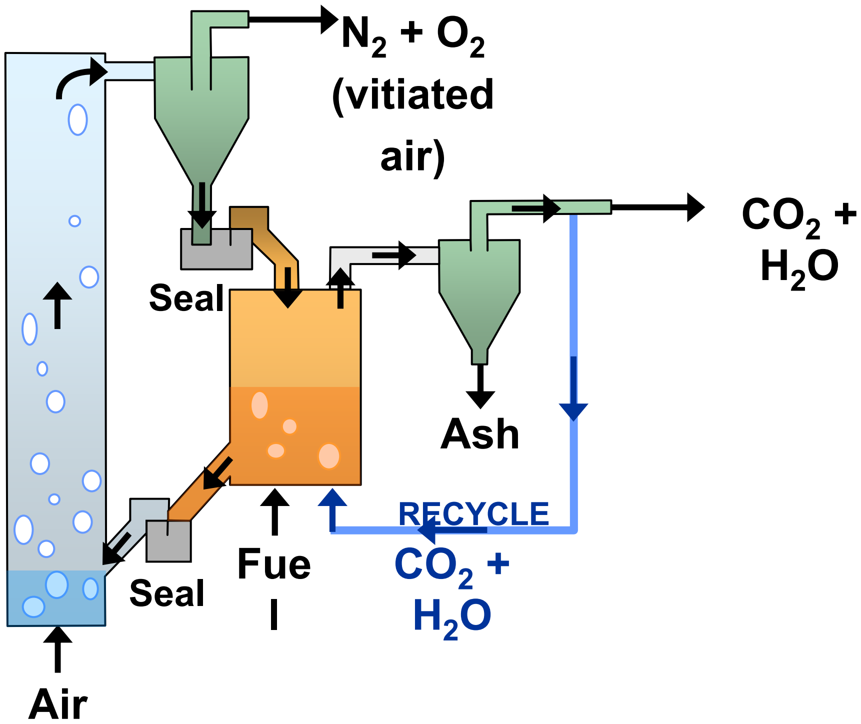


Issues in Chemical Looping Combustion

2006 NETL Multiphase Workshop

April 22-23, 2009

Thomas J. O'Brien, Chemist

Outline

- Backstory
- Description of Chemical Looping Combustion (CLC)
- Advantages/Disadvantages of the Technology
- History of the development of CLC
- Status of the technology
- CLC of solid fuels

Perspective

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

  ~1,015 million tons of coal in 2009,

  (~1,042 million tons in 2008, < 2.3%)

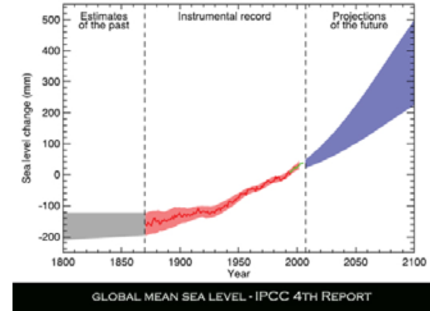
  ~10 million coal car loads (100 tons/car load)

  ~100,000 trains (100 cars/train)

  ~275 trains/day

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

Atmospheric CO_2 Overview



- **Atmospheric CO_2**

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

  - 284 ppm - pre-industrial level

  - 380 ppm – current

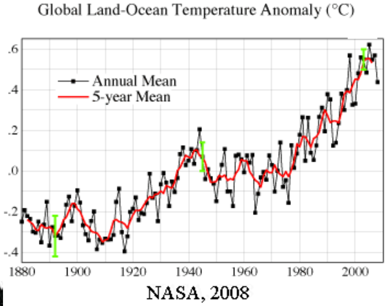
    (ΔT= 1 ºC/1.8 ºF)

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

  - 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)

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

EPA Endangerment Finding (4/17/2009)

Impacts that EPA believes may be significant for US citizens:

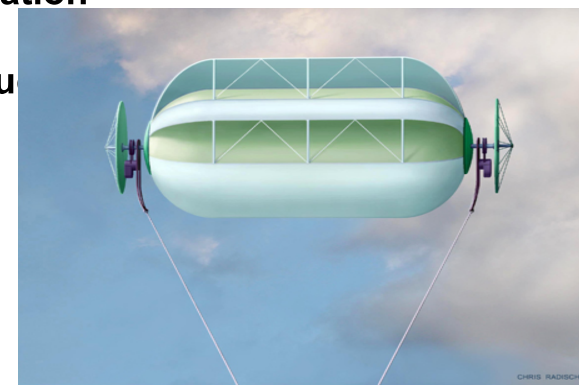
- an increased risk of droughts and floods
- sea level rise
- more intense storms and heat waves
- harm to water supplies, agriculture and wildlife

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

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

Options to Reduce CO_2 Emission

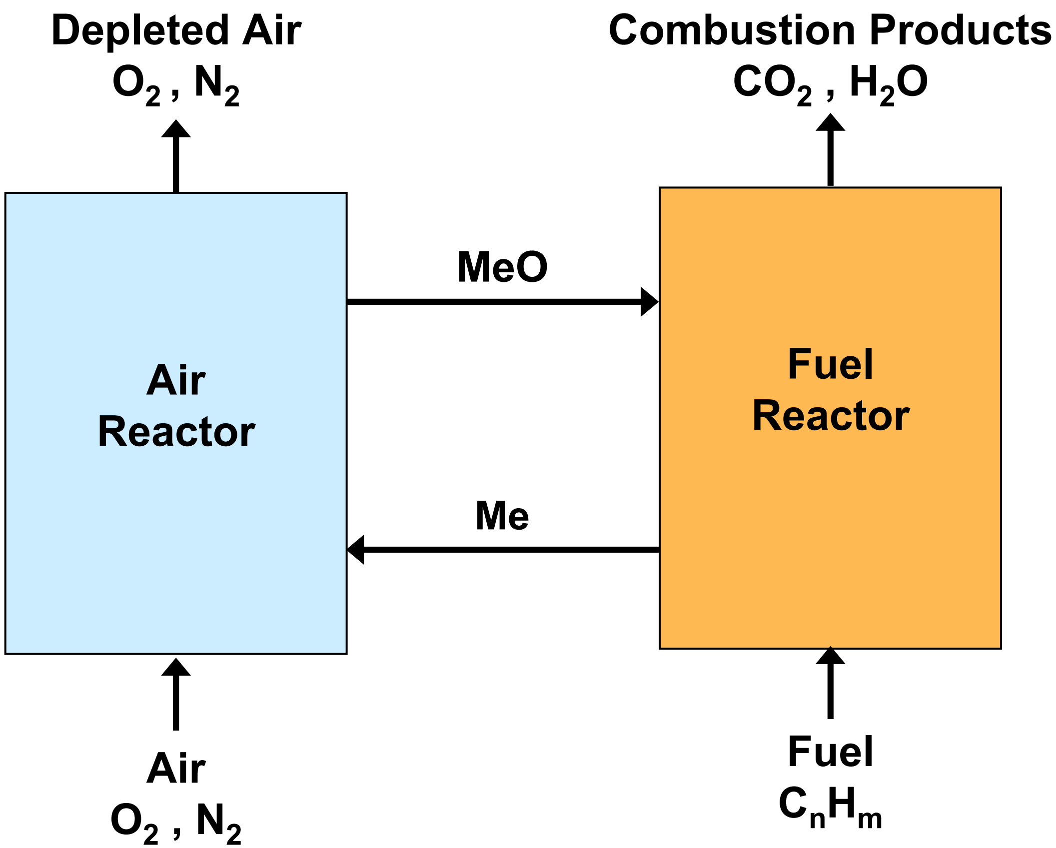
- **Conservation - modify life style and economy to reduce energy intensity**
- **Efficiency - increase efficiency of fuel conversion and utilization**
- **Fuel switching - Increase non-fossil fuel based power produ**
  - Solar
  - Nuclear
  - Biomass
  - Wind-power
  - Tidal
  - Geo-thermal
  - Hydro



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)

Schematic of a Chemical Looping Combustor



Generic CLC Reactions

Fuel Reactor (FR) – endothermic (usually) ($\Delta H_{FR} > 0$)

$$C_nH_{2m} + (2n+m)\ MeO \rightarrow (2n+m)\ Me + m\ H_2O + n\ CO_2$$

$$(CH_4 + 4\ NiO \rightarrow 4\ Ni + 2\ H_2O + CO_2)$$

Air Reactor (AR) – highly exothermic ($\Delta H_{AR} << 0$)

$$2\ Me + O_2 \rightarrow 2\ MeO$$

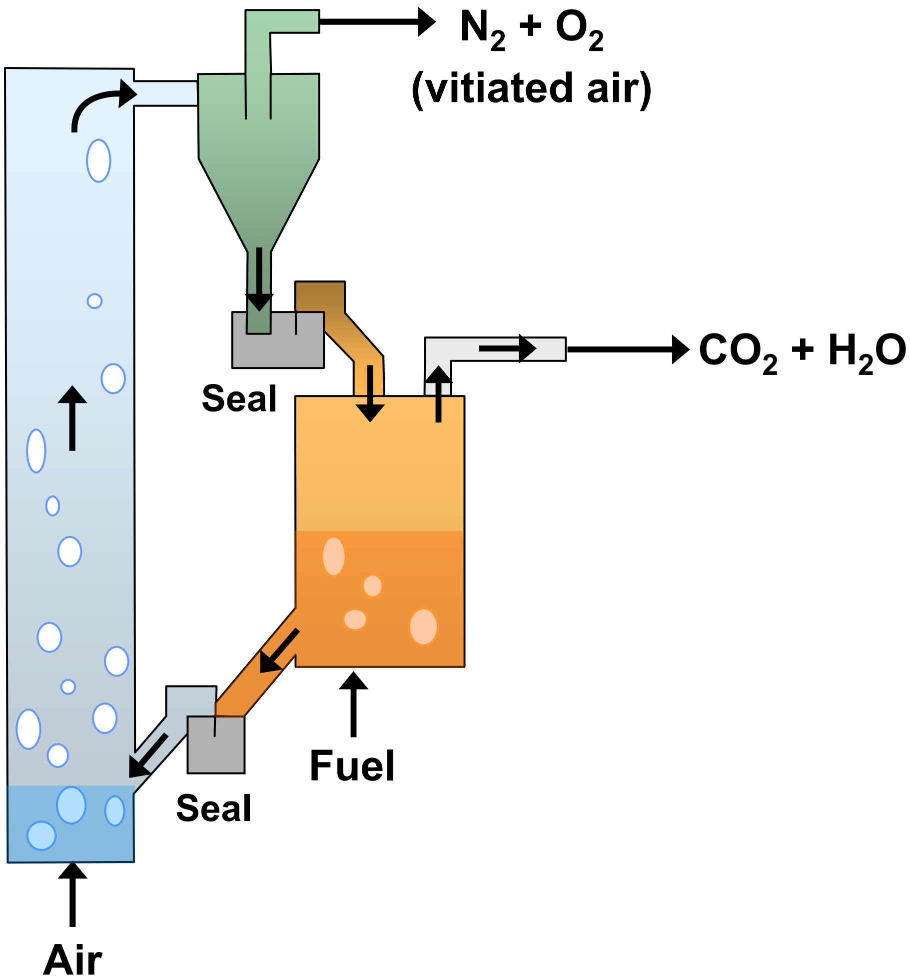
$$(2\ Ni + O_2 \rightarrow 2\ NiO)$$

Net Reaction – highly exothermic ($\Delta H_{FR} \equiv \Delta H_{FR} + \Delta H_{AR}$)

$$C_nH_{2m} + O_2 \rightarrow m\ H_2O + n\ CO_2$$

$$(CH_4 + O_2 \rightarrow 2\ H_2O + CO_2)$$

Chemical Looping Combustion Process (gaseous fuel)



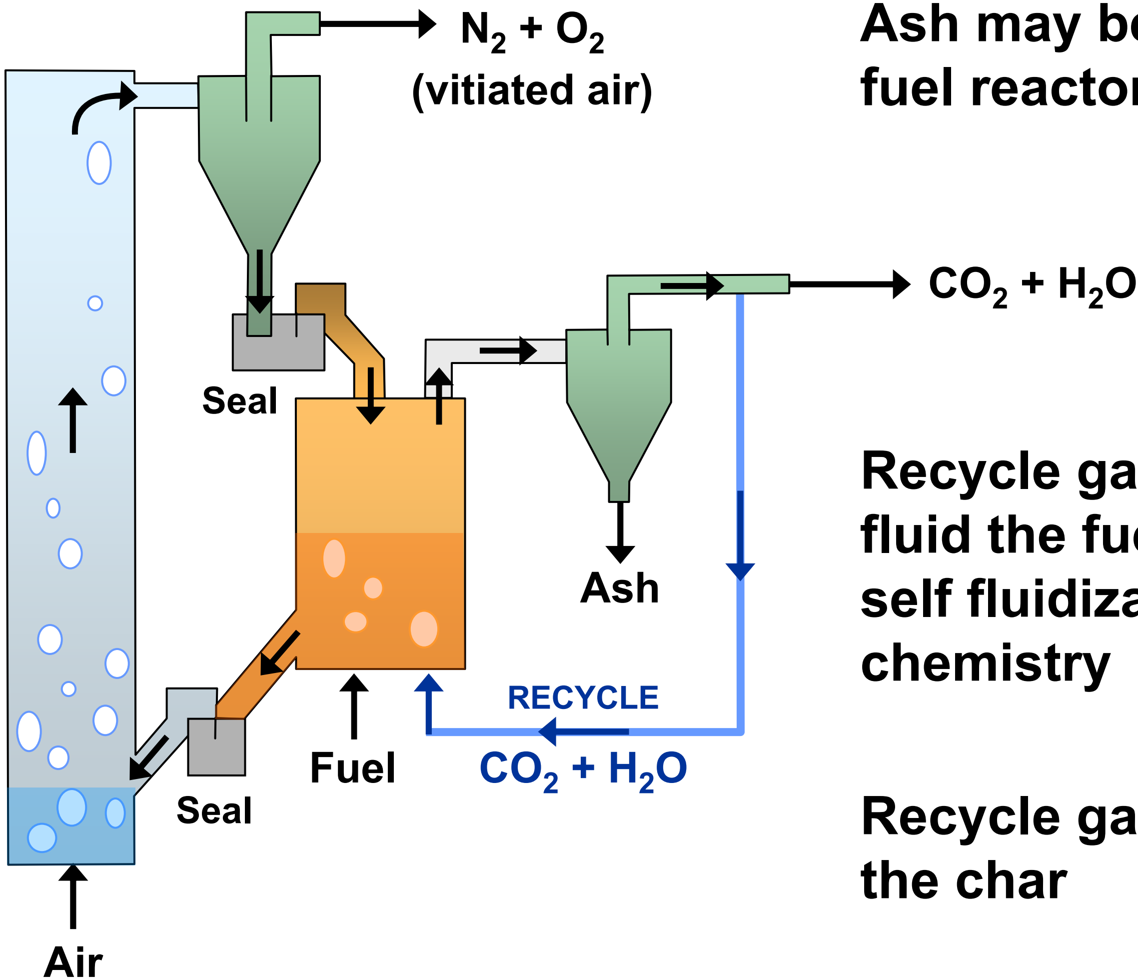
Air reactor – carrier is oxidized by air; heat is released

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).

Lyngfelt, *et al.*, 2001

Chemical Looping Combustion Process (solid fuel)



Ash may be elutriated from the fuel reactor

Recycle gas must be used to fluid the fuel reactor, along with self fluidization due to chemistry

Recycle gas must "burn out" the char

Advantages of CLC Technology

1) Produces 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)

(***Low temperature) fuel*** NO_x ***… not determined (???)***

3) Compatible with S-capture technologies

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 Fuel R
6) **Heavy metals (other than Hg) may stay with the ash**
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)

Disadvantages of CLC Technology

1) **Carrier circulation**

   Solids handling

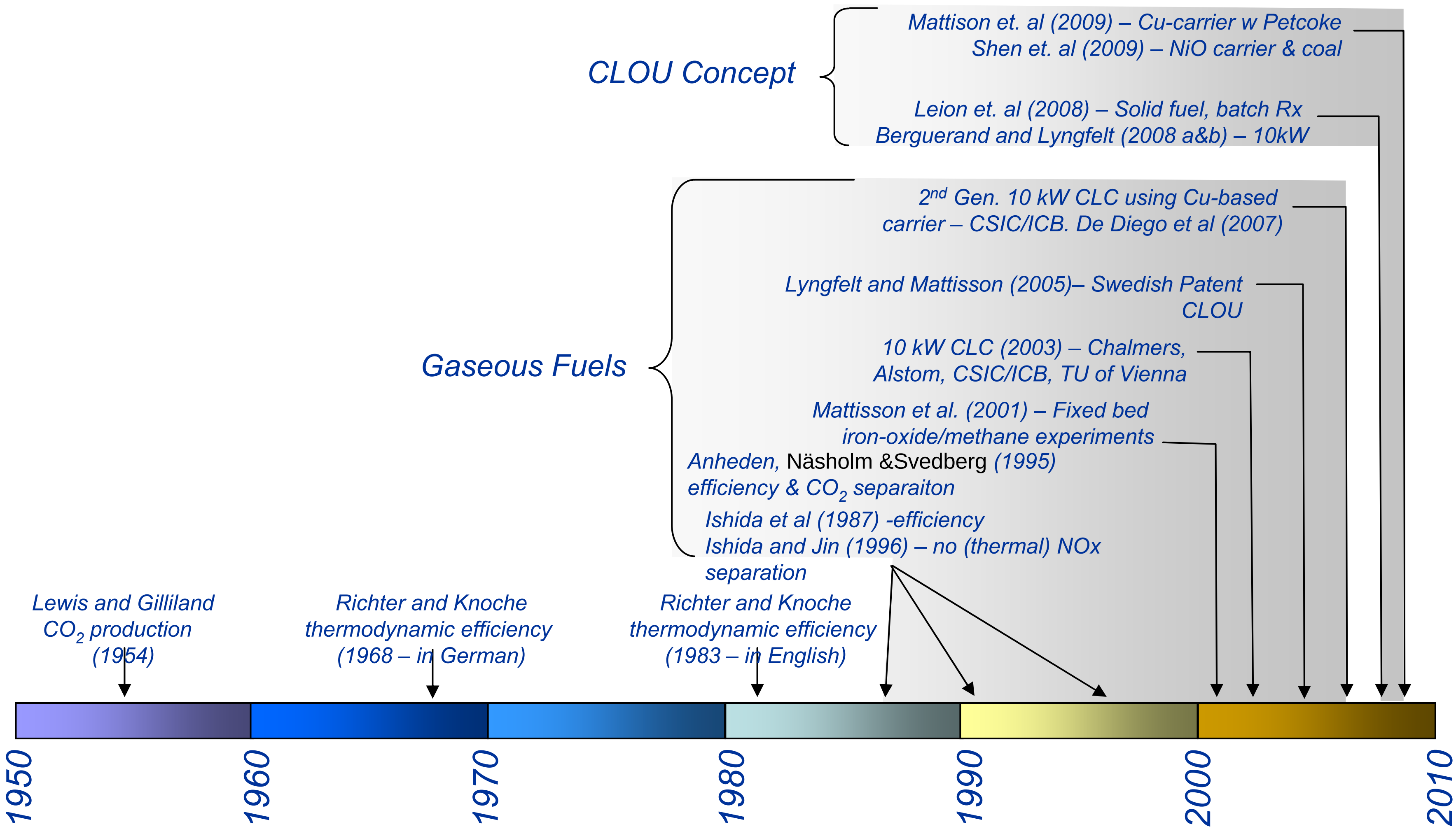
   Non-mechanical valves

2) **Dual reactors**

3) **Lower exhaust gas temperature (~1000 ºC)/pressure**

   Difficult to couple to a gas turbine – loss in efficiency

Overview – CLC Testing History



Ref: Anthony (2008) Ind. Eng. Chem res

History of the development of CLC

1) Method to produce pure CO_2
   Lewis and Gilliland (1954)
2) Proposed to improve combustion efficiency … reduce exergy
   Richter und Knoche (1968); Ishida (1982)
1) Implications for carbon capture are recognized
2) Chalmers program
3) European program
4) US effort

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

- **Chemical**
  - High reactivity – oxidation and reduction rates
  - Multiple oxidation states – oxygen carrying capacity
  - Light weight
  - Complete conversion at (T,P)
  - 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

Bed of Fuel Reactor

- **Fuel Reactor will have solid particles of different size and density.**
  - Carrier (Metal Oxide or $CaSO_4$)
  - Coal (Solid Fuel)
  - Ash
  - $CaCO_3$ for SO_x removal

Critical 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)

- **Char burnout**
  - Complete conversion
    - Large residence time/reactor size
    - Tendency to move to the AR

Critical Issues between FR & AR
(to be addressed by multi-phase CFD)

- **Flow from FR to AR must not contain unburned fuel**
  - Fuel combustion in the AR
    - Additional heat release in the AR
    - CO_2 released will escape capture

- **Air flow must not leak into the FR**
  - N_2 will contaminate the CO_2/H_20 stream
    - Additional compression costs
    - Inerts would be eturned to the AR

- **Char burnout**
  - Complete conversion
    - Large residence time/reactor size
    - Tendency to move to the AR

Process Design Issues

- **Air Reactor: Me + ½ $O_2 \rightarrow$ MeO**
  - Transport reactor
  - In-bed heat removal
- **Gas-Particle Separation after AR**
  - Cyclone separator
  - Heat removal (air stream and/or solids stream)
- **Fuel Reactor: solid fuel + MeO $\rightarrow$ Me + H_2O + CO_2**
  - Bubbling bed/Moving bed
- **Gas-Particle-Particle Separation after FR**
- **Heat Removal**
- **Non-mechanical Valve**

Pilot Plant Studies

- 10 kW_{th} scale
- Chalmers University (Tobias Mattisson, Anders Lyngfelt)
- 50 kW_{th} scale

- Vienna University of Technology (Hermann Hofbauer)
- 120 kW_{th} scale

- Alstom: Coal-CaS/$CaSO_4$ (Herb Andrus)
  - Phase II & III (<2009) 150 kW_{th}
  - Phase IV (>2009) 3 MW_{th}

- Ohio State University: Coal-Fe_2O_3 (L.S. Fan)

Vienna University of Technology
http://www.chemical-looping.at/start.asp

- Gaseous fuel

- 120 kW_{th} scale

ALSTOM Power, Inc.
(Heb Andrus)

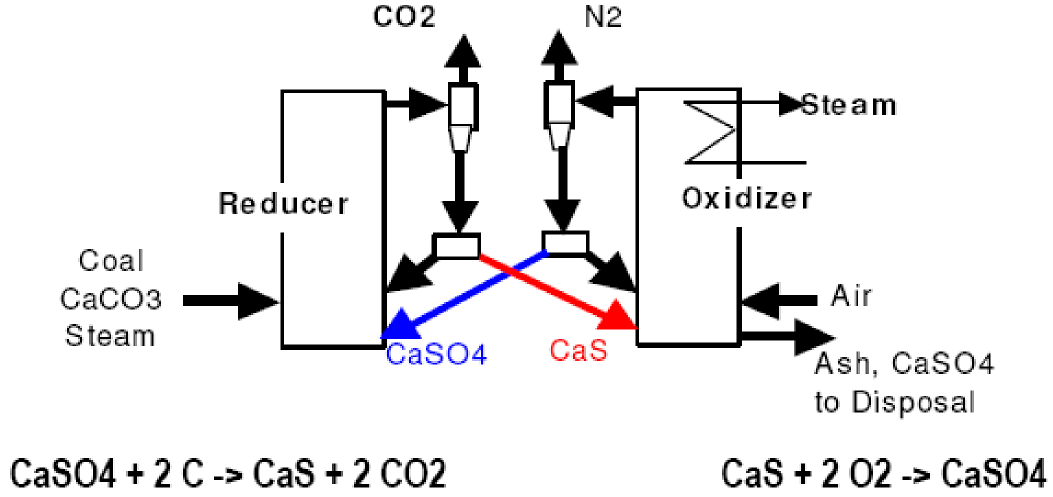


Figure 2-1 - Indirect Combustion with CO_2 Capture – Option 1.

- **$CaSO_4$/CaS carrier, formed from limestone**
- **Coal fuel**
- **150 kW_{th} PDU, building a 3 MW_{th} PDU**

Ohio State University

- **2.5 kW_{th}**
- **Patented iron oxide-based composite oxygen carrier particle.**
- **Cylindrical shape pellet,**

  (3-5 mm x 1.5-4.5 mm)
- **Coal**

  (75 to 250 micron)

Phase I Sub-Pilot Reactor

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}

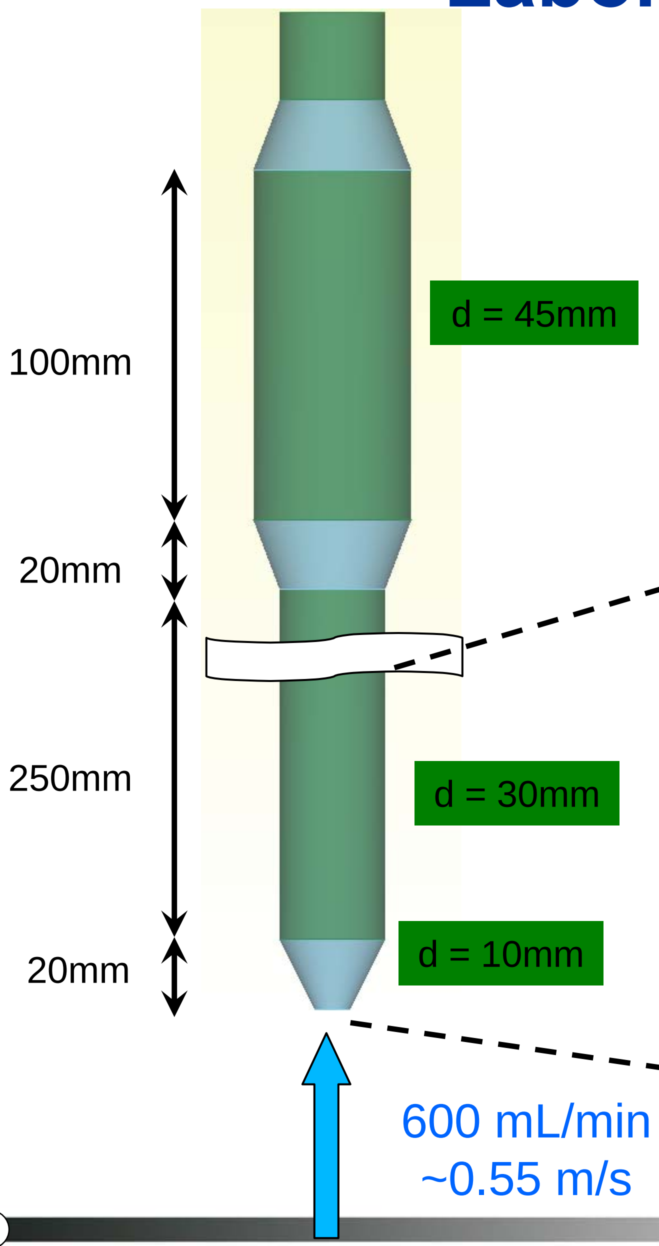
Chemical Kinetics	
Devolatilization	Nagpal (2005)
Gasification	Everson
Carrier Kinetics	Donskoi and McElwain (2001)

Thanks to …

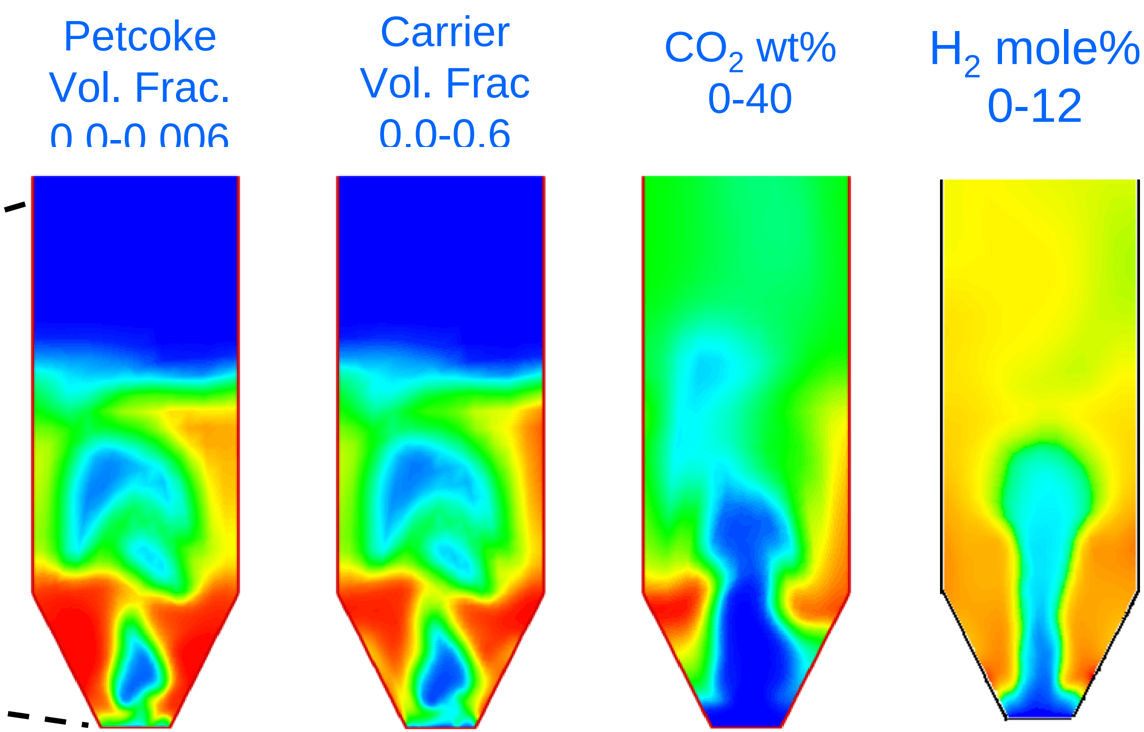
Kartikeya Mahalatkar (ANSYS-Fluent)
Dave Huckaby (NETL-DOE)
John Kuhlman (NETL-WVU

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

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

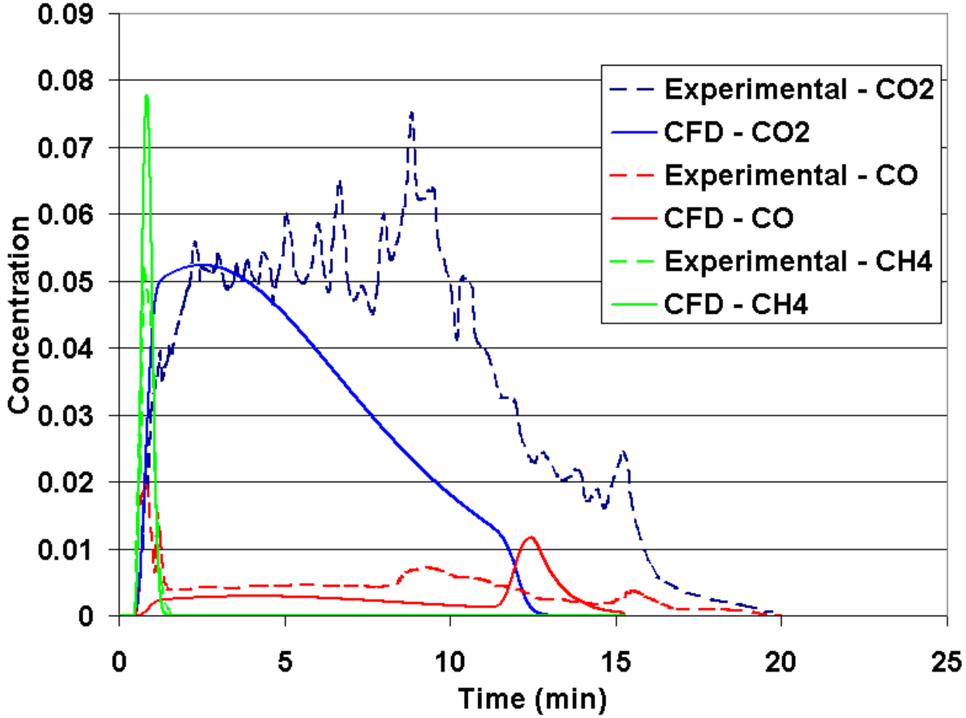
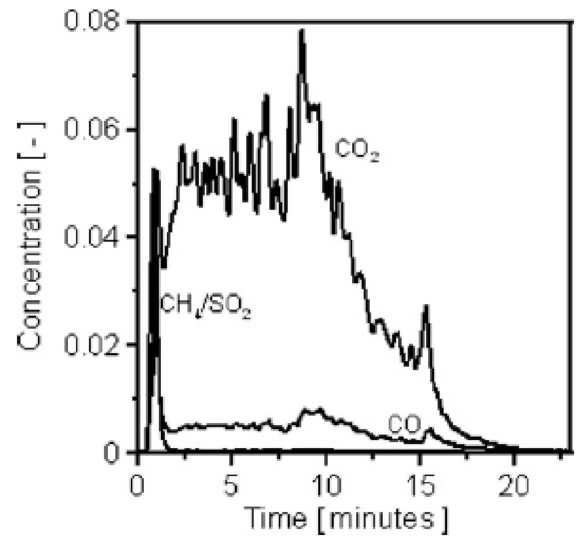


Fig 1: Concentration of CO2, CO and CH4 at Time delay of 30 seconds



- Lower Concentration of CO2 is a because of assumption of 2D Cartesian geometry

- Differences in experimental and numerical CH_4 and CO concentration is due to inherent uncertanities in the devolatile composition.

Thanks

E. David Huckaby

Kartikeya Mahalatkar

John Kuhlman