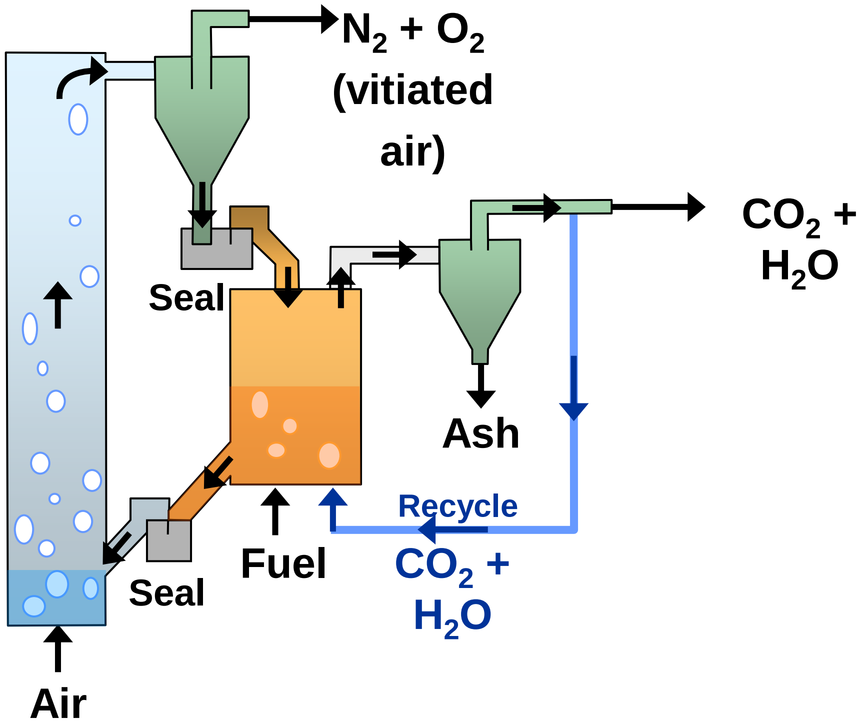
CFD Simulations of the Chemical Looping Combustion of Solid Fuels



NETL 2010 Workshop on Multiphase Flow Science

Pittsburgh Airport Marriott, Coraopolis, PA

May 4-6, 2010

Thomas O'Brien†, Kartikeya Mahalatkar*¶, John Kuhlman¶† and E. David Huckaby

†National Energy Technology Laboratory
**ANSYS-Fluent, Inc.*
¶West Virginia University, Morgantown, WV 26506, USA

Outline

- Backstory – USA & coal, climate change
- Chemical Looping Combustion (CLC) of Solid Fuels
- Carriers
- CFD Model
- Simulated Experiment
- Simulation Results

Perspective

US coal-fired power plants (~40% of US power)

~1 billion tons of coal in 2009 (2.3% < 2008)

~10 million coal carloads (100 tons/carload)

~100,000 trains (100 cars/train)

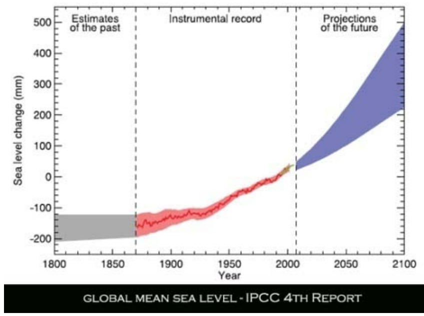
>>>>> ~275 coal trains/day in US alone >>>>>

The Powder River Basin alone contains

>100 billion tons of coal reserves

$$C + O_2 \rightarrow CO_2$$
$$12 + 32 = 44$$

Atmospheric CO_2 Overview



- **Atmospheric CO_2**

  (Global Temp Change; Sea Level Rise – thermal expansion only)

  - 284 ppm - pre-industrial level

http://news.bbc.co.uk/
April 15,2009

  - 380 ppm – current

    (ΔT= 1 ºC/1.8 ºF)

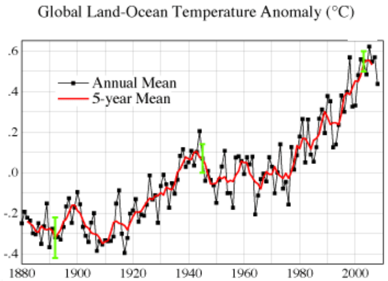
  - 450 ppm – 2100

    (+ ΔT= 0.6 ºC/1 ºF; $\Delta H_{sea\ level}$ = 14 cm/ 5.5 in)

    U.S. Climate Change Science Program "an attainable target if the world quickly adapts conservation practices and new green technologies to cut emissions dramatically."

  - 750 ppm - 2100 with current trends

    (+ ΔT= 2.2 ºC/4 ºF; $\Delta H_{sea\ level}$ = 22 cm/ 8.7 in)



NASA, 2008

Washington, *et al.*, "How Much Climate Change Can Be Avoided by Mitigation?" *Geophysical Research Letters*, (in press, 2009)

US Environmental Protection Agency (EPA) Endangerment Finding (4/17/2009)

Impacts that EPA believes may be significant for US citizens:

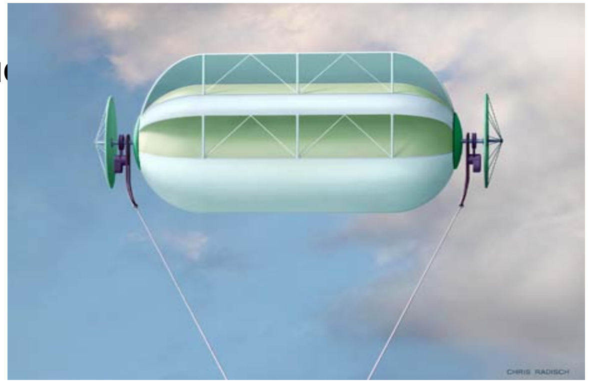
- an increased risk of droughts and floods
- sea level rise
- more intense storms and heat waves
- harm to water supplies, agriculture and wildlife

EPA - The science supporting the proposed endangerment finding was "compelling and overwhelming."

» E.P.A. has begun the process of regulating 5 green-house gases (climate-altering substances) under the Clean Air Act «

Options to Reduce CO_2 Emission

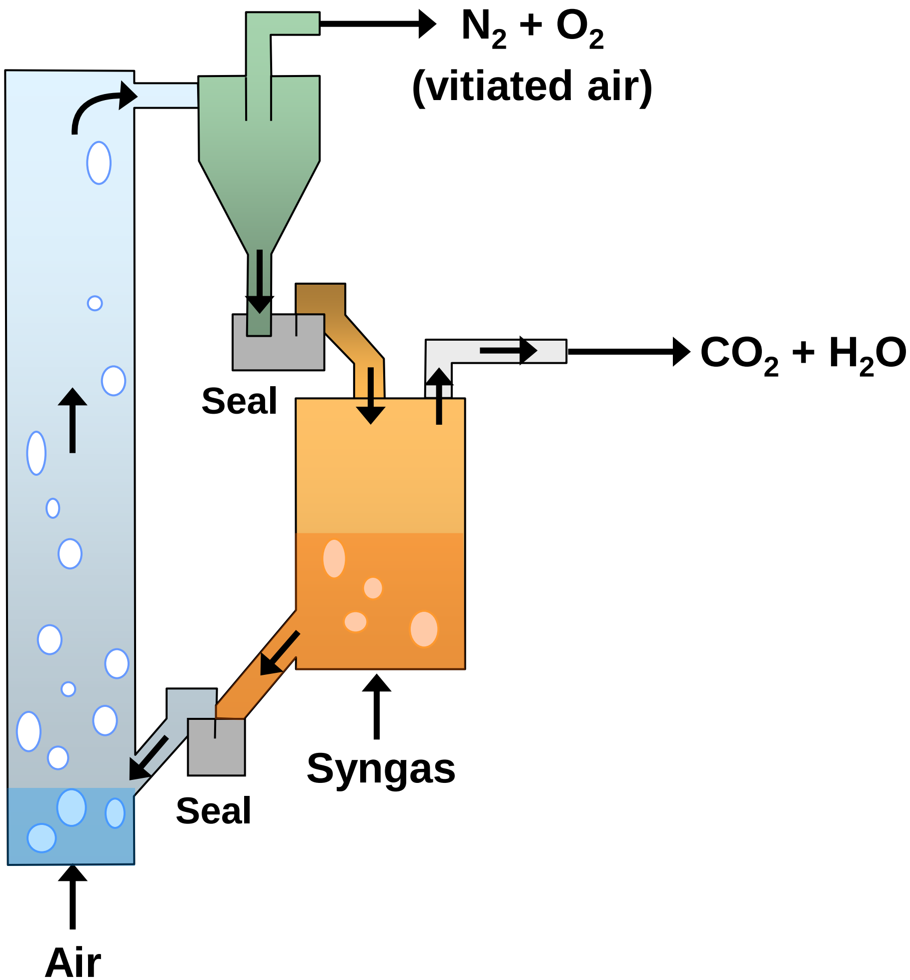
- **Reduce energy intensity - modify life style and economy to reduce energy demands**
- **Efficiency - increase efficiency of fuel conversion and utilization**
- **Fuel switching - Increase non-fossil fuel based power produc**
  - Solar
  - Nuclear
  - Biomass
  - Wind-power
  - Tidal
  - Geo-thermal
  - Hydro



The Magenn Power Air Rotor System
http://www.magenn.com/technology.php

- **Fossil Fuels with Carbon Capture and Sequestration**
  - Separation (75% of energy penalty ; 100-200 $/ton C)
    - Post-combustion
    - Oxy-fired
    - Pre-combustion
    - Un-mixed combustion
  - Compression & storage (25% of energy penalty; 4-8 $/ton C)

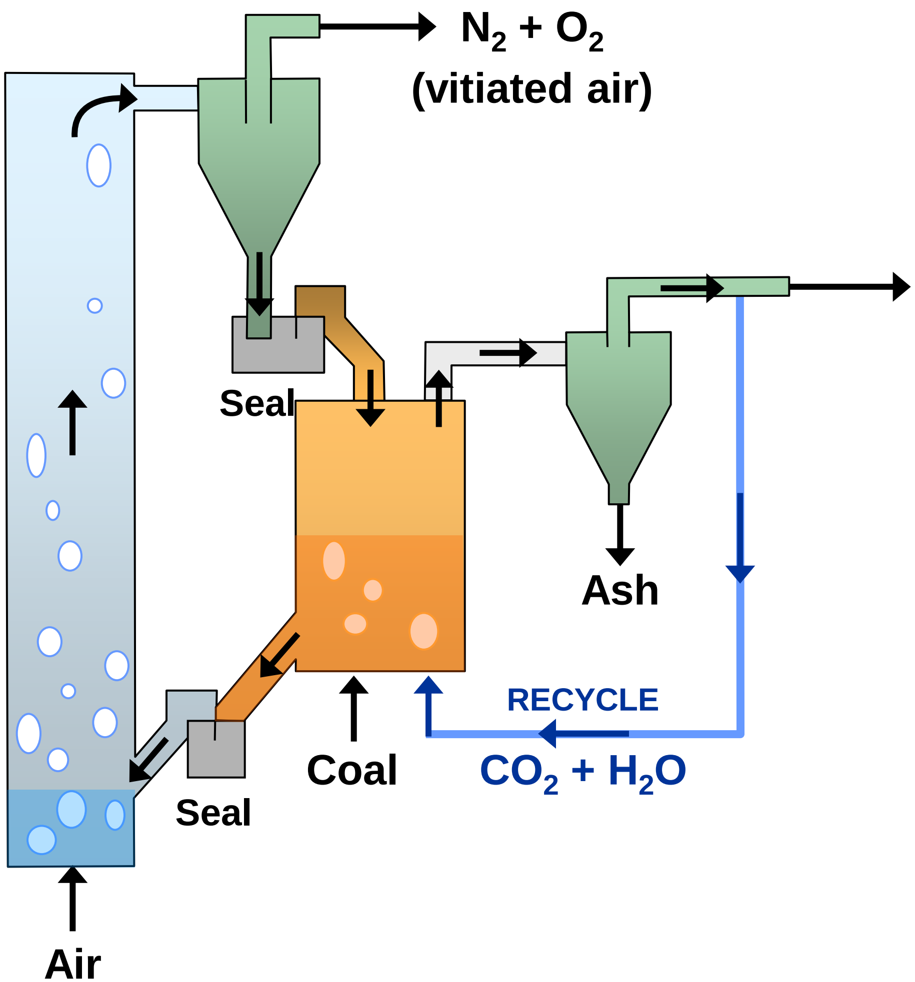
Chemical Looping Combustion of Coal (requires *ex-situ* gasification)



- Syngas is provided by an external oxygen-blown coal gasifier
- Air reactor – carrier is oxidized by air; heat is released
- Cyclone – hot oxidized carrier is sent to fuel reactor; hot vitiated air is used for power generation
- Fuel reactor – carrier oxidizes fuel to CO_2 and H_2O (usually endothermic); reduced carrier is returned to the air reactor (without any fuel).

Lewis and Gilliland (1954);Knoche und Richter (1968); Ishida (1994); Lyngfelt, *et al.*, 2001

Chemical Looping Combustion of Coal (involves *in-situ* gasification)



- **Recycle gas must:**
  - **1) help to fluidize the fuel reactor**
  - **(there is extensive self fluidization due to reactions)**
  - **2) gasify (burn out) the char.**
- **Char must be stripped from the FR → AR solids return.**
- **Ash may be elutriated from the fuel reactor and/or separated from the FR → AR solids return.**

Lewis and Gilliland (1954); Andrus et al. (2005), Scott et al. (2006), Cao and Pan (2006), Fan et al. (2007), Leion, Mattisson and & Lyngfelt (2007); Berguerand, N., and A. Lyngfelt (2008)

Advantages of CLC Technology

1) **Produces a separate CO_2/H_2O gas stream**
   - No cost of separation
   - Separation of H_2O on cooling/compression
   - CO_2 stream at process pressure
   - Could contain CO, H_2, unburned fuel, SO_2, fuel-N, Hg, …

2) **No/Low NO_x**
   - No thermal or prompt NO_x (low T of Air Reactor)
   - No “hot-spots” (fluidized bed processes)
   - ***Fuel NO_x … not determined (???)***

3) **In-bed tar cracking and control**
   - Metal oxides are currently used to catalyze tar cracking

4) **Compatible with S-capture technologies**
   - S sorbent could be added to the bed.

Advantages of CLC Technology (cont.)

4) **CLC uses well-established boiler technology**
similar to CFB boilers

5) **Hg removal would be facilitated**
smaller volume, more concentrated stream from FR

6) **Heavy metals (including Hg) may stay with the ash at lower T**

7) **Fewer materials concerns**
lower temperatures than conventional combustion

8) **Small vessel sizes/ lower construction costs**
higher volumetric heat release rate than conventional combustion

9) **Higher thermodynamic efficiency**
possible for some systems (decrease irreversibility)

10) **Improved H_2O utilization**

Disadvantages of CLC Technology

1) **Carrier circulation**

   Solids handling

   Non-mechanical valves

2) **Dual reactors**

3) **Carrier issues: fabrication, durability, poisoning, …**

4) **Lower exhaust gas temperature (<1000 ºC)/pressure**

   Difficult to couple to a gas turbine – loss in efficiency

Criteria for Carriers (Ni-, Cu-, Fe-, … ; $CaSO_4$/CaS)

- **Chemical**
  - Complete conversion at (T,P)
  - High reactivity – cyclic oxidation and reduction rates
  - Multiple oxidation states – oxygen carrying capacity
  - Light weight
  - No carbon deposition
  - Interaction with support & trace elements: S, N, Al, Si, Fe, Hg, K, Na, …
- **Physical**
  - Attrition
  - Agglomeration
- **Economics**
  - Raw materials (carrier + support)
  - Fabrication
  - Durability
- **Environmental - Benign**
  - CLC process
  - Extraction process

Carrier Properties
$3\ MO + HC \rightarrow M + CO_2 + ½\ H_2O$

- **Thermodynamic – fully convert HC to CO_2 & H_20**

  Fe_2O_3 >> Fe_3O_4 >> FeO >> Fe

  100% 70% 40% conversion

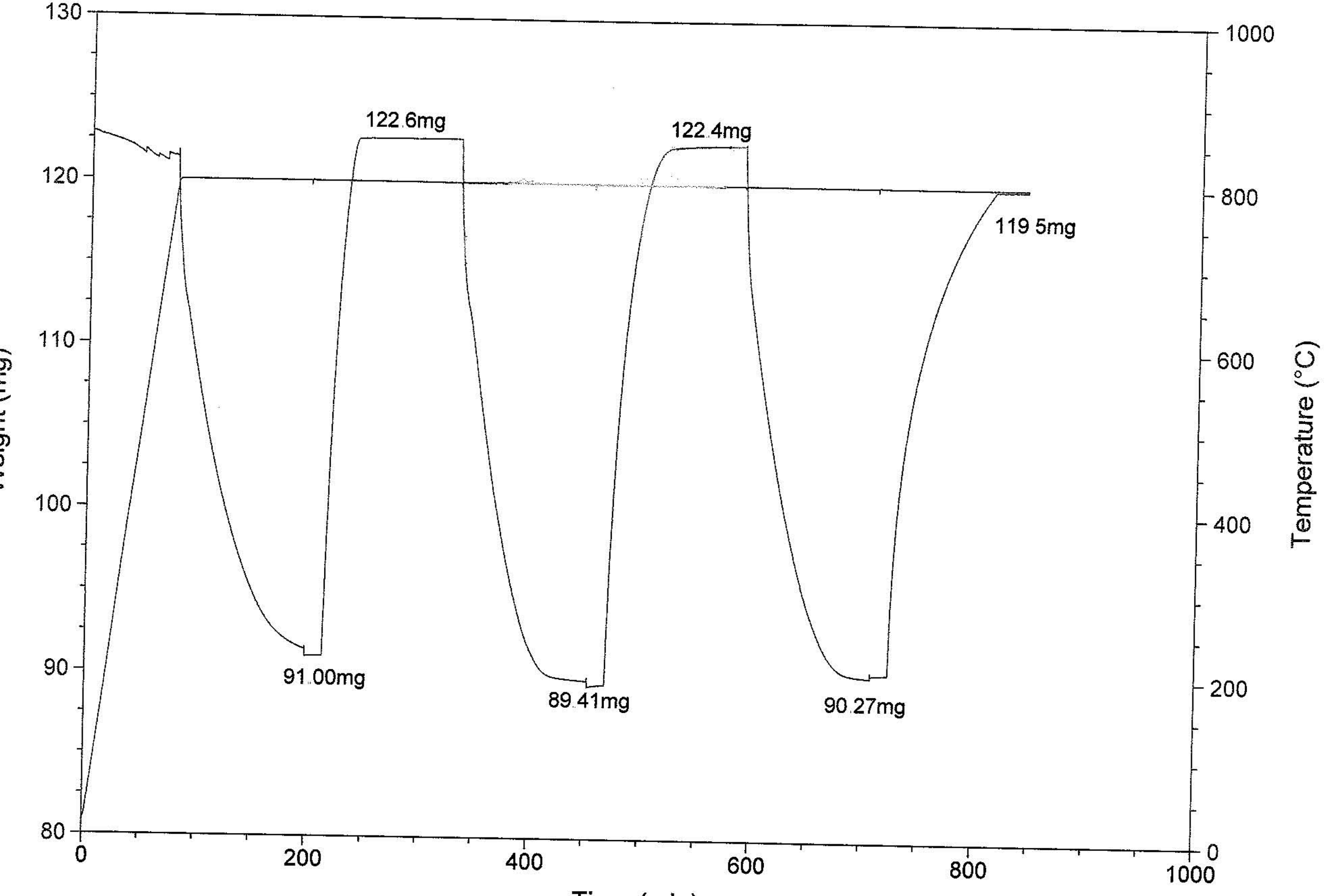
  CuO >> Cu_2O >> Cu

  NiO >> Ni
- **Kinetic – reactive for red/ox**
- **Durability – cycling (physical, chemical, thermal)**
- **Cost – materials, fabrication, lifetime**
- **Environmental - benign**

Sample: Empire Standard Pellet, 3/02/09
Size: 122.8720 mg
Method: 10cycle.mth
Comment: 800 degrees C with syn.gas; Tom O'brien

TGA

File: C:\TA\Data\TGA\Data.390
Operator: TS
Run Date: 3-Mar-09 09:32
Instrument: 2050 TGA V5.4A



Carrier Types

- **Pure material vs supported**
- **Fabricated vs natural**
- **Cu, Ni, Fe, limestone (CaS/$CaSO_4$)**

Carrier Types

- **Pure material vs supported**
- **Fabricated vs natural**
- **Cu, Ni, Fe, limestone ($CaS/CaSO_4$)**

…. Natural Commodity Carriers

- taconite
- iron ore
- magnetite sand
- ilmenite
- limestone pellets

Taconite
mineral <> concentrate <> pellet

Taconite mineral: hard rock

~ 20% Fe (Fe_3O_4, magnetite)

Taconite concentrate: ~20-40 µm powder,

~ 65% Fe (Fe_3O_4, magnetite)

Taconite pellets: ~ 8 mm sintered sphere

~ 65% Fe (Fe_2O_3, hemtite)

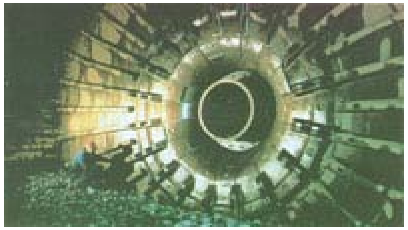
$50/tonne

reactive

durable

commodity (natural??)

Taconite (ore-to-pellet) Process



- **Crushing - the taconite ore is crushed to pea size, then mixed with water and ground in rotating mills until it is a fine powder (~10 micron).**

- **Separation - the iron ore concentrate is separated from the taconite using magnetism. The tailings are dumped into a holding basin.**

- **Pellets - the concentrate (the wet taconite powder) is rolled with clay in large rotating furnaces, forming marble-sized balls. These are dried and sintered to form taconite pellets.**

- **Steel - the taconite pellets are shipped to steel-making facilities.**
  - Filter cake (~10 micron, 80% Fe)
  - Pellet formation (to spec)
  - Tailings (~10 micron, 20% Fe)

www.dnr.state.mn.us/education/geology/digging/taconite.html

Taconite Rock Aggregate

Taconite Pellet Shipping Facility
Silver Bay, MN

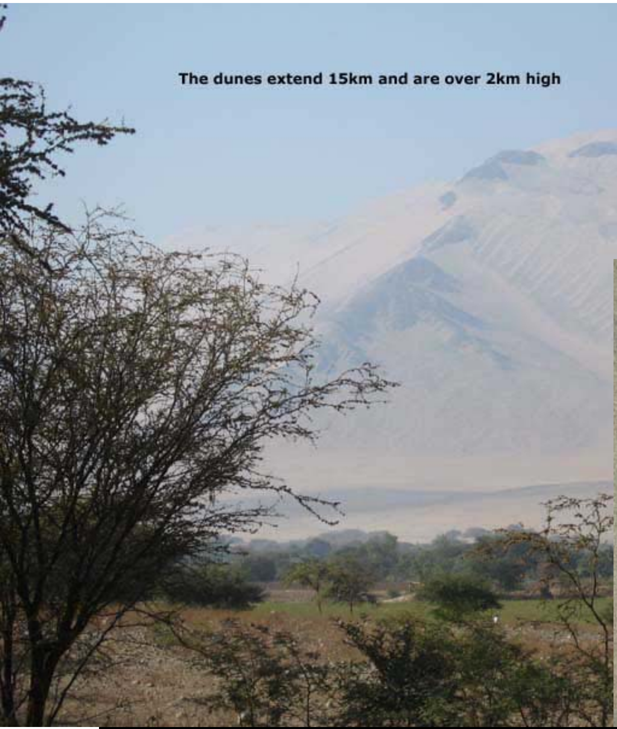
Michigan (Escanaba)

Iron Ore

- **Pellets are preferred for blast furnace operation**
- **Ores are of various types**
  - Rock >>> sinters
  - Powder >>> pellets
- **Durability – support the blast furnace “burden”**
- **Reactivity – H_2, CO, CH_4**
- **Cost – dirt cheap (but not as cheap as limestone)**
- **Benign!**

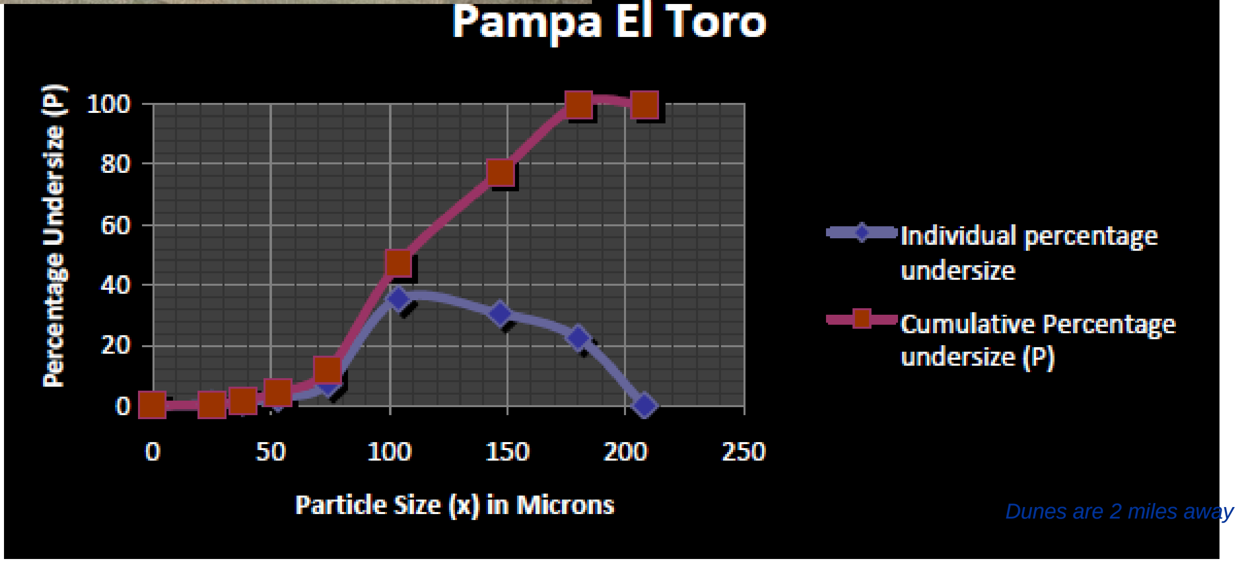
Australian (Tom Price)

Peru - Cardero black sand



	Particle size in microns (x)	Individual percentage undersize	Cumulative Percentage undersize (P)
mesh	0	0	0
500	25	0.4	0.4
400	38	1.3	1.7
270	53	2.7	4.4
200	74	7.2	11.6
150	104	35.4	47
100	147	30.5	77.5
80	180	22.4	99.9
65	208	0	99.9

Fe particles are magnetic



Dunes are 2 miles away

Peru - Cardero Fe Ore

Critical Design Issues in the Fuel Reactor
(to be addressed by multi-phase CFD)

- **Volatile fuel … must be converted in the bed**
  - Fuel, CO or H_2 will escape the FR
    - Additional compression costs
    - Returned to the FR (or used as syngas for topping)
- **Char … must be burned out**
  - Incomplete conversion
    - Large residence time/reactor size
    - Tendency to move to the AR

Critical Issues between FR & AR

(to be addressed by multi-phase CFD)

- **Char … must not flow into the AR from FR**
  - Fuel combustion in the AR
    - Additional heat release in the AR
    - CO_2 released will escape capture
- **Air … must not leak into the FR from AR**
  - N_2 will contaminate the CO_2/H_20 stream
    - Additional compression costs
    - Inerts would be returned to the AR

CFD Model
Heavily-loaded, Reactive Multiphase Flow (Interpenetrating Continua)

- **Each granular material (coal & carrier) is an inter-penetrating continua >>> a "Navier-Stokes" eq.**
- **The interstitial fluidizing gas >>> a Navier-Stokes eq.**
- **Temperature eq. for each phase**
- **"Granular temperature" equation for the granular phases**
- **Global homogeneous and heterogeneous chemistry**

These PDE's are closed by a variety of constitutive laws and coupled by transfer of mass, momentum, and energy.

Fluent-ANSYS (http://www.fluent.com/) or MFIX (https://mfix.netl.doe.gov/)

Chalmers Quartz FB Reactor

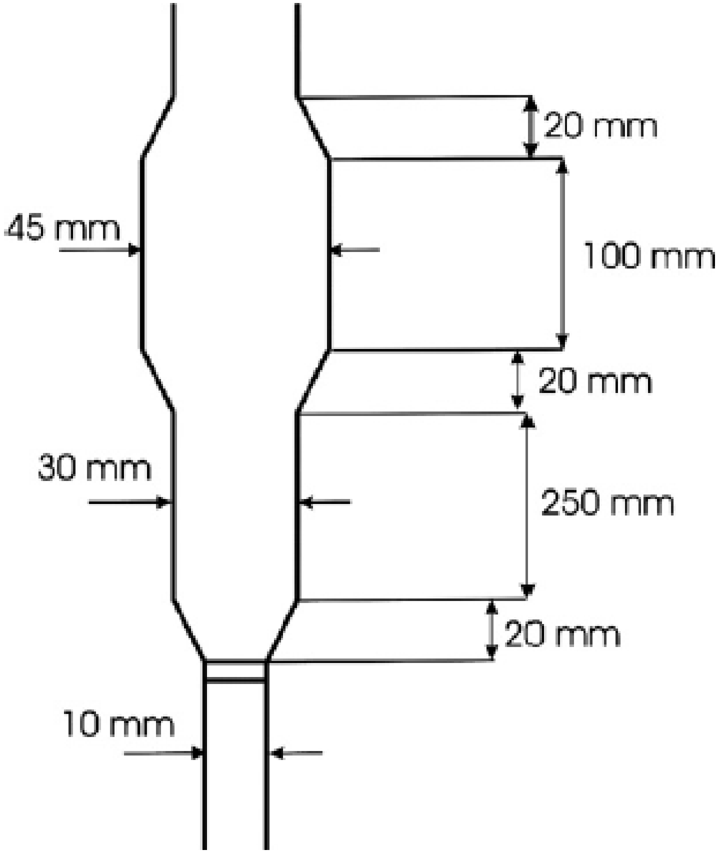


Fig. 2. Fluidized-bed reactor of quartz.

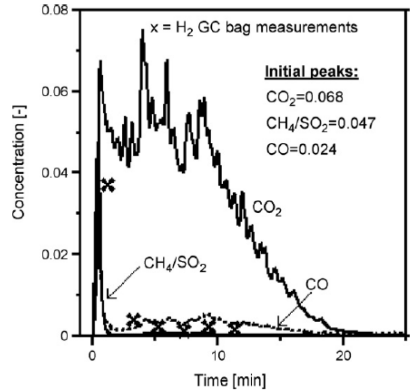


Fig. 4 – Concentration profile during the reduction of 40 g $Fe_2O_3/MgAl_2O_4$ with 0.2 g petroleum coke. The inlet concentration of H_2O is 50%. The temperature is 950 °C.

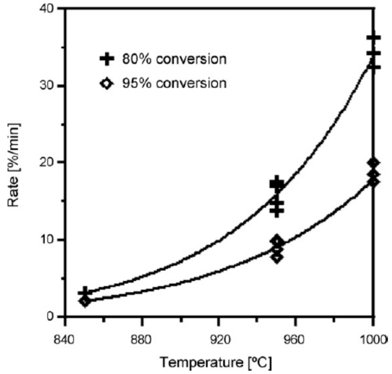


Fig. 15 – Average rate of reaction to reach 80% and 95% conversion for 0.2 g of South African coal in 40 g of ilmenite as a function of temperature. The fluidizing gas contained 50% H_2O.

Leion, H., T. Mattisson and A. Lyngfelt,
“Solid fuels in chemical-looping combustion,”
*Inter. J. Greenhouse Gas Control **2,** 180–193, 2008.*

Chemical Reaction Scheme
(*in-situ* gasification)

Coal devolatilization

$$Coal \rightarrow aChar + b\underset{Soot}{C} + cCH_4 + dC_2H_6 + eCO + fCO_2 + gH_2 + hH_2O + iAsh$$

The coefficients (*a* through *i*) are determined from the ultimate and proximate analysis of the coal

Char gasification … by H_2O

$$Char\left(CH_{0.0245}O_{0.001531}\right) + H_2O \rightarrow CO + 1.00842H_2 + 0.001531H_2O$$

Char gasification … by CO_2

$$Char\left(CH_{0.0245}O_{0.001531}\right) + CO_2 \rightarrow 2CO + 0.00842H_2 + 0.001531H_2O$$

Chemical Reaction Scheme

Hematite/Magnetite reduction: CO, H_2, CH_4, and C_2H_6

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

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$

$$12Fe_2O_3 + CH_4 \rightarrow 8Fe_3O_4 + 2H_2O + CO_2$$

$$21Fe_2O_3 + C_2H_6 \rightarrow 14Fe_3O_4 + 3H_2O + 2CO_2$$

Water-Gas-Shift Reaction

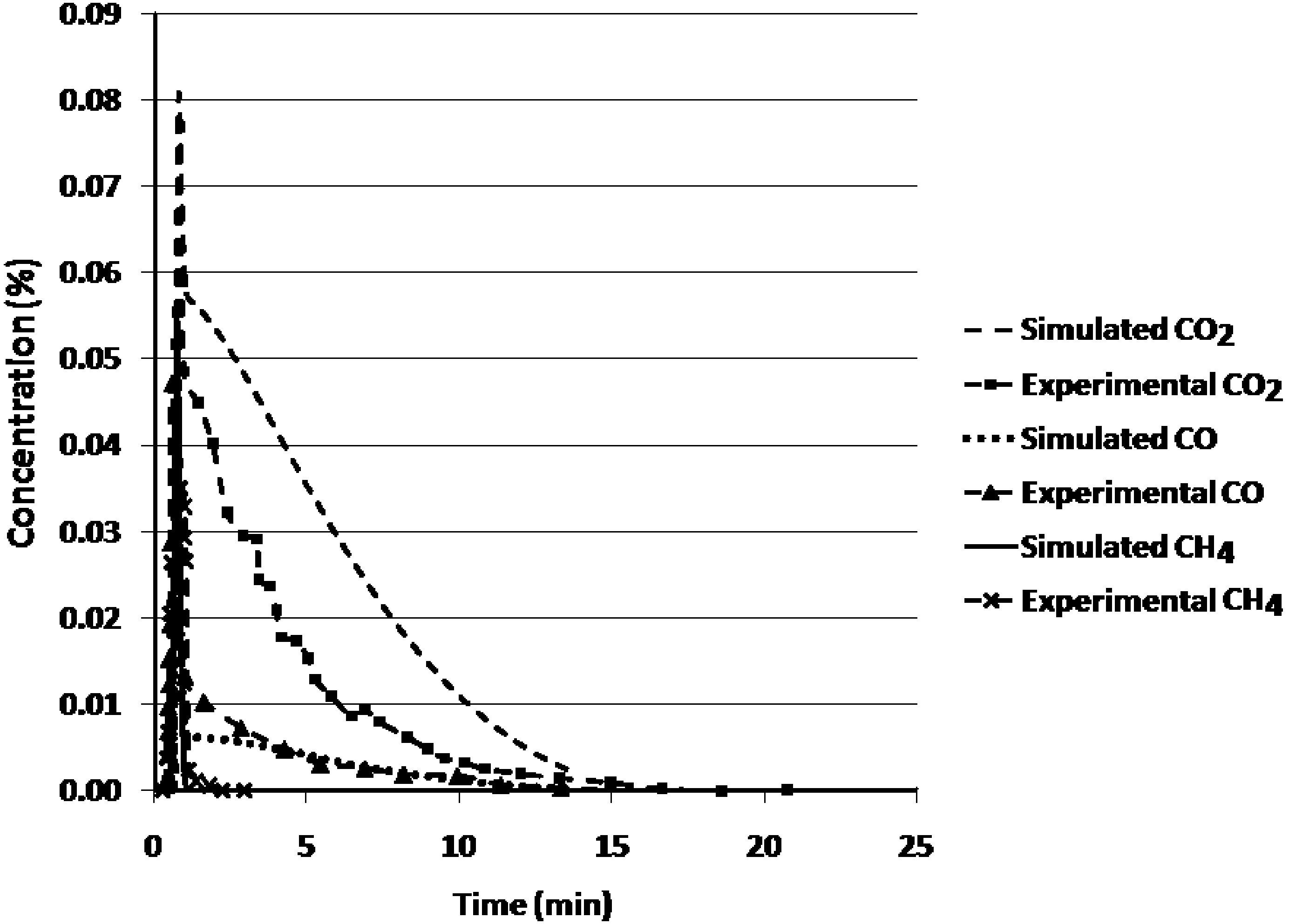
$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

Simulated fuel reactor properties (Leion *et al., 2008)*

Diameter of bed	**10 – 30 mm**
Gas flow rate (STP): 50%H_2O/50%N_2	**600 ml/min**
Mass of Fe_2O_3 carrier particles	**40 g**
Mass of injected coal	**0.1 g**
Mean diameter of carrier particles	**105 μm**
Mean diameter of SA coal particles	**150 μm**
Mean density of carrier particles (including support)	**4500 kg/m^3**
Initial density of coal particles	**2000 kg/m^3**

H. Leion, T. Mattisson, A. Lyngfelt, Solid fuels in chemical-looping combustion, Inter. J. Greenhouse Gas Control, 2 (2008) 180-193.

Concentrations of CO_2, CO and CH_4 calculated vs. experimental Leion *et al.*, 2008.



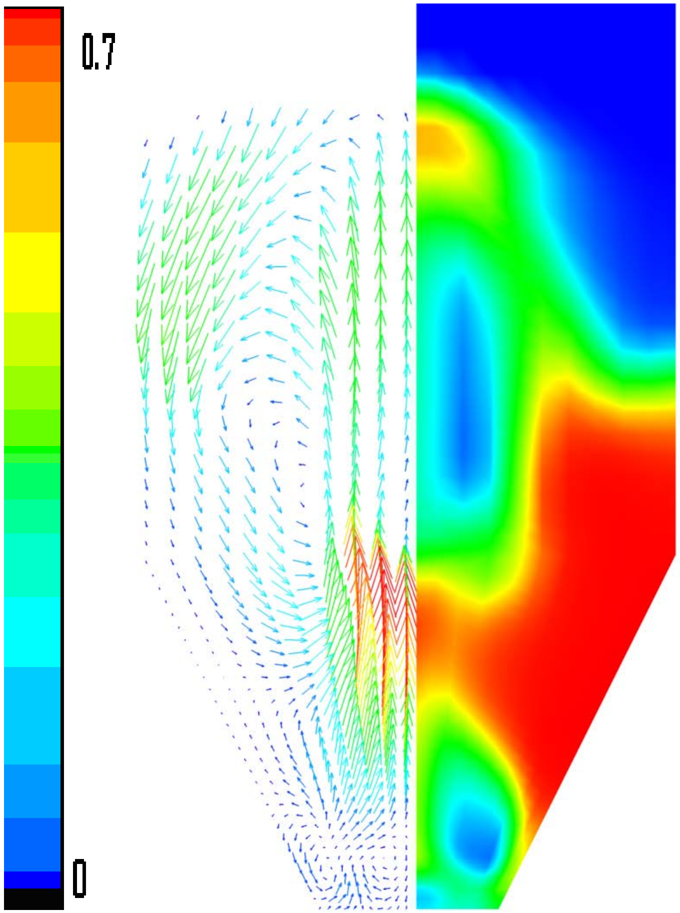
H. Leion, T. Mattisson, A. Lyngfelt, Solid fuels in chemical-looping combustion, Inter. J. Greenhouse Gas Control, 2 (2008) 180-193.

Peak Concentration of Gas Species

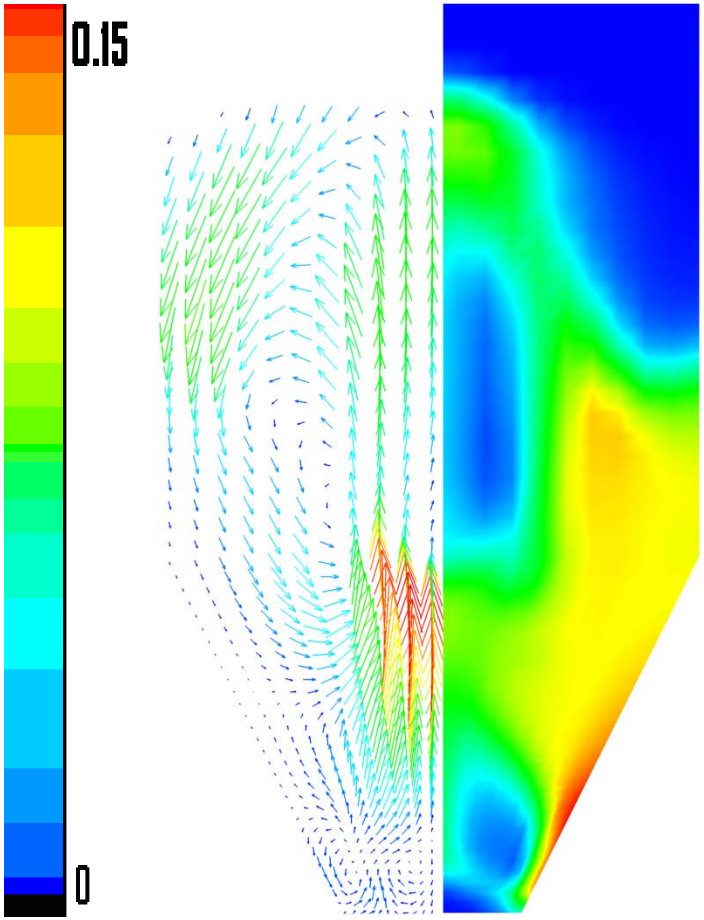
	Peak Concentration (Experimental)	Peak Concentration (Simulation)
CH_4	0.036	0.049
CO_2	0.078	0.081
CO	0.047	0.032

H. Leion, T. Mattisson, A. Lyngfelt, Solid fuels in chemical-looping combustion, Inter. J. Greenhouse Gas Control, 2 (2008) 180-193.

Vol. fract. & velocity of Fe oxide and coal at 175 seconds

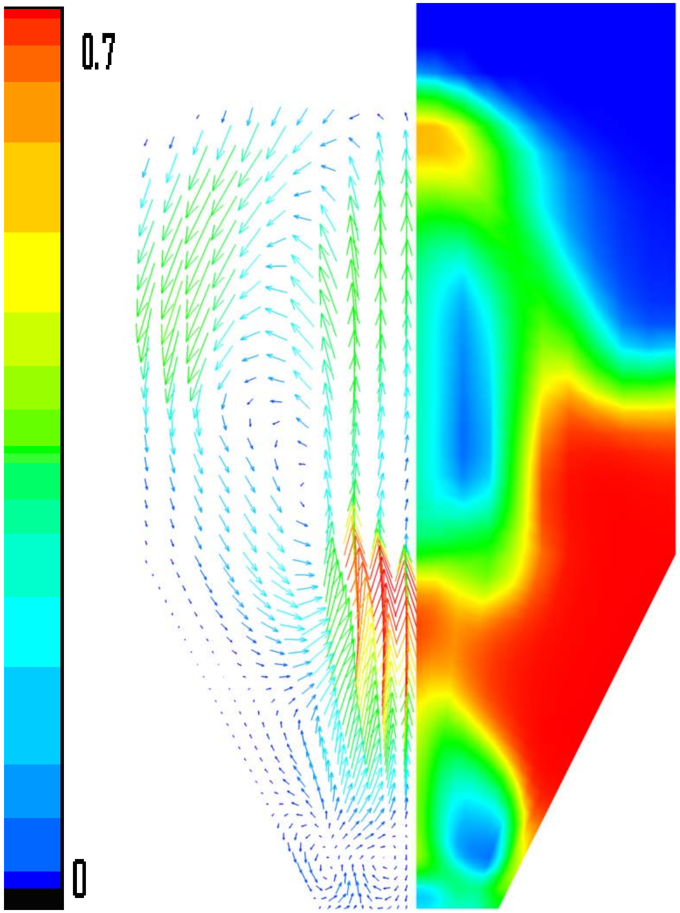


Fe oxide

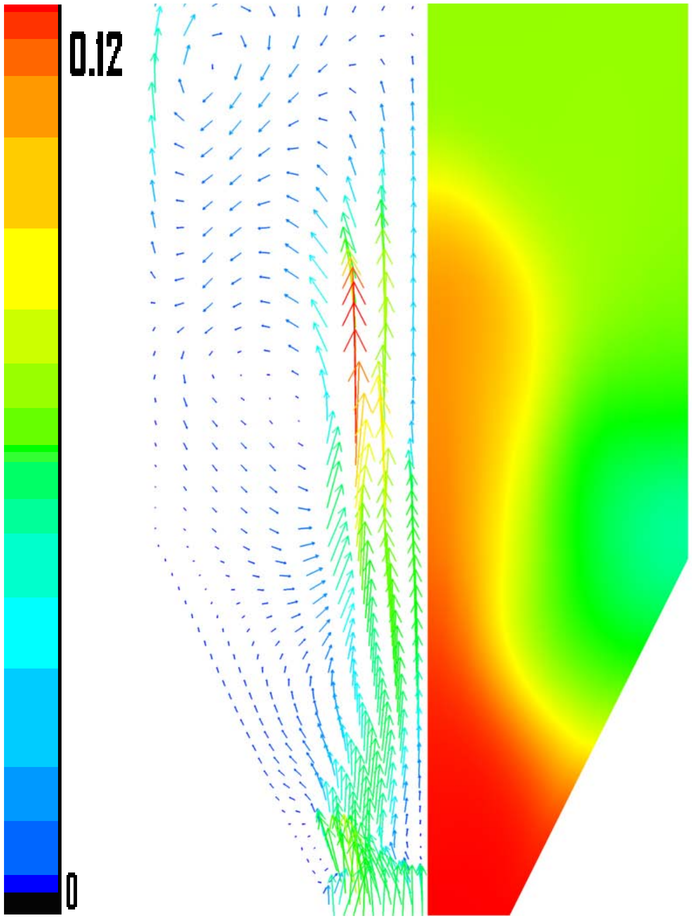


Coal (x100)

Volume fraction & velocity of Fe oxide
Mass fraction & velocity of CO_2
at 175 seconds

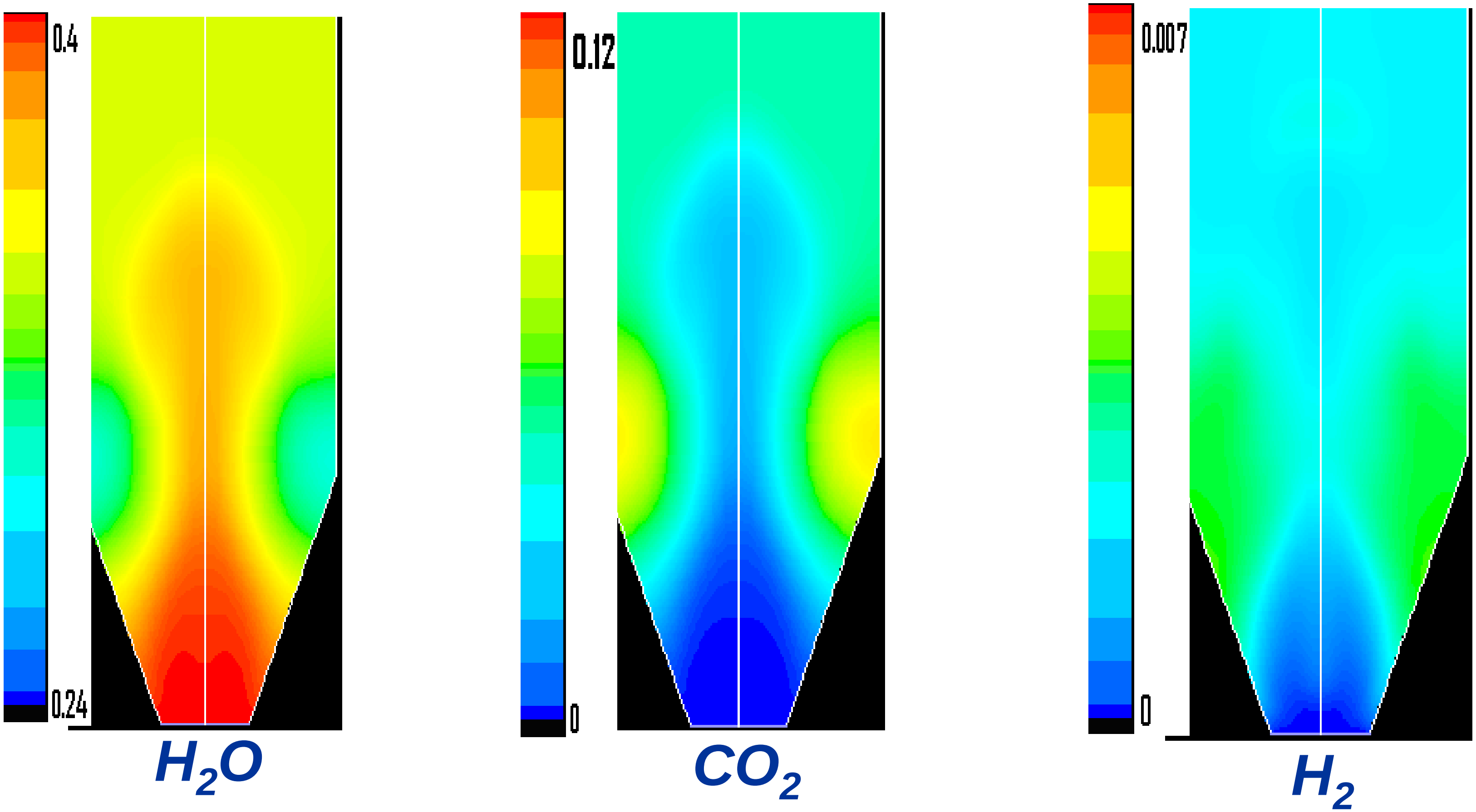


Fe oxide



CO_2

Gas species mass fractions at 175 seconds



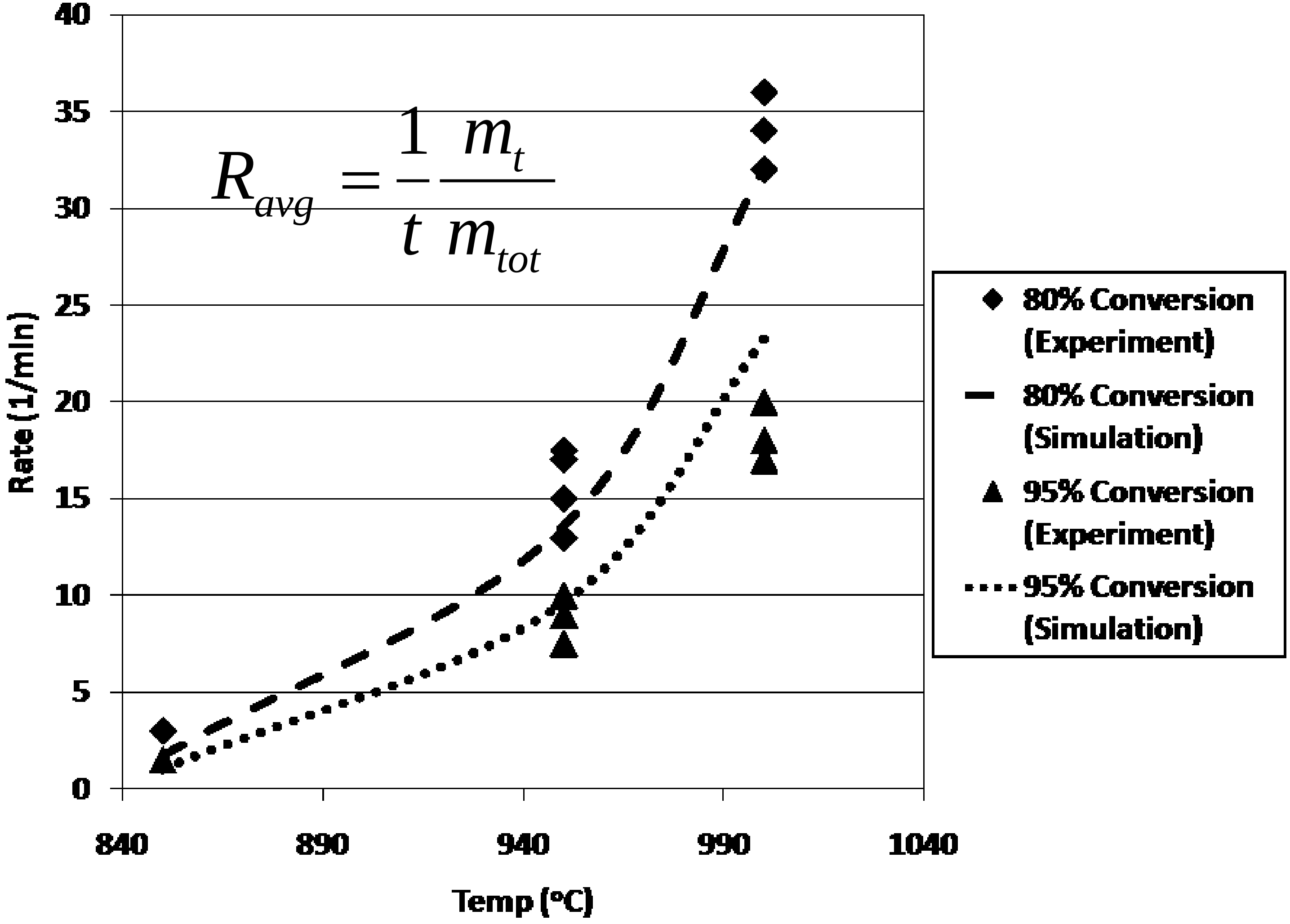
$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$

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

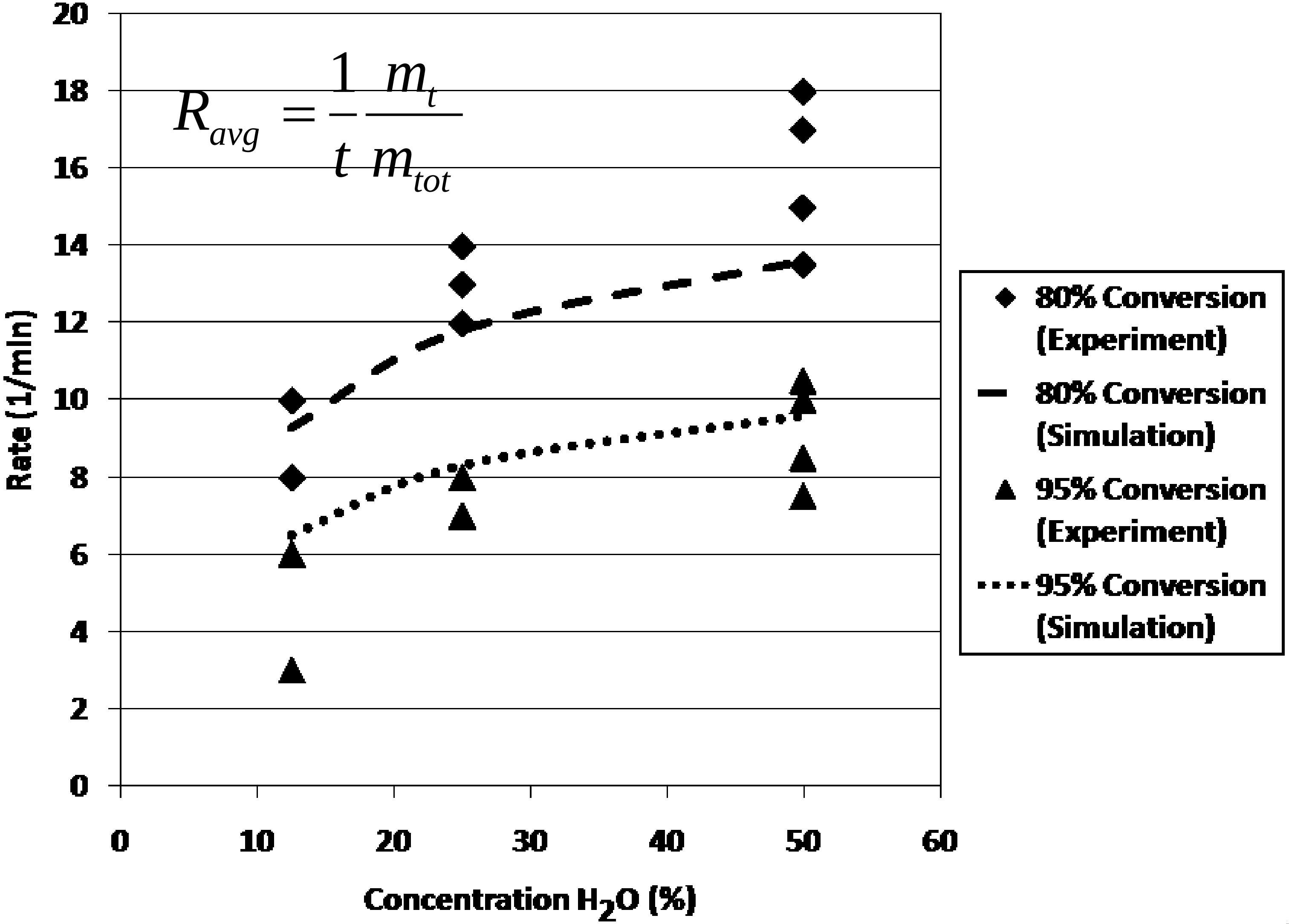
$$Char + H_2O \rightarrow CO + 1.00842H_2 + 0.001531H_2O$$

$$Coal \rightarrow aChar + cCH_4 + eCO + fCO_2 + gH_2 + hH_2O$$

The average coal reaction rate at different operating temperatures



The average coal reaction rate at different steam concentrations



Simulation of Lab-Scale CLC of Petcoke

(Leion *et al.*, 2007)

Experimental Parameters	
Temperature	1223 K (950 C)
Pressure	1 atm
Carrier	Fe_2O_3
Fluidization Vel.	0.55 m/s ~50 u_{mf}

Chemical Kinetics	
Devolatilization	Nagpal (2005)
Gasification	Everson
Carrier Kinetics	Donskoi and McElwain (2001)

Thanks to …

Kartikeya Mahalatkar (ANSYS-Fluent)
Dave Huckaby (NETL-DOE)
John Kuhlman (NETL-WVU

Leion, H., T. Mattisson and A. Lyngfelt,
"The use of petroleum coke as fuel in chemical-looping combustion,"
Fuel **86**, 1947–1958, 2007.

Chemistry Scheme

Coal Devolatilization

$$Coal \rightarrow aChar + b\underset{Soot}{C} + cCH_4 + dC_2H_6 + eCO + fCO_2 + gH_2 + hH_2O + iAsh$$

Water-Gas Shift Reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Char Gasification by CO_2

$$Char(CH_{0.0245}O_{0.001531}) + CO_2 \rightarrow 2CO + 0.00842\ H_2 + 0.001531\ H_2O$$

Char Gasification by H_2O

$$Char(CH_{0.0245}O_{0.001531}) + H_2O \rightarrow CO + 1.00842H_2 + 0.001531H_2O$$

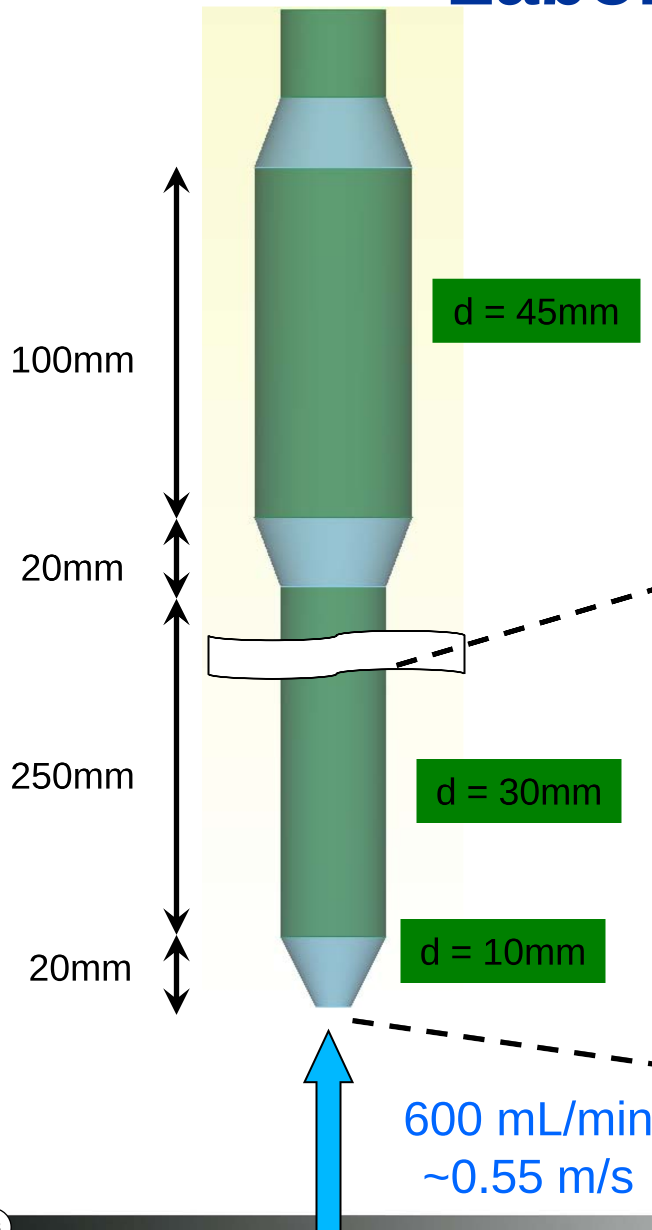
Hematite Reduction

$$12Fe_2O_3 + CH_4 \rightarrow 8Fe_3O_4 + 2H_2O + CO_2$$

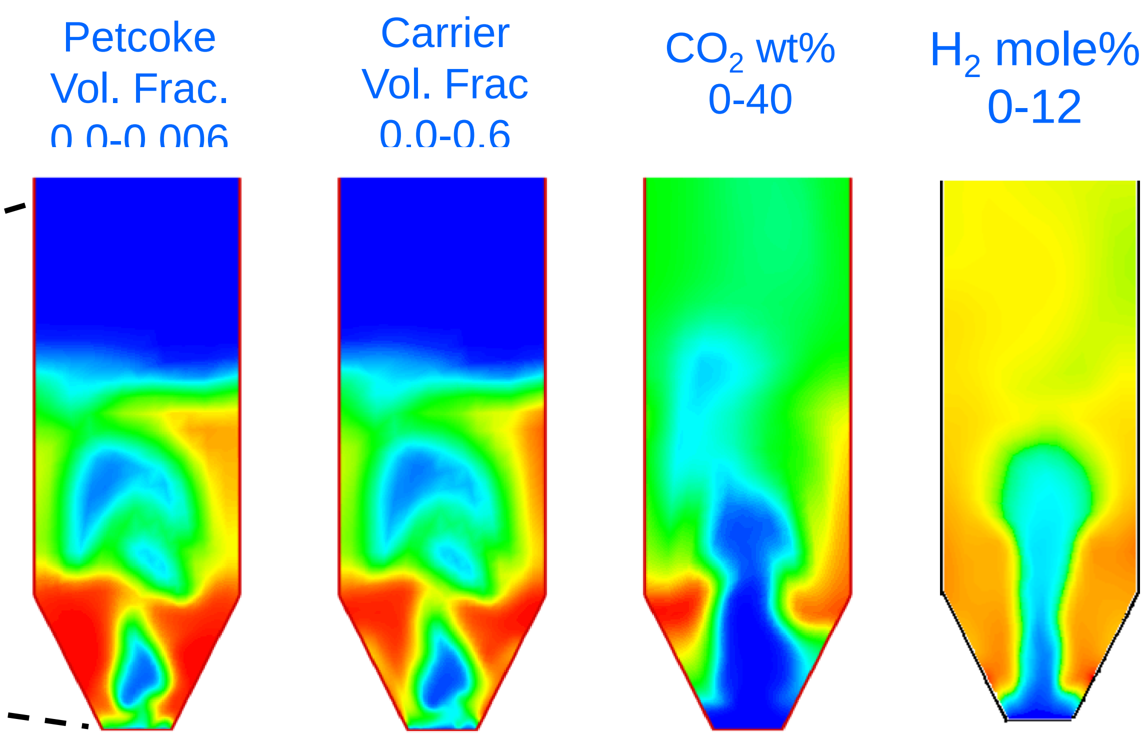
$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$

Laboratory Petcoke CLC



- **Petcoke and Metal Oxide are well mixed**
- **Only small quantities of H_2 leak through bubbles**



- Fuel Consumption: 50/50 wt% H_2O/N_2
- Carrier Oxidation: 10/90 wt% O_2/N_2

Laboratory Petcoke CLC

Results from y = 10m

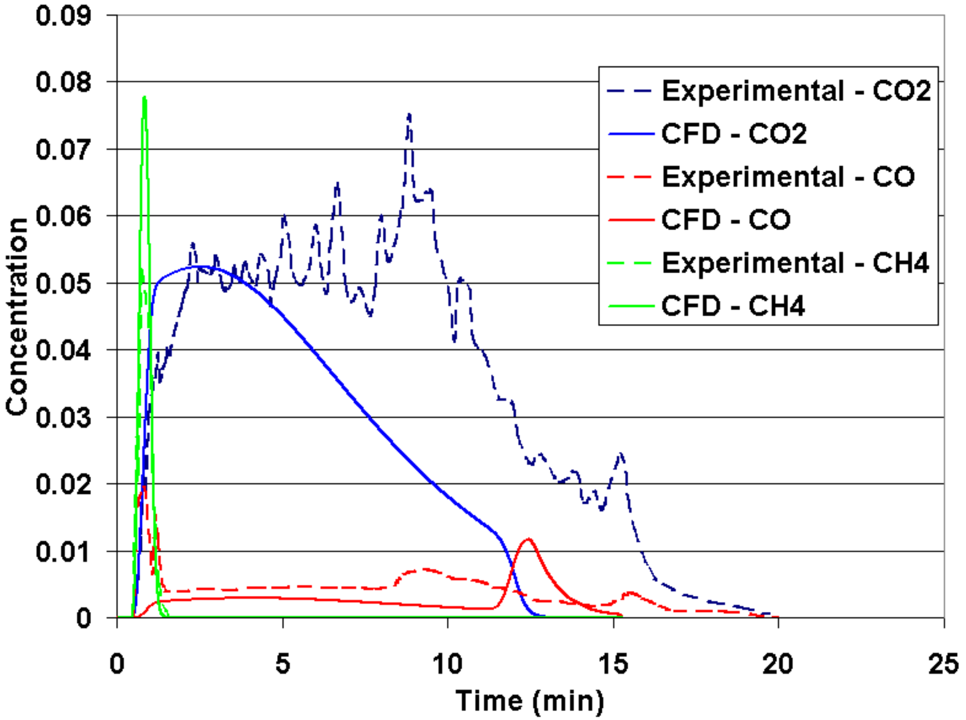
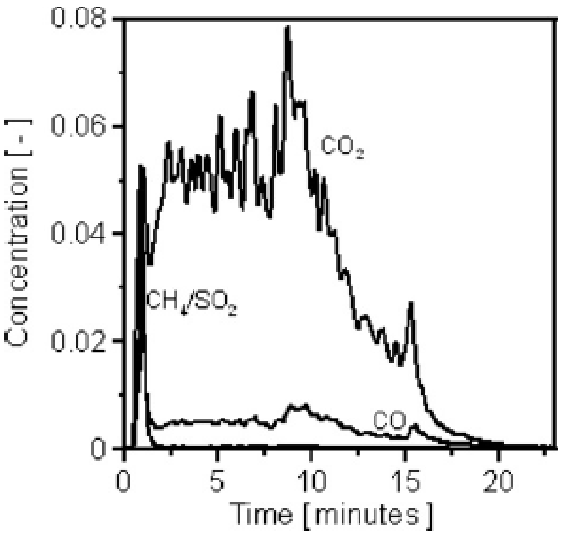
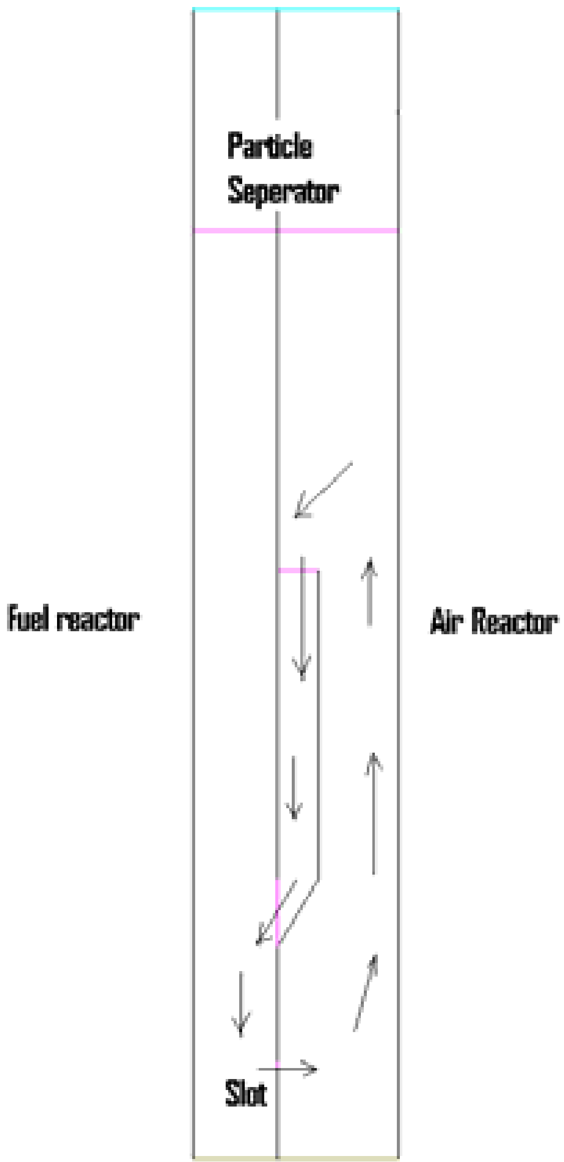


Fig 1: Concentration of CO_2, CO and CH_4 at time delay of 30 seconds

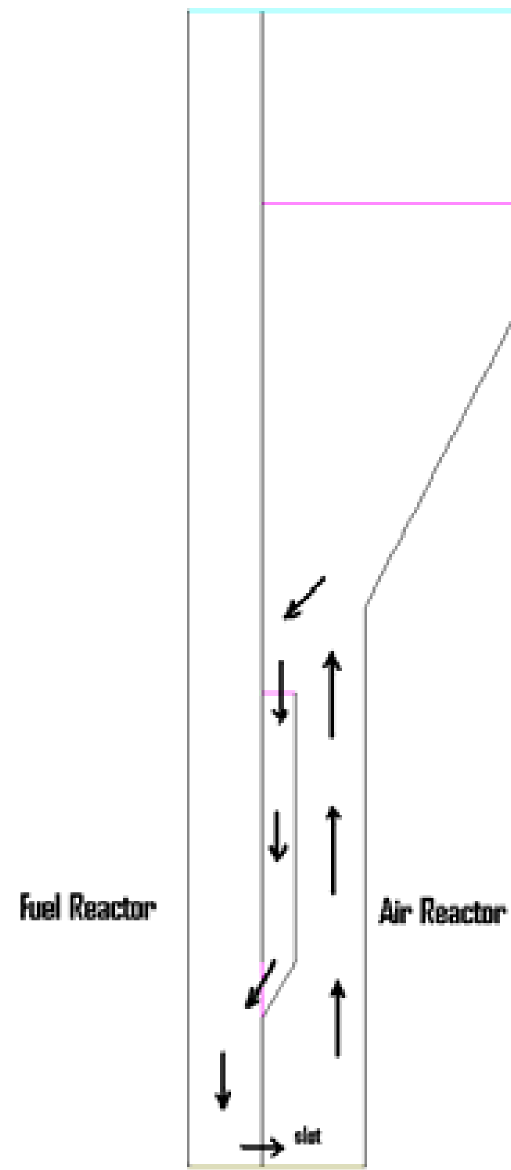


- **Lower concentration of CO_2 is because of assumption of 2D Cartesian geometry**
- **Differences in experimental and numerical CH_4 and CO concentration is due to inherent uncertainties in the volatile composition.**

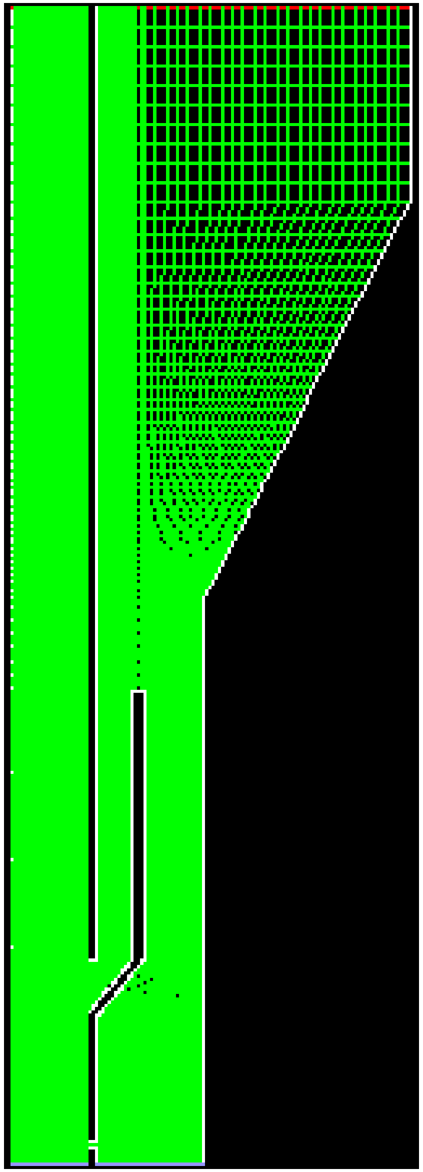
Full CLC system: Kronberger *et al.*(2004)

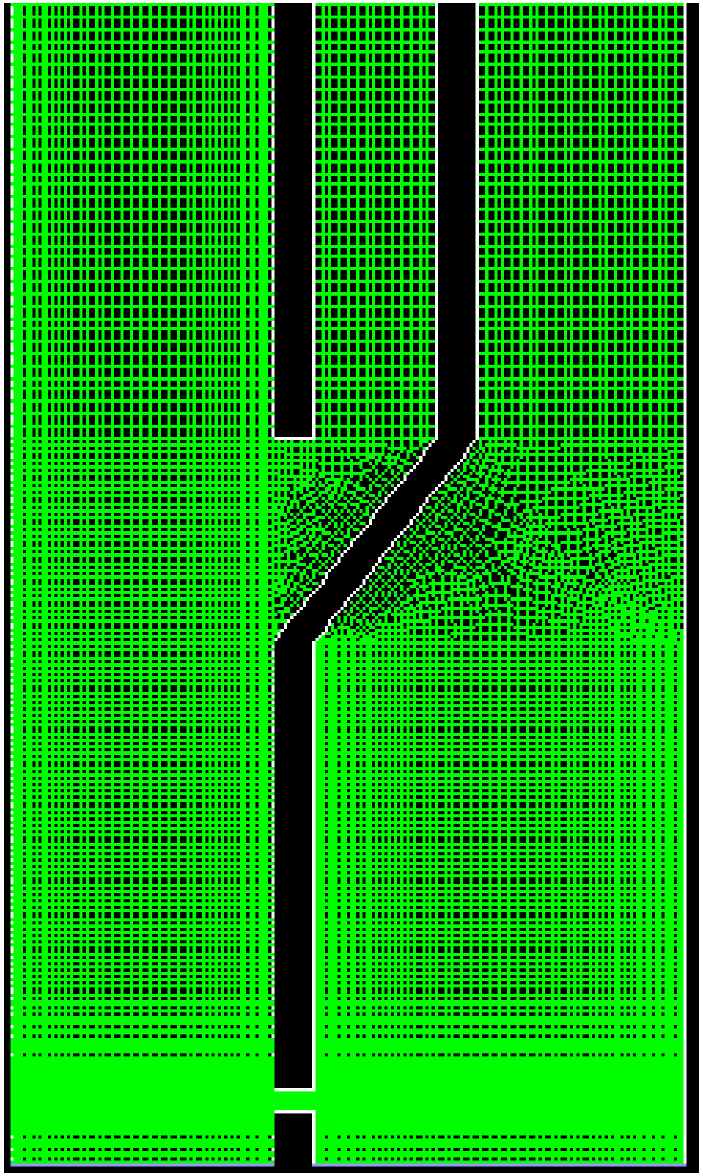


Actual experimental geometry



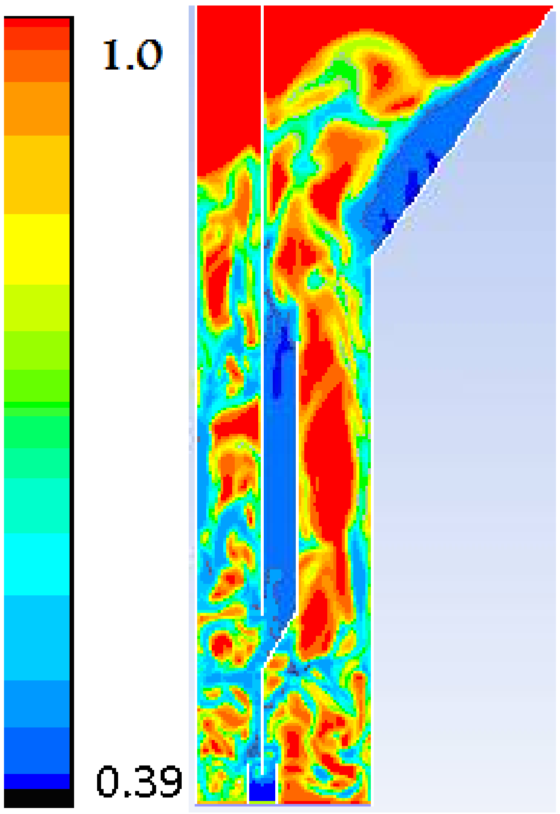
Simulated geometry





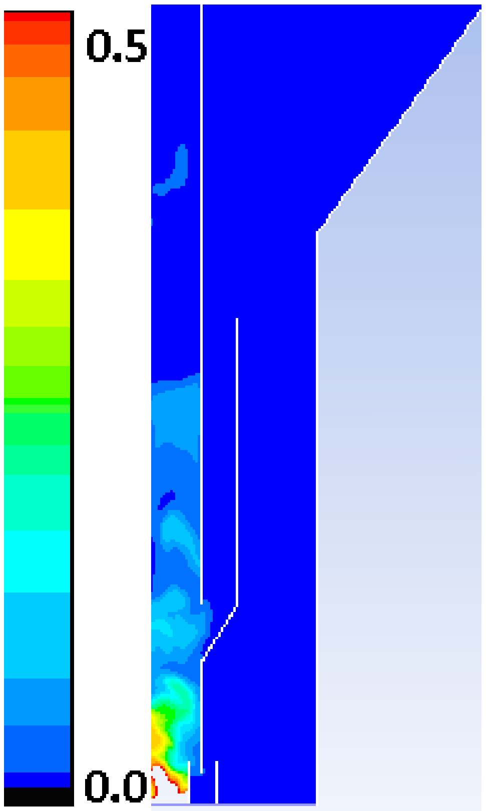
Gas phase snap shot

Operating temperature = 1123 K
FR flow rate of 7.5 x 10^{-6} m^3/s
AR flow rate of 83 x 10^{-6} m^3/s



Gas volume fraction

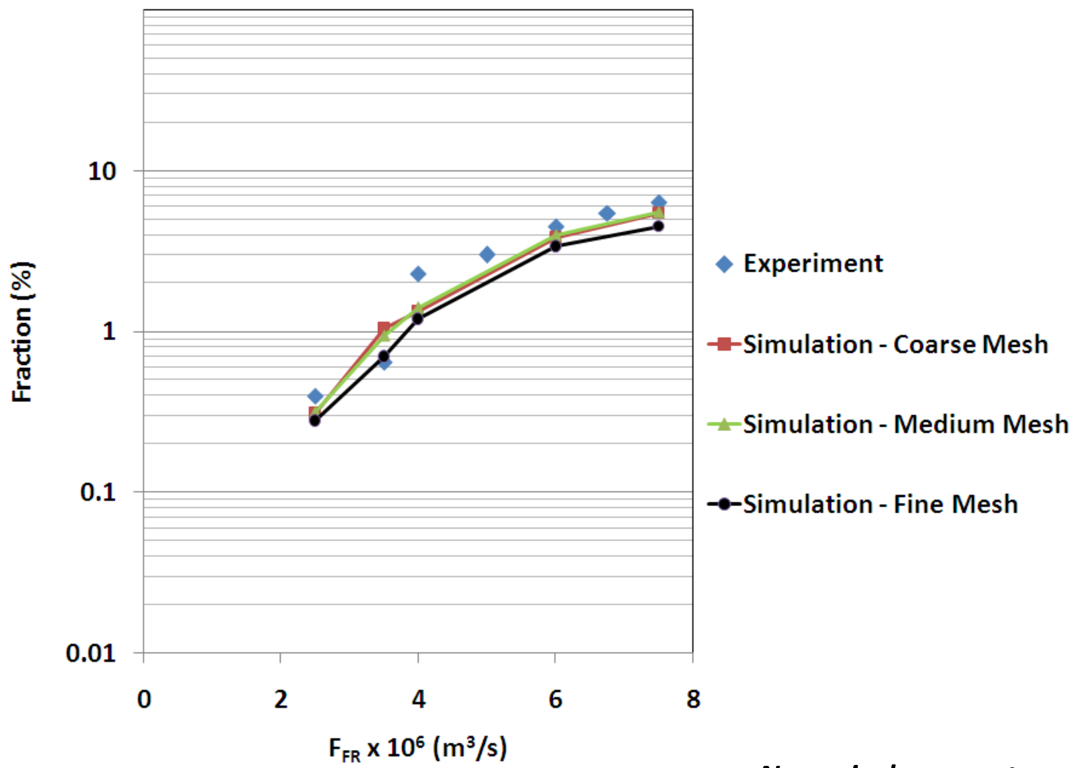
Oxidation Reaction:
$12MnO + 2O_2 \rightarrow 4Mn_3O_4$



CH_4 mole fraction

Reduction Reaction:
$4Mn_3O_4 + CH_4 \rightarrow 12\ MnO + CO + 2H_2O$

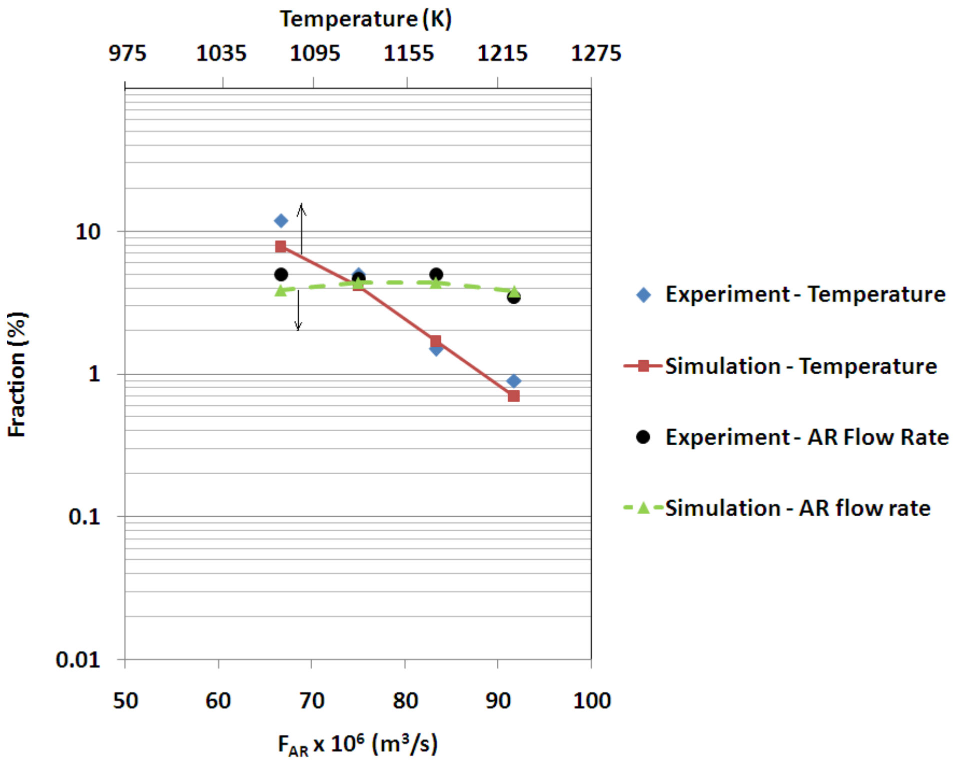
Variation in outlet CH_4 fraction ($X_{CH4}/(X_{CH4}+X_{CO}+X_{CO2})$) with change in FR flow rates



Numerical parameters of the simulation

	Coarse Mesh	Medium Mesh	Fine Mesh
Cell count	8822	17562	33745
Δt (sec)	2×10^{-4}	1×10^{-4}	2.5×10^{-5}

Variation in outlet CH_4 fraction $(X_{CH4}/(X_{CH4}+X_{CO}+X_{CO2}))$ with change operating T



Numerical parameters of the simulation

	Coarse Mesh	Medium Mesh	Fine Mesh
Cell count	8822	17562	33745
Δt (sec)	2×10^{-4}	1×10^{-4}	2.5×10^{-5}

Thanks you for your attention

Thanks to my co-authors

??? Questions ????