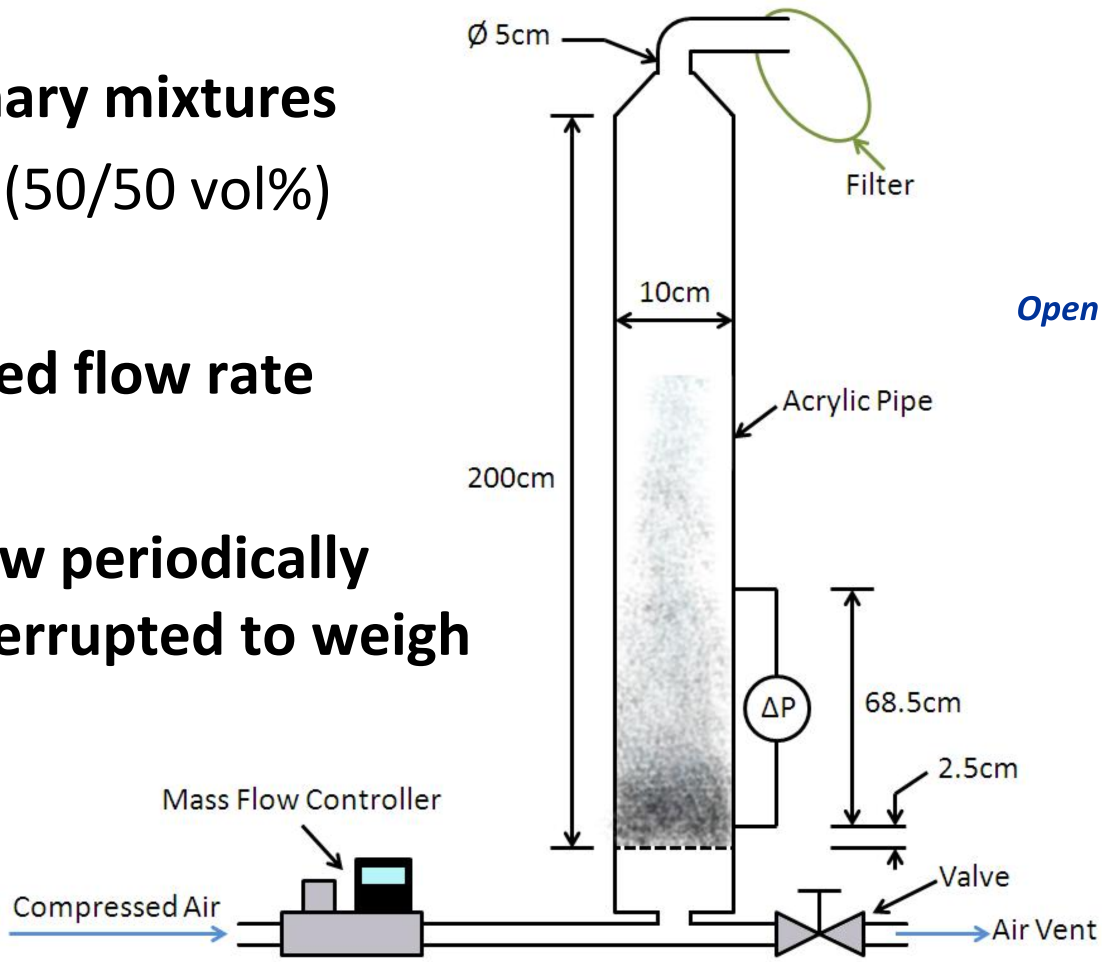
O'Brien et al. [2010] – 1st Chemical Looping Conference

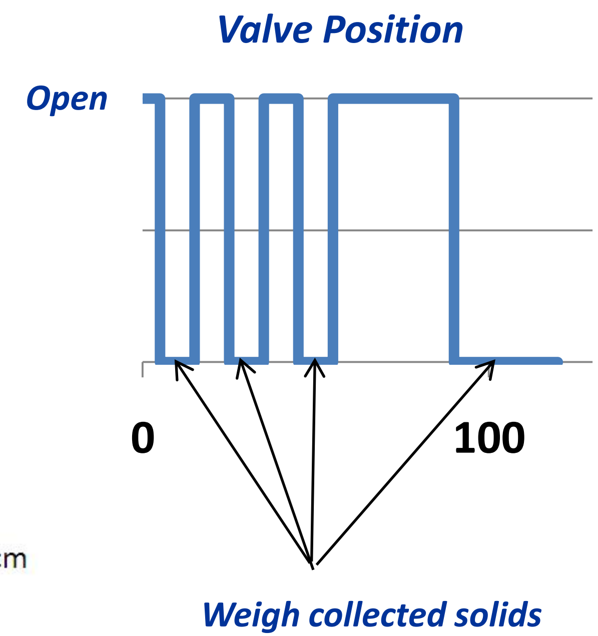
Challenges

- **Carrier selection**
  - balance carrier performance (reactivity, capacity), cost and availability
- **Fuel utilization**
  - bypass of fuel in the bed
  - gas residence time
  - gasification of coal is rate limiting
- **Solids Handling**
  - carrier, coal, ash separation
  - circulation rate & inventory control
- **Heat integration**
  - fuel reactor is endothermic

Solid separation fluid bed

- **Binary mixtures**
  - (50/50 vol%)
- **Fixed flow rate**
- **Flow periodically interrupted to weigh**





Dalton, Weber, Straub, and Mei, 2011, Clearwater Coal Conference

Several Different Materials

Oxygen Carriers

Alumina Oxide

Copper Oxide

Ilmenite

Pseudo Ash

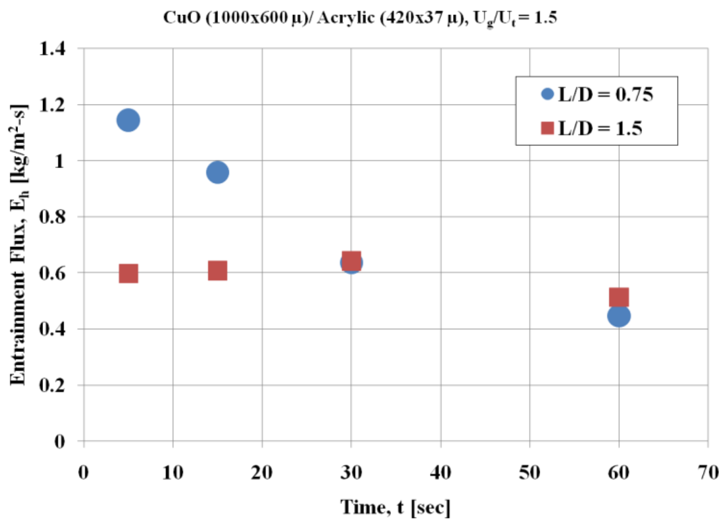
Glass Beads

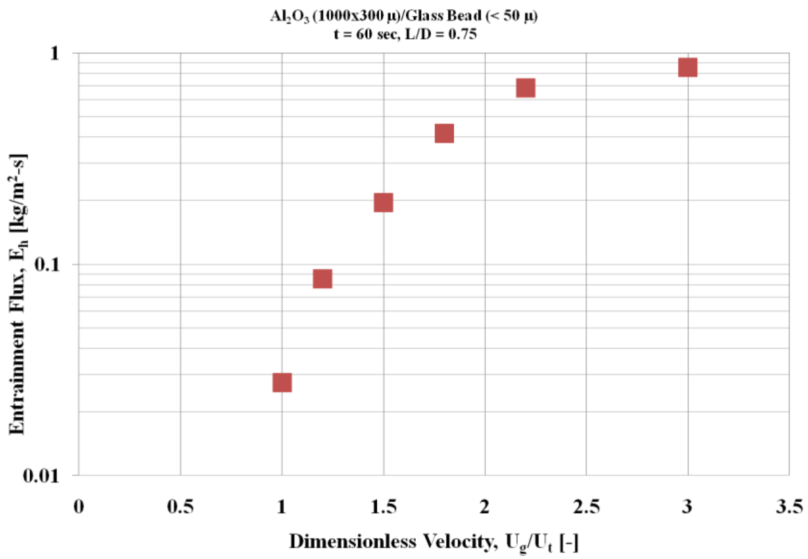
Acrylic

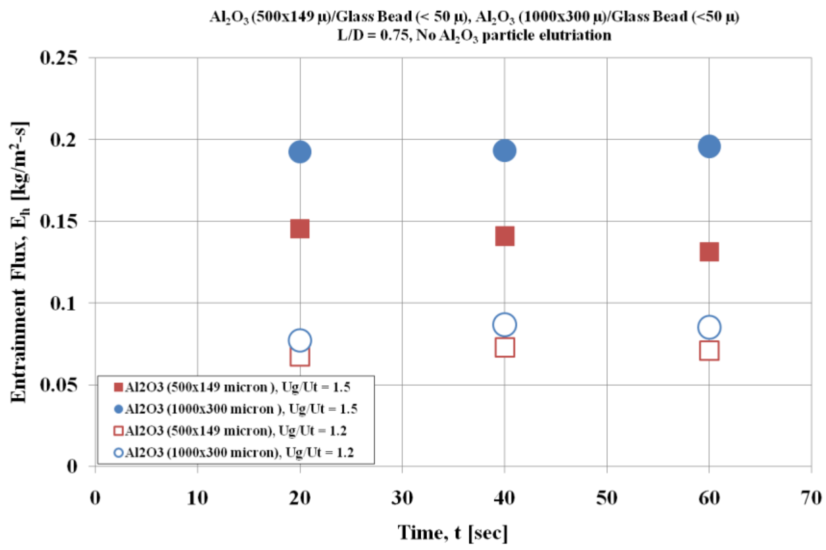
Material	Size (µm)		Density (kg/m³)	Ut (m/s) Smallest	Ut (m/s) Largest
Copper Oxide	1000	600	3424	5.68	X
Ilmenite	250	74	4457	0.88	X
Al_2O_3 (small)	500	149	3968	1.60	X
Al_2O_3 (large)	1000	300	3968	3.18	X
Acrylic	420	37	1216	X	2.00
Glass Beads	50	less	2464	X	0.39

Separation Results

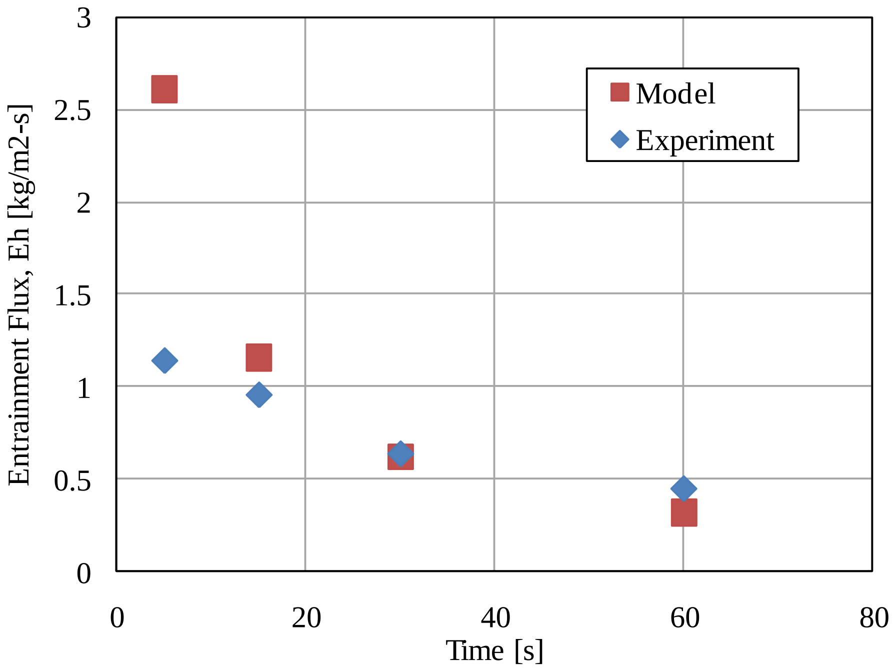
- **Elutriation Increases with:**
  - *decreased* particle size
  - *decreased* bed height
  - *increased* gas flow

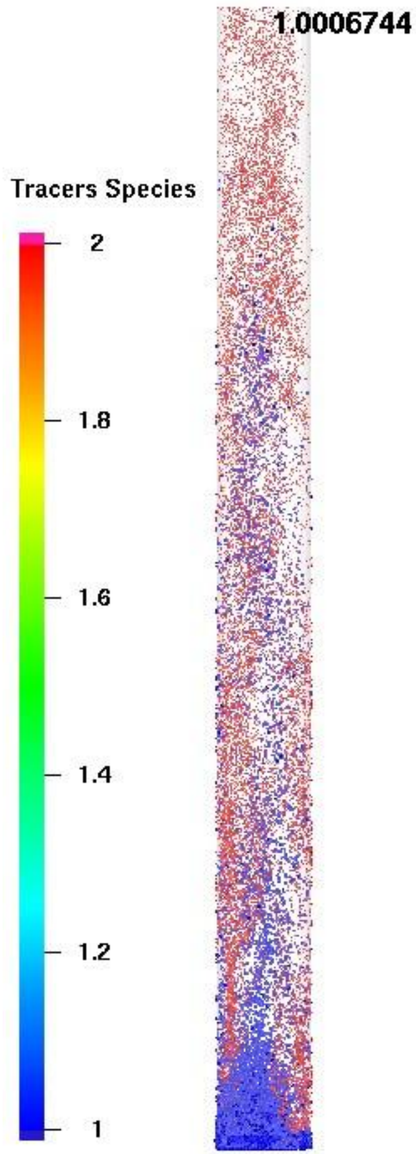






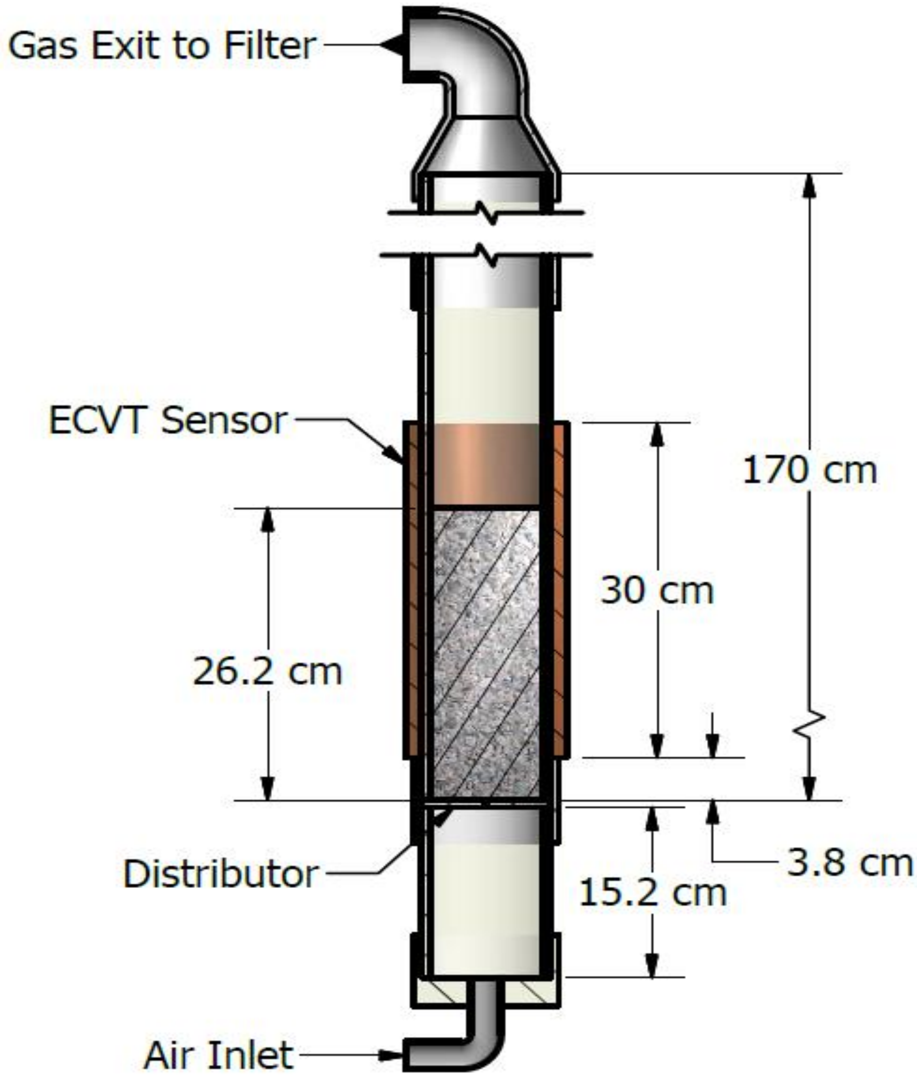
Simulations



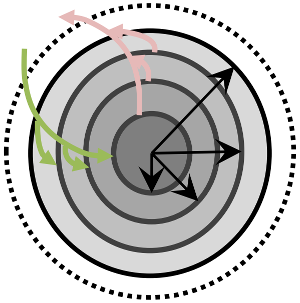


- **MPIC (Barracuda)**
- **43k cells**
- **Wen-Yu drag**
- **Model overpredicts entrainment**

Solid Separation with ECVT



Reaction Models for Metal Oxide Reduction



- **Differential Models & Parameter Estimation**
  - Homogenous
  - Three Front Shrinking Core
  - Implemented using python/scipy/Cantera

- **Reaction Model Identification Tool**
  - Least squares fit of reduction curves vs. analytical models of reduction
    - Homogenous, Shrinking Core (1D,2D,3D), Avrami-Erofeev
  - Implemented as an Excel Workbook

Arne Scholtissek, 2011, Thesis – TU Bergakademie Freiberg
TU-Freiberg-WVU-NETL Exchange Program

Iron Reduction

- **Several Iron Oxide Phases**
- **Multistep reduction**

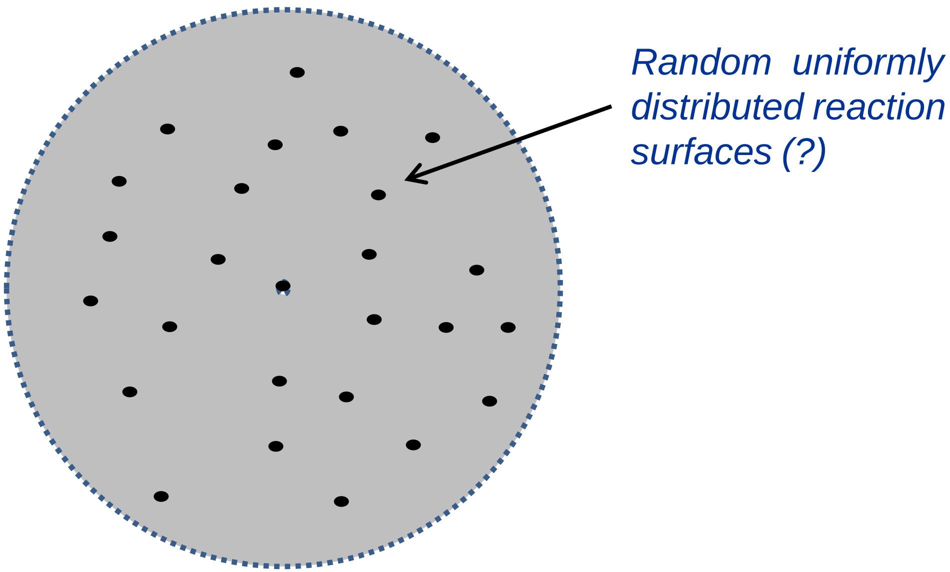
$Fe_{0.95}O$ $Fe_{0.88}O$

$$3Fe_2O_3 \longleftrightarrow 2\,Fe_3O_4 \longleftrightarrow 6\,FeO \longleftrightarrow 6\,Fe$$

	+ 1 O	+ 2 O	+ 6 O
hematite	*magnetite*	*wustite*	

Pineau, Kanari, Gaballah [2007]

Homogenous Reaction Model



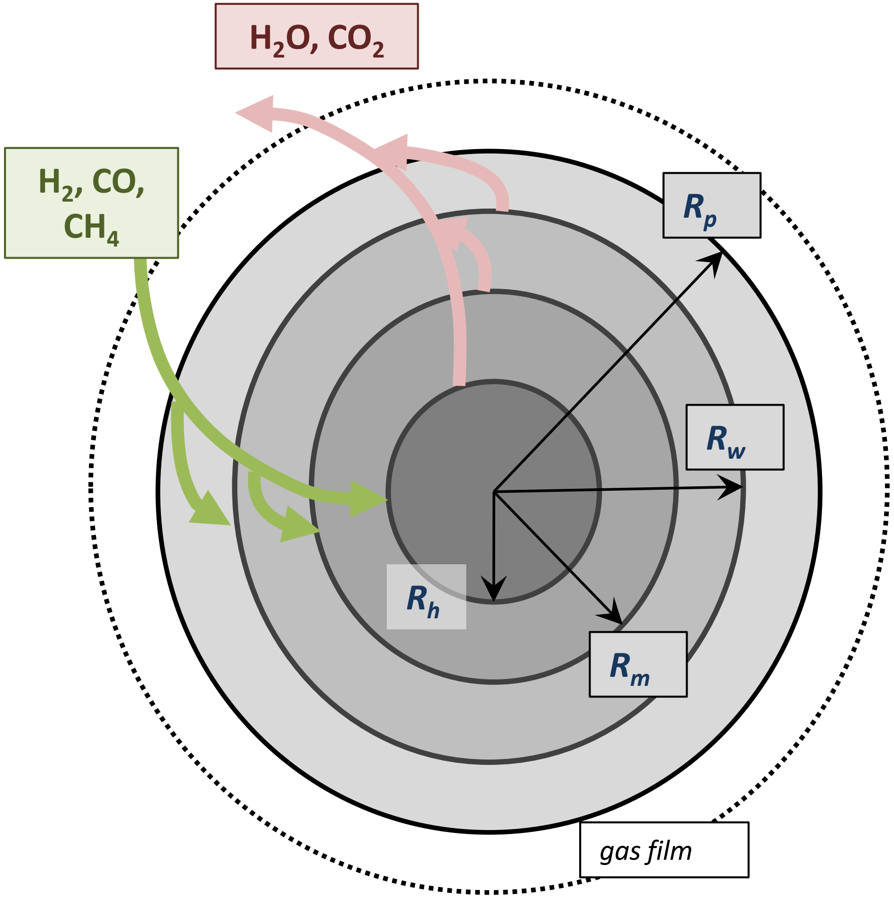
Fe_2O_3	$\frac{dc_h}{dt} = -k_h\, c_h\,,$
Fe_3O_4	$\frac{dc_m}{dt} = u\, k_h\, c_h - k_m\, c_m\,,$
FeO	$\frac{dc_w}{dt} = v\, k_m\, c_m - k_w\, c_w\,,$
Fe	$\frac{dc_{iron}}{dt} = w\, k_w\, c_w\,,$

$$k_t = A_t \exp\left(-\frac{E_t}{RT}\right) f(c_{i,gas})$$

- **isothermal**
- **chemical reaction controlled**
  - neglect film diffusion and internal diffusion
- **uniform solid composition**

Chowdury and Roy **[2008]**

3-Front Shrinking Core

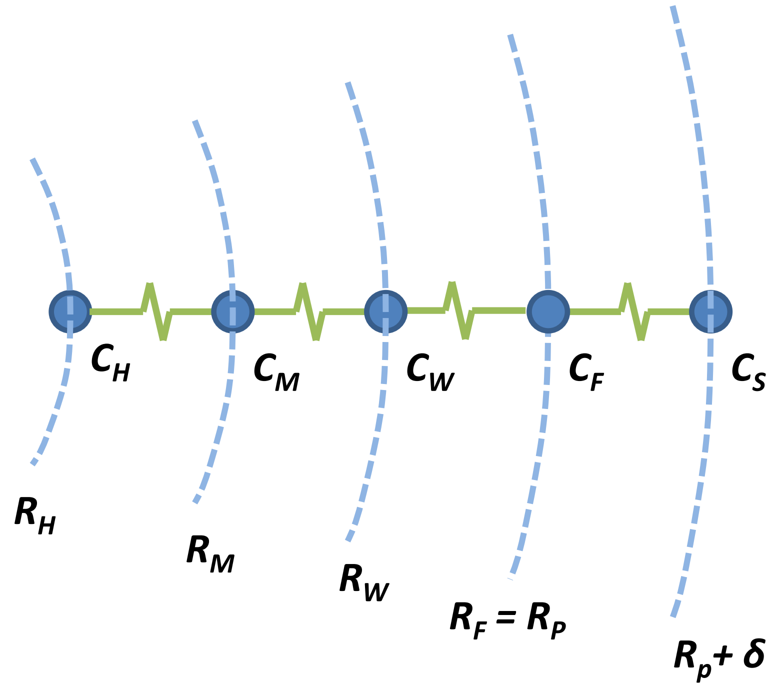


- reversible, first order reactions at each front
- film diffusion
- gas diffusion (Fickian) through porous layers
- isothermal
- constant external gas composition and temperature
- quasi-steady state gas composition

Spitzer, Manning, Philbrook [1966]
Tsay, Ray, Szekely [1976]
Negri, Alfano, Chiovetta [1988]

3-Front Shrinking Core

- **Differential Algebraic System**
- **Mass balance at the reaction surface**
  - (Flux of Fuel to Surface – Flux of Fuel from Surface) = Consumption at the Surface
- **Reaction surfaces from solid mass (volume) balance**
  - porosity changes in the layer to account for material density differences

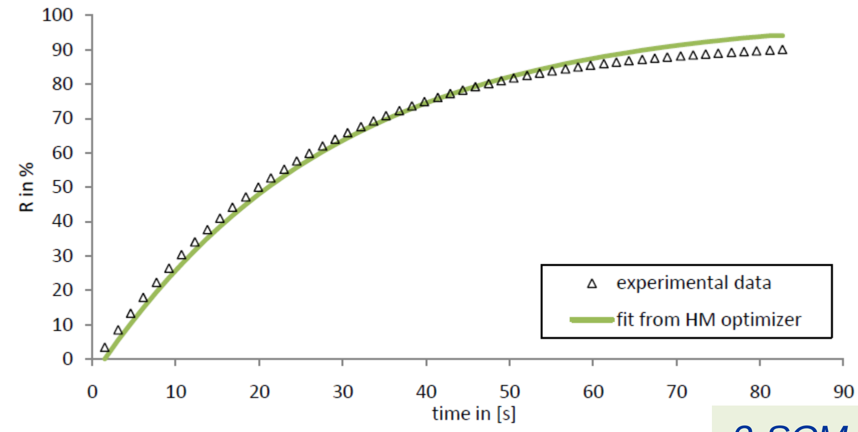


Results

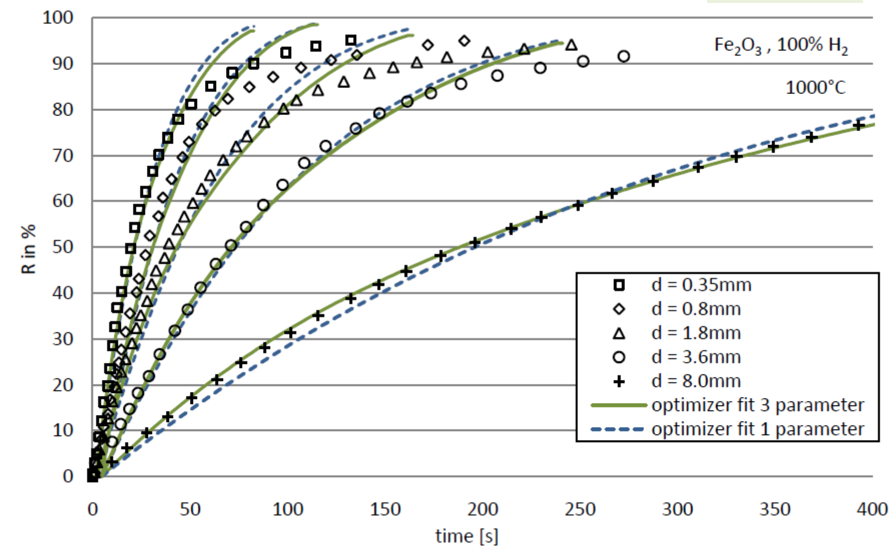
- **Optimize rate coefficients by with experimental reduction curves**

- **Fit could be better - need to revise model**
  - Distinct reaction fronts at the particle radius scale ?

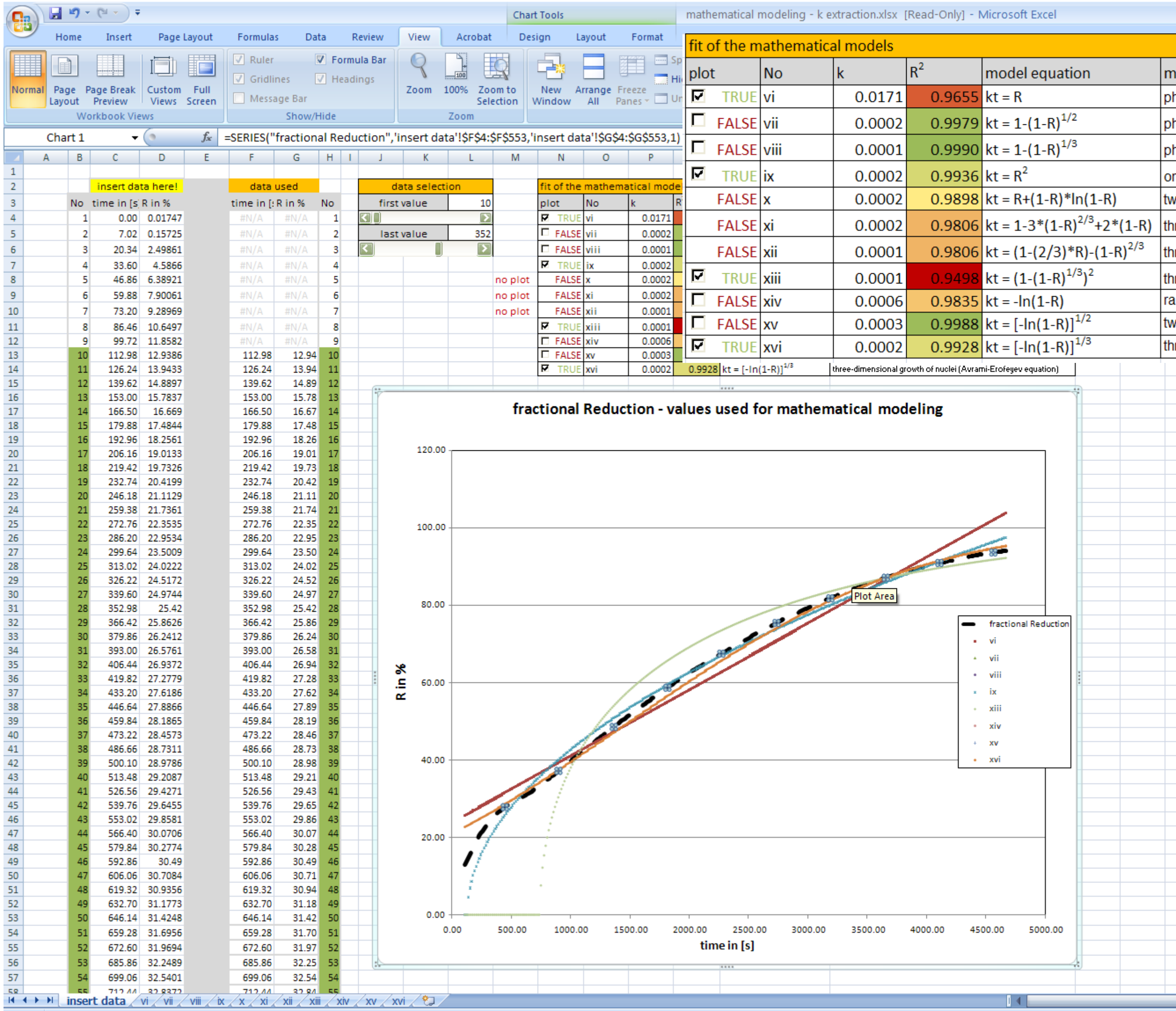
HM, d = 350 um



3-SCM



Reaction Model Identification Tool



fit of the mathematical models					
plot	No	k	R^2	model equation	mechanism
☑ TRUE	vi	0.0171	0.9655	kt = R	phase boundary controlled reaction (infinite slabs)
☐ FALSE	vii	0.0002	0.9979	$kt = 1-(1-R)^{1/2}$	phase boundary controlled reaction (contracting cylinder)
☐ FALSE	viii	0.0001	0.9990	$kt = 1-(1-R)^{1/3}$	phase boundary controlled reaction (contracting sphere)
☑ TRUE	ix	0.0002	0.9936	$kt = R^2$	one-dimensional diffusion
FALSE	x	0.0002	0.9898	kt = R+(1-R)*ln(1-R)	two-dimensional diffusion
FALSE	xi	0.0002	0.9806	$kt = 1-3*(1-R)^{2/3}+2*(1-R)$	three-dimensional diffusion
FALSE	xii	0.0001	0.9806	$kt = (1-(2/3)*R)-(1-R)^{2/3}$	three-dimensional diffusion (Ginstling-Brounshtein equation)
☑ TRUE	xiii	0.0001	0.9498	$kt = (1-(1-R)^{1/3})^2$	three-dimensional diffusion (Jander equation)
☐ FALSE	xiv	0.0006	0.9835	kt = -ln(1-R)	random nucleation, unimolecular decay law (first-order)
☐ FALSE	xv	0.0003	0.9988	$kt = [-ln(1-R)]^{1/2}$	two-dimensional growth of nuclei (Avrami-Erofeyev equation)
☑ TRUE	xvi	0.0002	0.9928	$kt = [-ln(1-R)]^{1/3}$	three-dimensional growth of nuclei (Avrami-Erofeyev equation)

Fuel Reactor Simulations

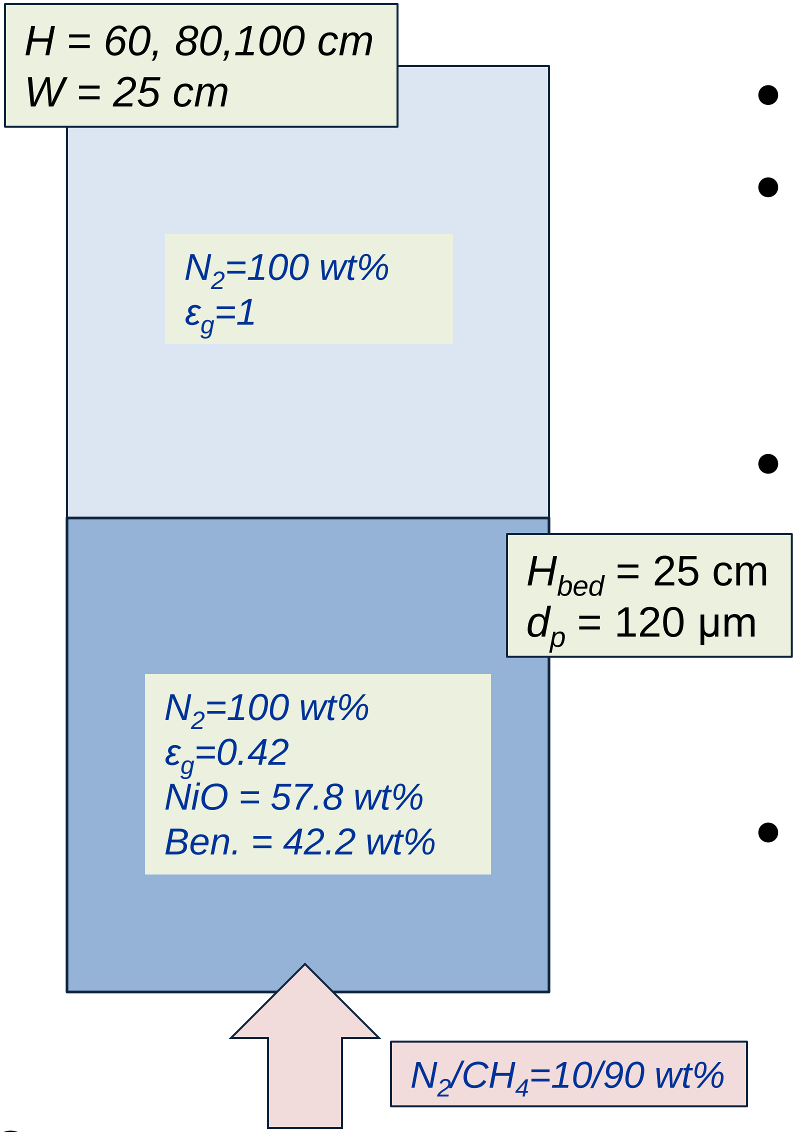
- **Batch Fuel Reactor**
  - NiO & CH_4
  - Jung & Gamwo [2008], Shuai et al. [2010]

- **Parameter Sensitivity of a Continuous Fuel Reactor**
  - CuO & CO/H_2
  - CBIC Zaragoza – Forero et al. [2009]

- **MFIX Euler-Euler**

Carsten Olm, 2011, Thesis – TU Bergakademie Freiberg
TU-Freiberg-WVU-NETL Exchange Program

Configuration - Batch CH_4-NiO Reactor



- **Bubbling Fluidized Bed Reactor**
- **2 baseline simulations**
  - Jung & Gamwo (no turb)
  - Shaui et al. (turb)
- **1 modified simulation**
  - Increase domain height (100 cm)
  - Refine mesh (24K to 32K) cells
  - Modify gas viscosity
- **3 more**
  - fine grid, upwind, lower particle diameter (80 um)

Batch Reactor – Oxygen Carrier Kinetics

- Shrinking core model (SCM)
  - Ryu et al. [2001]

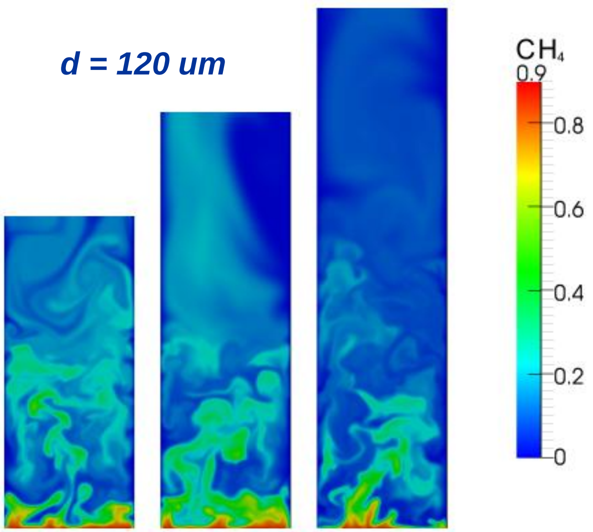
$$CH_4(g) + 4 \cdot NiO(s) \rightarrow CO_2(g) + 2 \cdot H_2O(g) + 4 \cdot Ni(s) \quad (\Delta H_c^0 = +156.5\ kJ/mol)$$

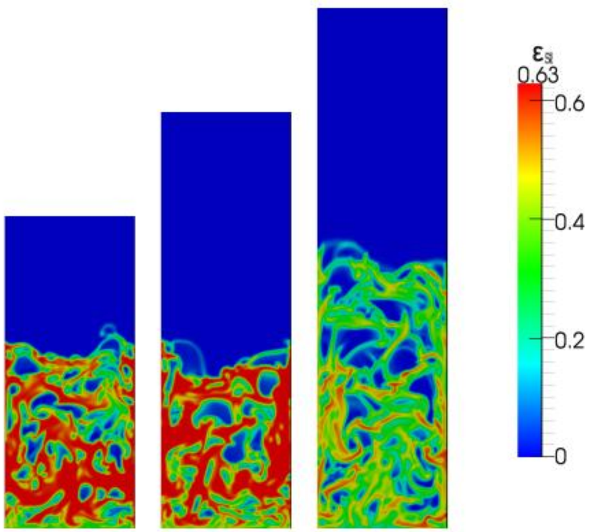
$$-r = k \cdot S_0 \cdot \varepsilon_g \cdot \frac{\rho_g \cdot w_{CH_4}}{M_{CH_4}} \qquad \left[\frac{mol}{cm^3 \cdot s}\right]$$

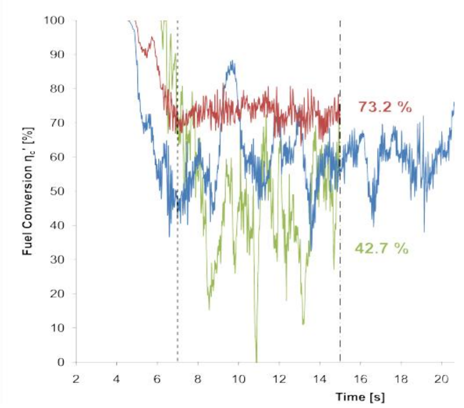
Results - Batch CH_4-NiO Reactor

d = 120 um

d = 80 um







Jung & Gamwo

~43%

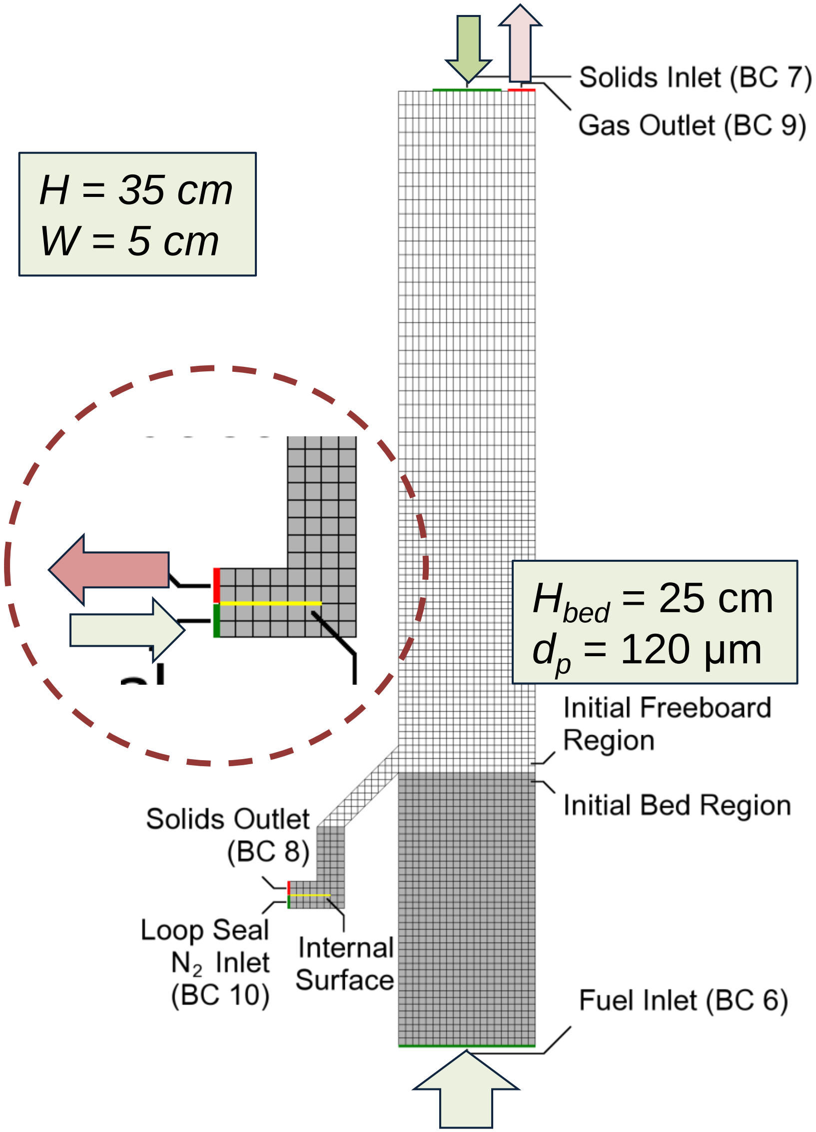
Shaui et. al.

~60 %

Current

- **Note: Large domain w/ 120 um particles is similar to center**

Continuous Syngas Reactor



- **2.4 K active cells**
  - Cut-cell
  - Non-uniform
- **18 operating conditions**
  - Fuel flow rate
  - Fuel composition
  - Circulation Rate

Forero et al., Fuel Processing Technology 90 (2009), p. 1473

Reaction Model

$$H_2(g) + CuO(s) \rightarrow H_2O(g) + Cu(s) \quad (\Delta H_c^0 = -85.8\ kJ/mol)$$
$$CO(g) + CuO(s) \rightarrow CO_2(g) + Cu(s) \quad (\Delta H_c^0 = -126.9\ kJ/mol)$$

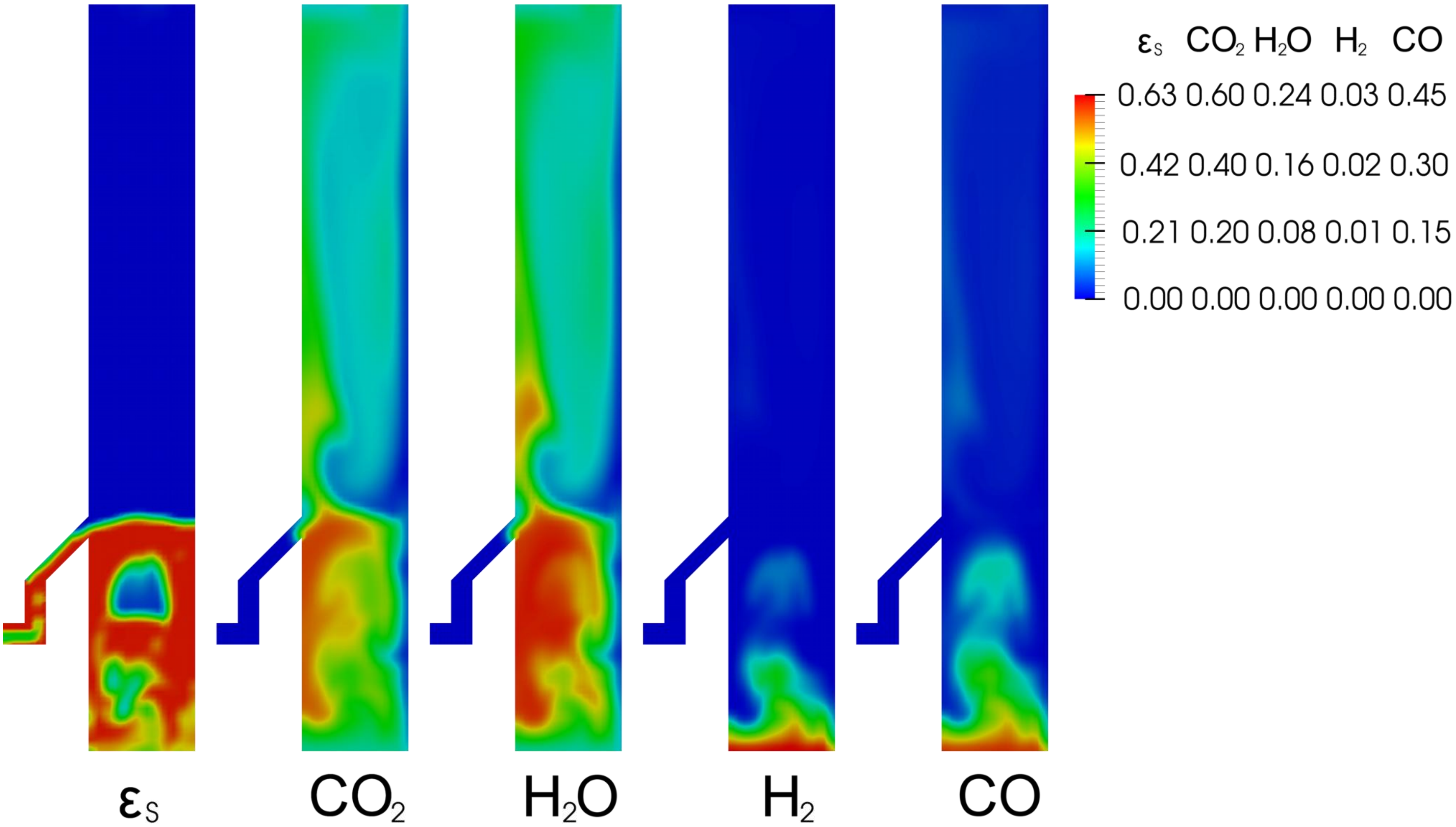
- **Assume**
  - reactions are additive
  - Plate-like shrinking core –> homogenous model at low CuO mass fractions

$$-r_i = \varepsilon_s \cdot \frac{dC_{CuO}}{dt} = -\varepsilon_s \cdot \frac{C_{CuO,0}}{\tau_i} \quad \left[\frac{mol}{cm^3 \cdot s}\right]$$

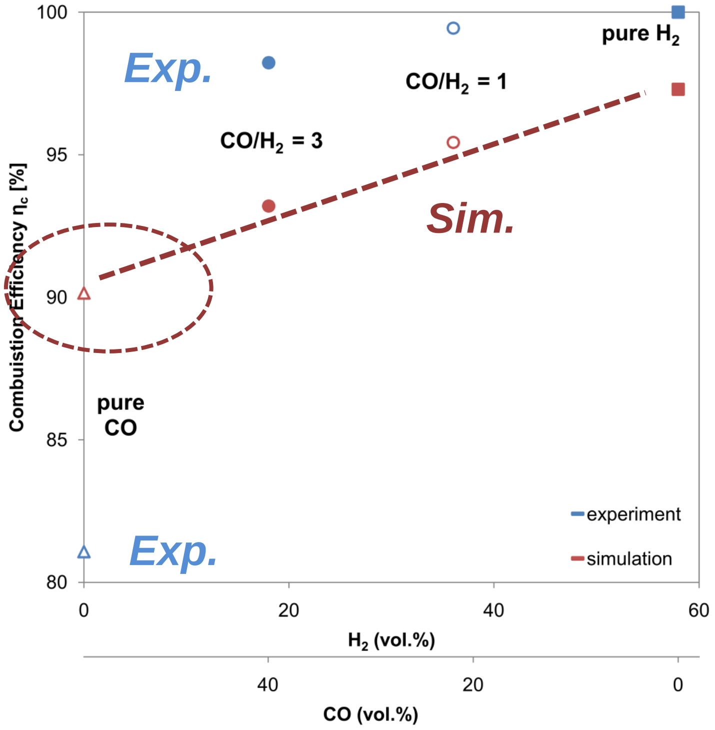
$$k = k_0 \cdot e^{\left(-\frac{E_A}{R \cdot T_s}\right)} \quad \left[\frac{mol^{(1-n)} \cdot cm^{(3n-2)}}{s}\right] \qquad X_s = \frac{t}{\tau_i}, \quad \tau_i = \frac{\rho_{m,CuO} \cdot L}{b_i \cdot k_i \cdot C_{g,i}^n}$$

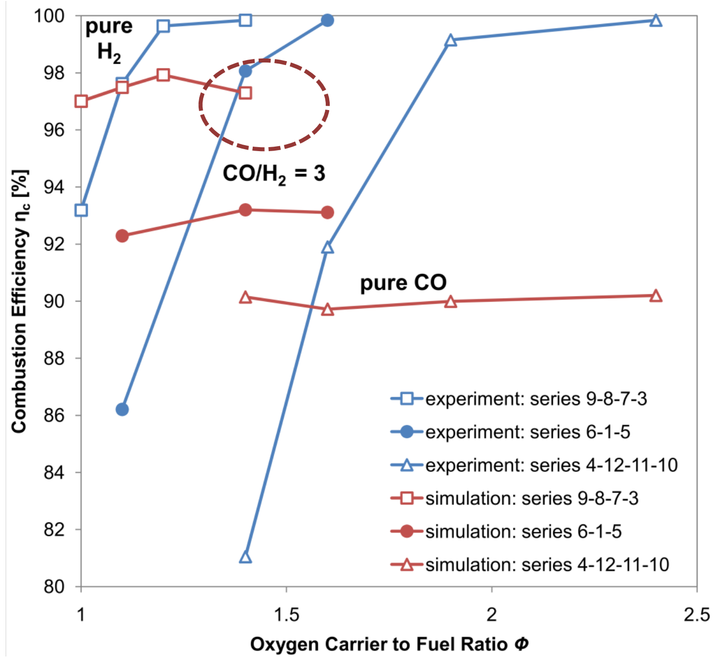
Abad et. al [2007]

Continuous Reactor – Results



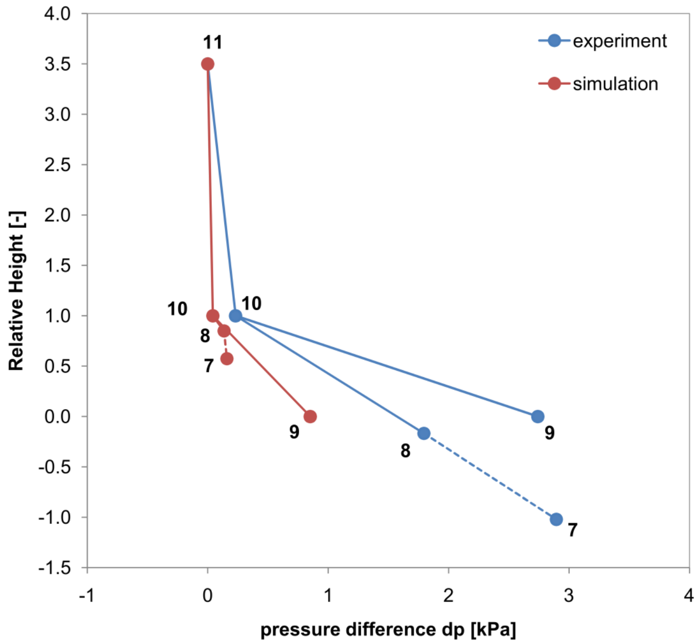
Combustion Efficiency

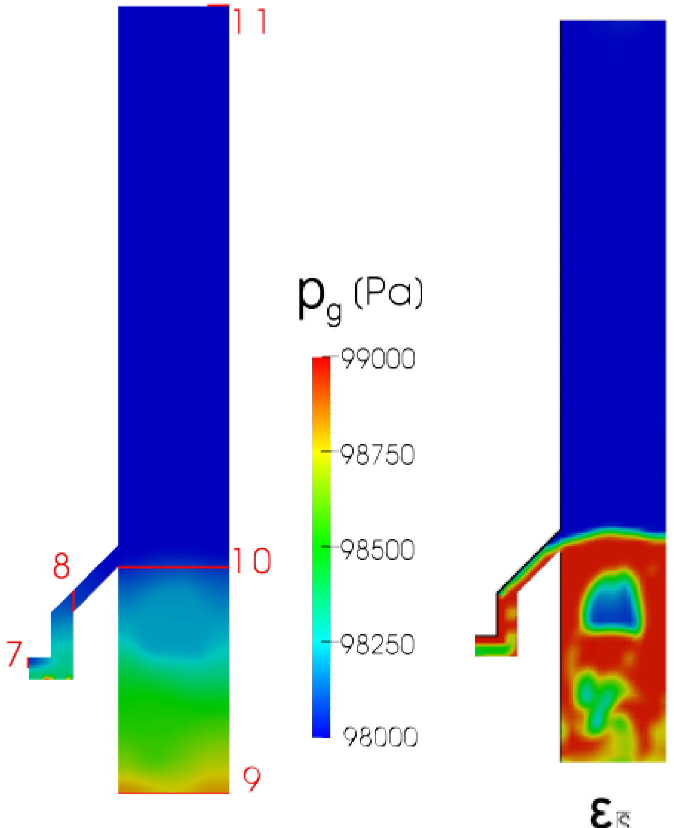




- Simulations are less sensitive to operating conditions than the experiment
  - CO reaction rate is too fast & H2 cooperative effect
  - More analysis on decrease

Pressure Drop





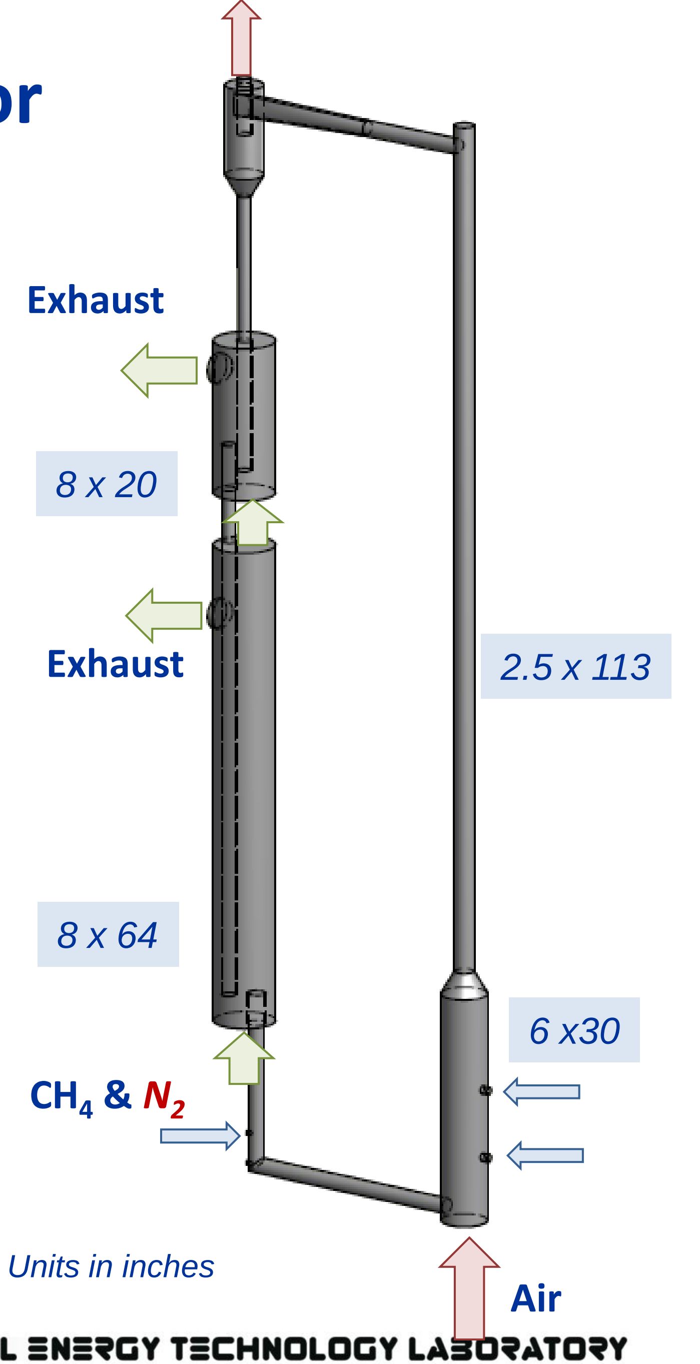
- Pressure drop (solid inventory) is under-predicted
  - 9-10 - resolution ?
  - 10-11 – 3D effects

Future Plans

- **Pair experiments with simulations**
  - 25kW Reactor
    - Non-reacting ("clear") & reacting
  - Solid-separation (ECVT)
  - Attrition tests
  - Single Fluid Bed Reactor
- **Use TGA and Fixed Bed Experiments to develop carrier specific reaction models**
- **Continued validation with external data**

25kW CL Reactor

- **Objectives**
  - eval. integrated CLC performance
  - eval. control, solids handling, and sensor performance
  - provide validation data
- **Status**
  - Procurement
  - Installation - Jan 2012
- **Design conditions**
  - Self-sustaining operation at ~ 25kW$_{th}$
    - (3 lb/hr CH_4)
  - Independent control of preheat temperature for air and fuel reactors
  - Back-pressure control valves provide additional pressure balance capability
  - Iron & copper carriers
  - Fluidized Beds and Riser



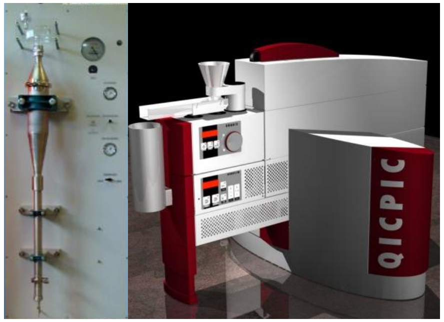
Attrition and TGA

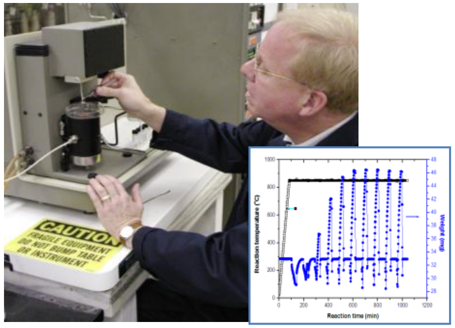
Attrition Tests

- **Evaluate statistical models to predict attrition rates**
  - ASTM 5757
  - ASTM 4058
- **Provide input for systems analyses and technology evaluations**

TGA Lab Studies

- **Review published kinetics data**
- **Evaluate alternative oxygen carriers**
- **Provide kinetic rate data for simulations of CL systems**





Fluid Bed and Cold Flow

Single Fluid Bed Reactor

- Quantify reaction rates at FB conditions
- Calibrate reacting CFD simulations in single fluid bed reactor
- Provide exposed samples for attrition testing and evaluate carriers in FB environment

Cold Flow with ECVT

- Evaluate solids handling and controls for integrated system
- Non-reacting conditions
- Provide hydrodynamic benchmark data for simulations
- Provide control data for reacting unit