ENHANCED HYDROGEN PRODUCTION INTEGRATED WITH CO_2 SEPARATION IN A SINGLE-STAGE REACTOR

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Project ID # PDP1

Overview

Timeline

- Project start date: Oct 2003
- Project end date: Sept 2005
- Percent complete: 50 %

Budget

- Total project funding: $501,300
  - DOE share: $ 399,713
  - Contractor share: $ 101,587
- Funding for FY04: $160,000
- Funding for FY05: $200,000

Barriers

Technical Target:

- Cost reduction of H_2 production from fossil fuels. For natural gas sources
  - $ 3.00/ggeH_2 (by 2005)
  - $1.50/gge$H_2$ (by 2010)

Technical Barriers:

- Cost effective CO_2 avoidance
- Reduction in impurities (CO, H_2S)
- Selectivity towards H_2 capture
- Desired Operating Temp range
- Cost of H_2 production

Partners

Ohio State University

Project Objectives

To assist DOE in the development of hydrogen production technologies by maximizing H_2 production from fossil fuels

- To develop a high temperature reaction based process from syn gas ($CO + H_2$) which:
  - Maximizes H_2 production at high temperature & pressure (current year)
  - Maximizes H_2 purity by enhancing water-gas-shift reaction
  - Creates a sequestration ready CO_2 stream
- To identify process conditions for maximizing CaO reactivity
  - Thermodynamic analyses for optimizing carbonation, hydration and sulfidation
  - Testing of mesoporous calcium sorbents
  - Optimizing carbonation and calcination reactions (current year)
  - Multicyclic testing (current year)

Overall Technical Approach

- ***In-situ*** **CO_2 removal from the Water gas mixture**
- **Drive the equilibrium limited WGS reaction forward**
  - ✓ **Maximize H_2 production**
  - ✓ **High T/P/Purity H_2 possible**
  - ✓ **Reduce Steam consumption**
  - ✓ **Remove CO and CO_2 to ppm levels**
  - ✓ **Integrated CO_2 separation making this H_2 Production process CO_2 sequestration ready as well**
  - ✓ **In membrane reactors, H_2 production limited by WGS catalysis and not H_2 diffusion**

$$CO + H_2O \rightarrow CO_2 + H_2$$

Removed (CO_2)

Approach: Experimental

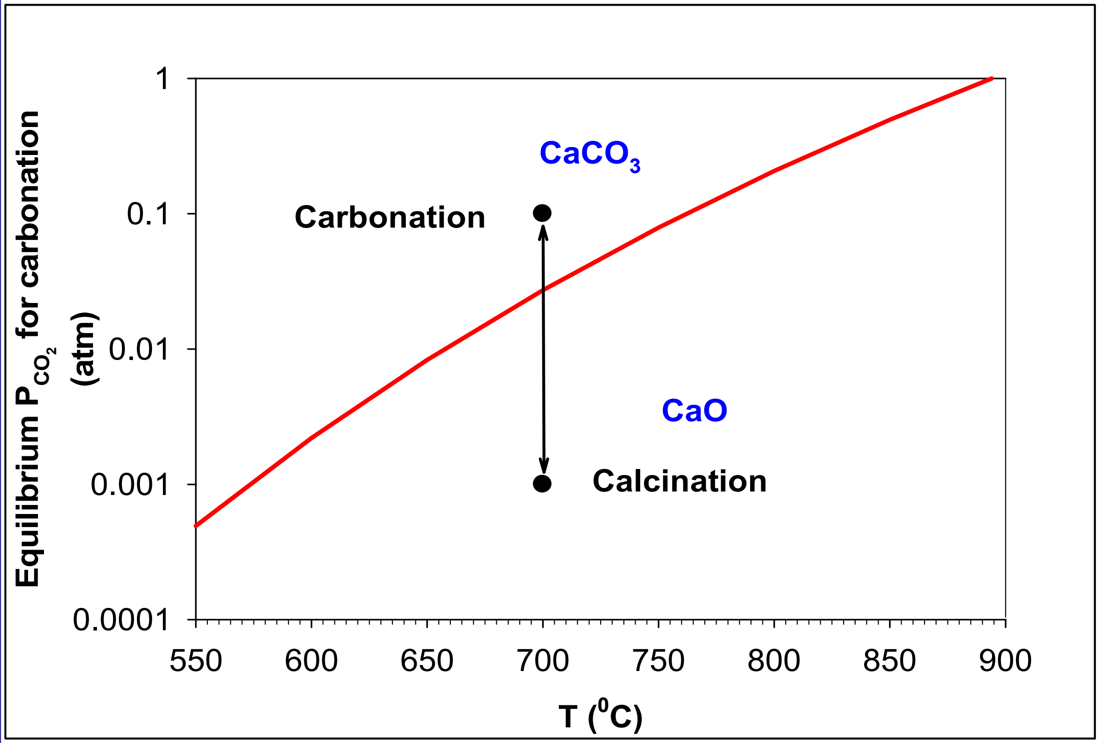
- **Integral bed for simultaneous WGS and Carbonation**
  - Breakthrough studies for extent/purity of hydrogen production
  - Sorbent reactivity
  - Catalyst activity (blank testing)
  - Catalyst deactivation avoidance

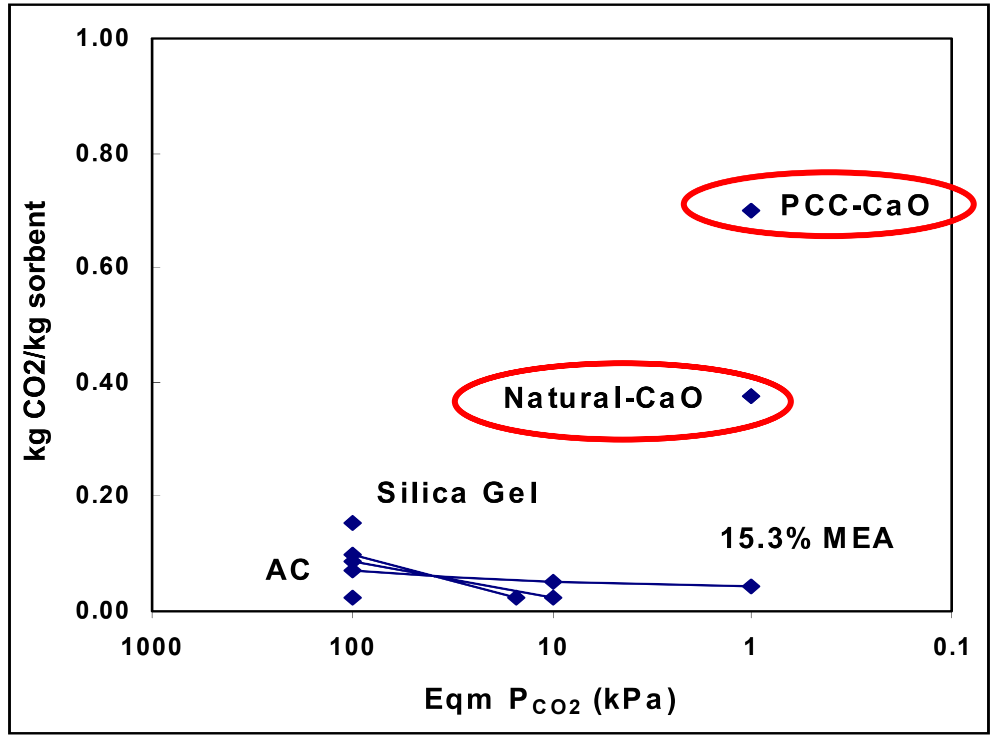
- **MSB-TGA testing**
  - Extent of carbonation (High pressures)
  - Multicyclic carbonation-calcination reaction testing
  - Competing carbonation/sulfidation reactions

- **Sub-atmospheric calcination**
  - Vacuum calcination
  - Steam calcination

Carbonation Calcination Reaction System (CCR)

$$CaO + CO_2 \longleftrightarrow CaCO_3$$





- **Regenerable metal oxides**
- **Carbonation**
  $MO + CO_2 \longrightarrow MCO_3$
- **Calcination**
  $MCO_3 \longrightarrow MO + CO_2$

Computed from HSC Chemistry v 5.0

[a]15.3% MEA, [b]AC, 1393 m^2/g, [c]AC: Norit R1, [d]Silica Gel, [e]AC 1018 m^2/g

[a]Song et al., 1996; [b]Heuchel et al., 1999; [c]Dreisbach et al., 1999; [d]Zhang et al., 1998; [e]Sarkar and Bose, 1997

Reaction Schemes

Reaction phase:

WGSR:	$CO + H_2O \rightarrow CO_2 + H_2$
Carbonation:	$CaO + CO_2 \rightarrow CaCO_3$

Regeneration phase:

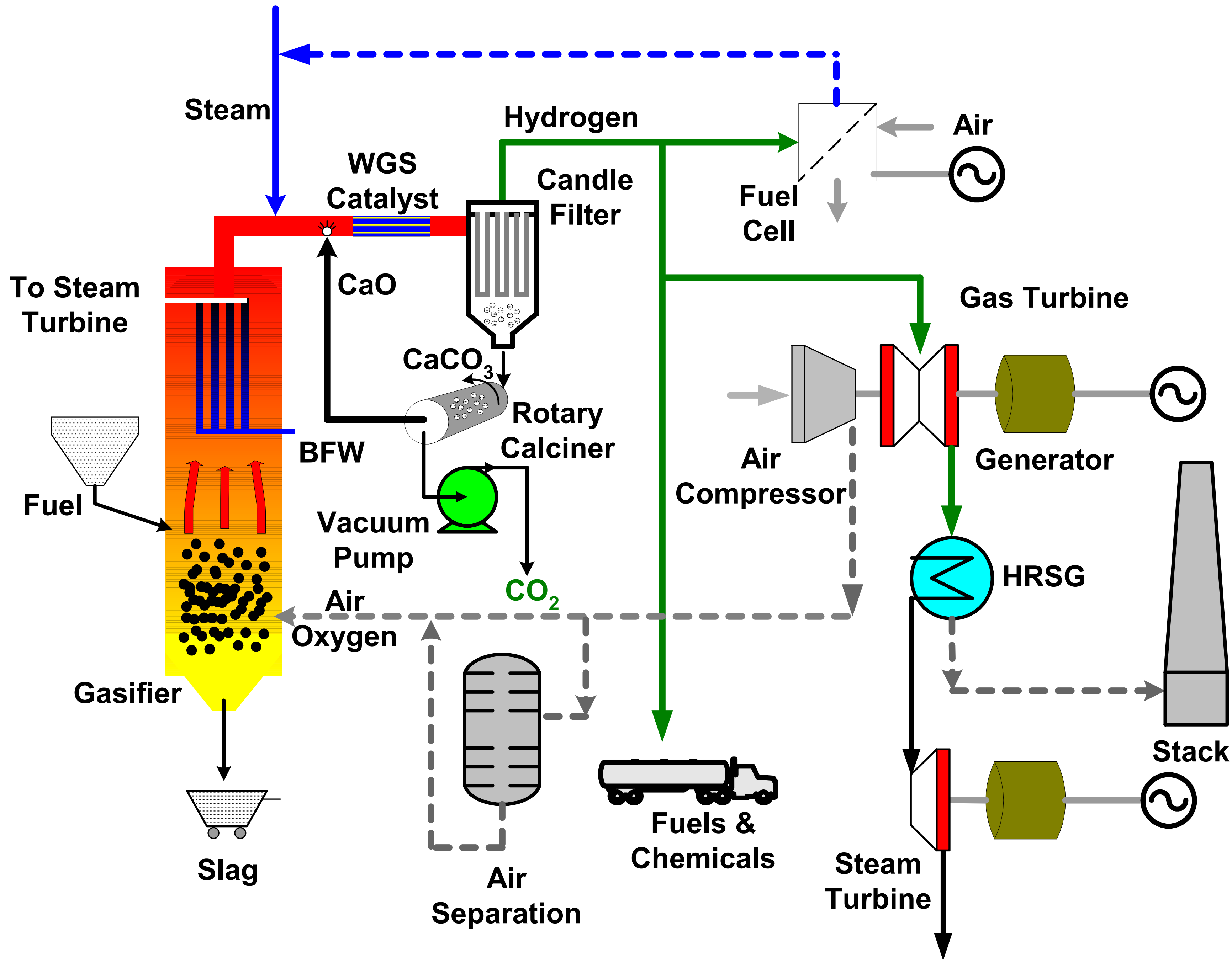
Calcination:	$CaCO_3 \rightarrow CaO + CO_2$

Parasitic Reactions:

***Hydration*:**	$CaO + H_2O \rightarrow Ca(OH)_2$
***Sulfidation*:**	$CaO + H_2S \rightarrow CaS + H_2O$

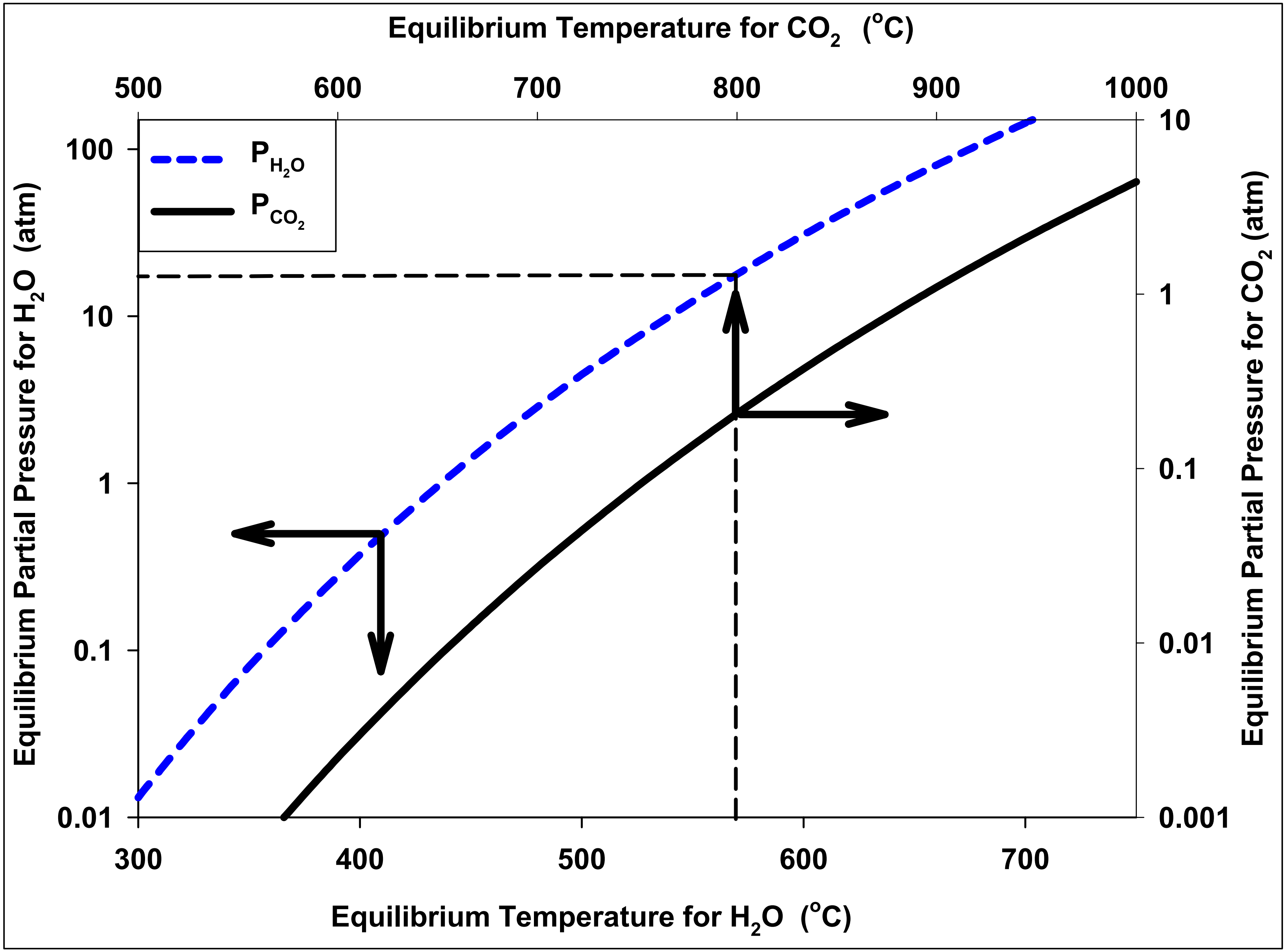
- **High Steam/CO**
- **H_2/CO ratio can be improved**
- **But can never maximize H_2 production**
- **Further CO cleanup required for PEM fuel Cells (ppm levels)**

Overall integration scheme



Thermodynamic Analyses

$CaO + CO_2 \leftrightarrow CaCO_3$ $CaO + H_2O \leftrightarrow Ca(OH)_2$

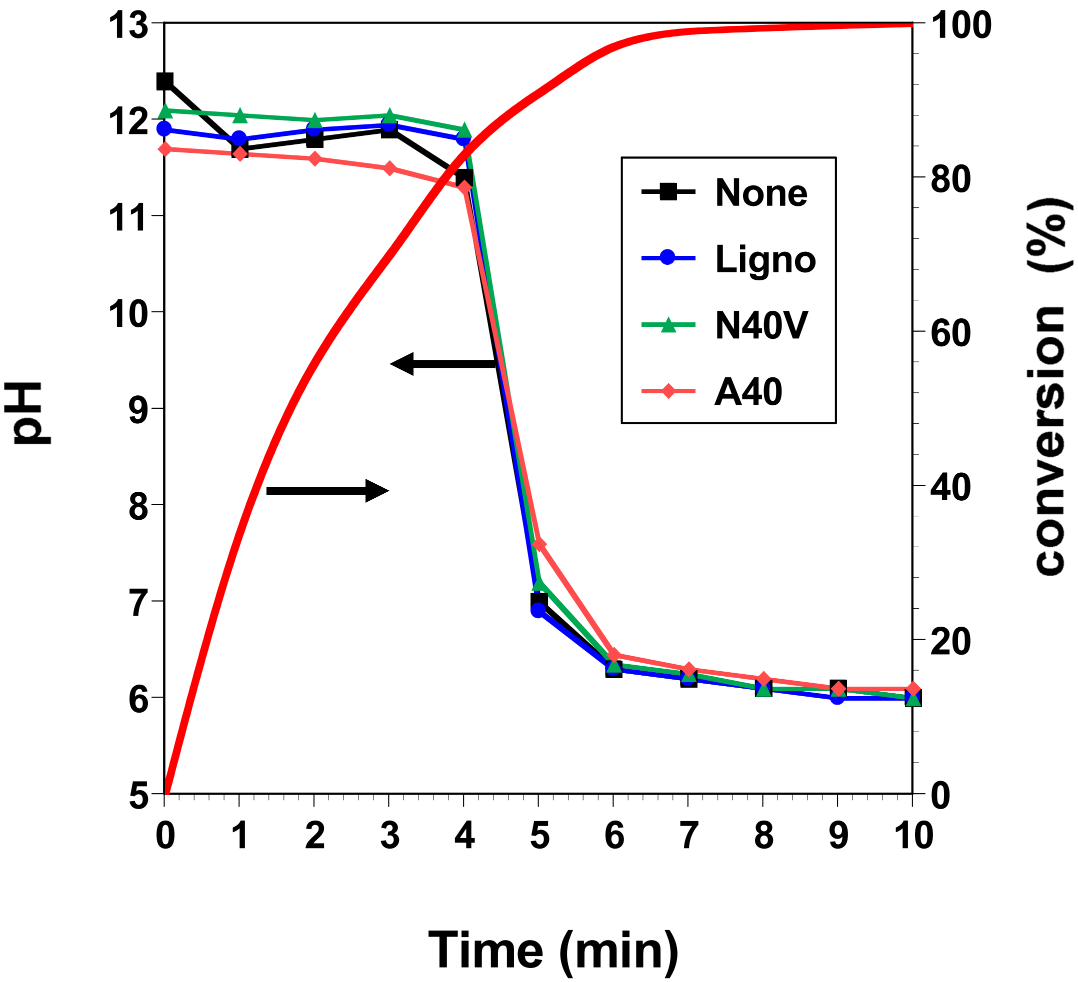


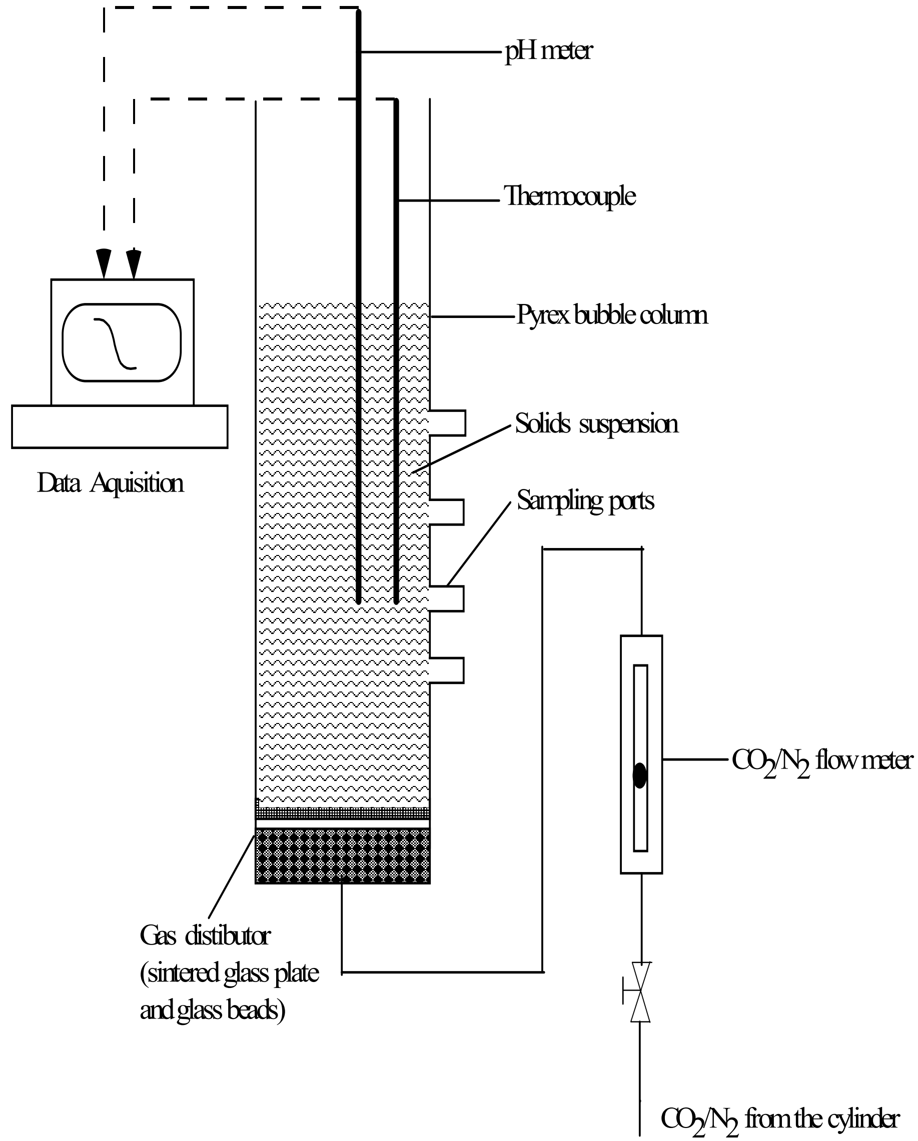
Fuel Gas Compositions

	Moving Bed, dry	Moving Bed slagging	Fluidized Bed	Entrained Flow, slurry	Entrained Flow, dry
Oxidant	air	Oxygen	Oxygen	Oxygen	Oxygen
Fuel	Sub Bituminous	Bituminous	Lignite	Bituminous	Bituminous
Pressure (psi)	295	465	145	615	365
CO	17.4	46	48.2	41	60.3
H2	23.3	26.4	30.6	29.8	30
CO2	14.8	2.9	8.2	10.2	1.6
H2O	…	16.3	9.1	17.1	2
N2	38.5	2.8	0.7	0.8	4.7
CH4+ HCs	5.8	4.2	2.8	0.3	…
H2S + COS	0.2	1.1	0.4	1.1	1.3

- Typical gasifier P_{CO_2}: 0.4 - 4.3 atm
- Equilibrium Temperature: 830 - 1000 ^{o}C
- Operate below T_{eq} for carbonation to occur
- Typical gasifier P_{H_2O}: 12 - 20 atm
- Equilibrium Temperatures: 550 - 575^{o}C
- Operate above T_{eq} to prevent hydration of CaO

PCC Synthesis*





Solids loading: 2.56 wt%

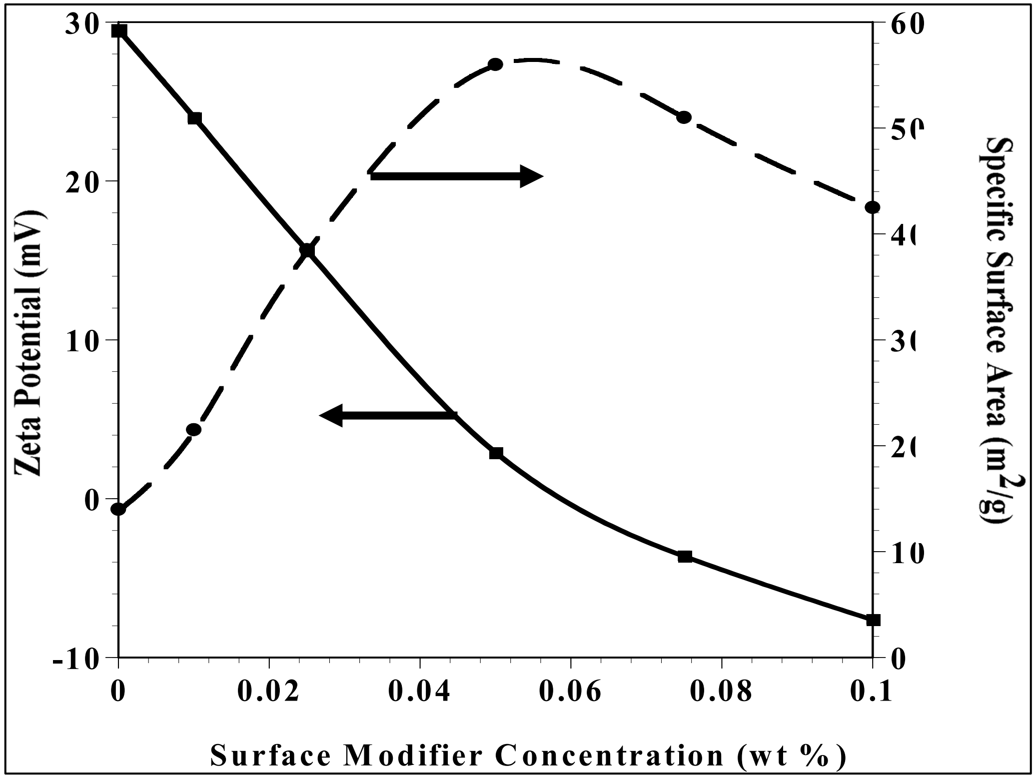
CO_2 flow rate: 5 scfh

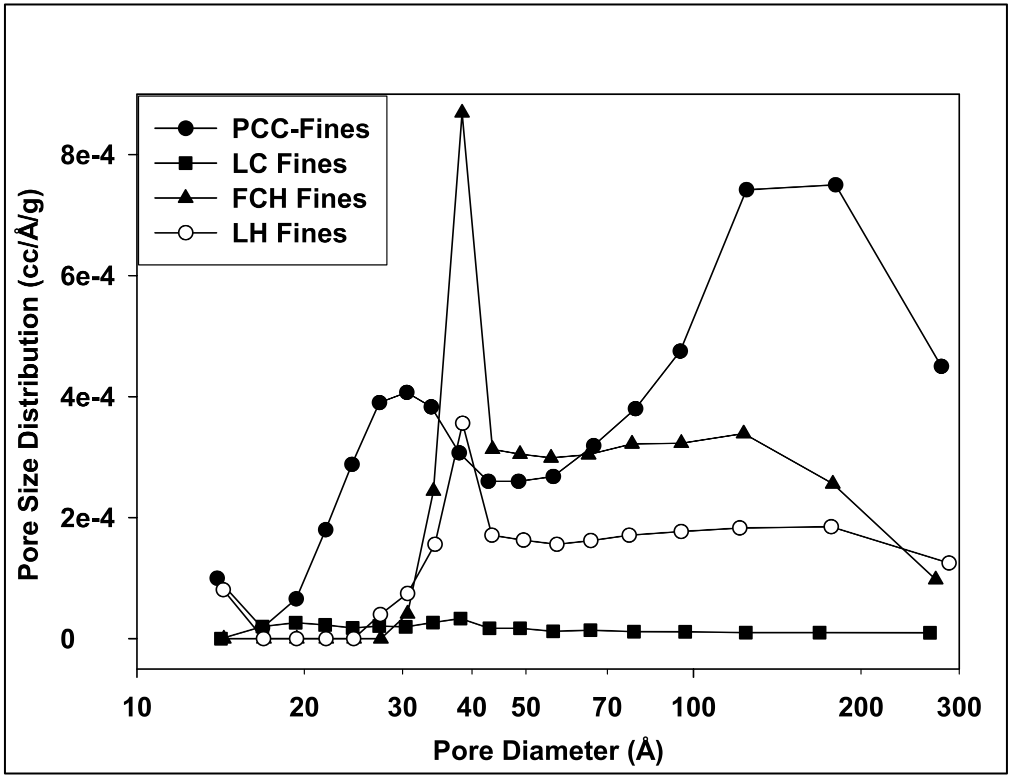
CO_3^{2-} and HCO_3^{-} ions

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

Agnihotri et al., (1999)

Optimization of Sorbent Morphology





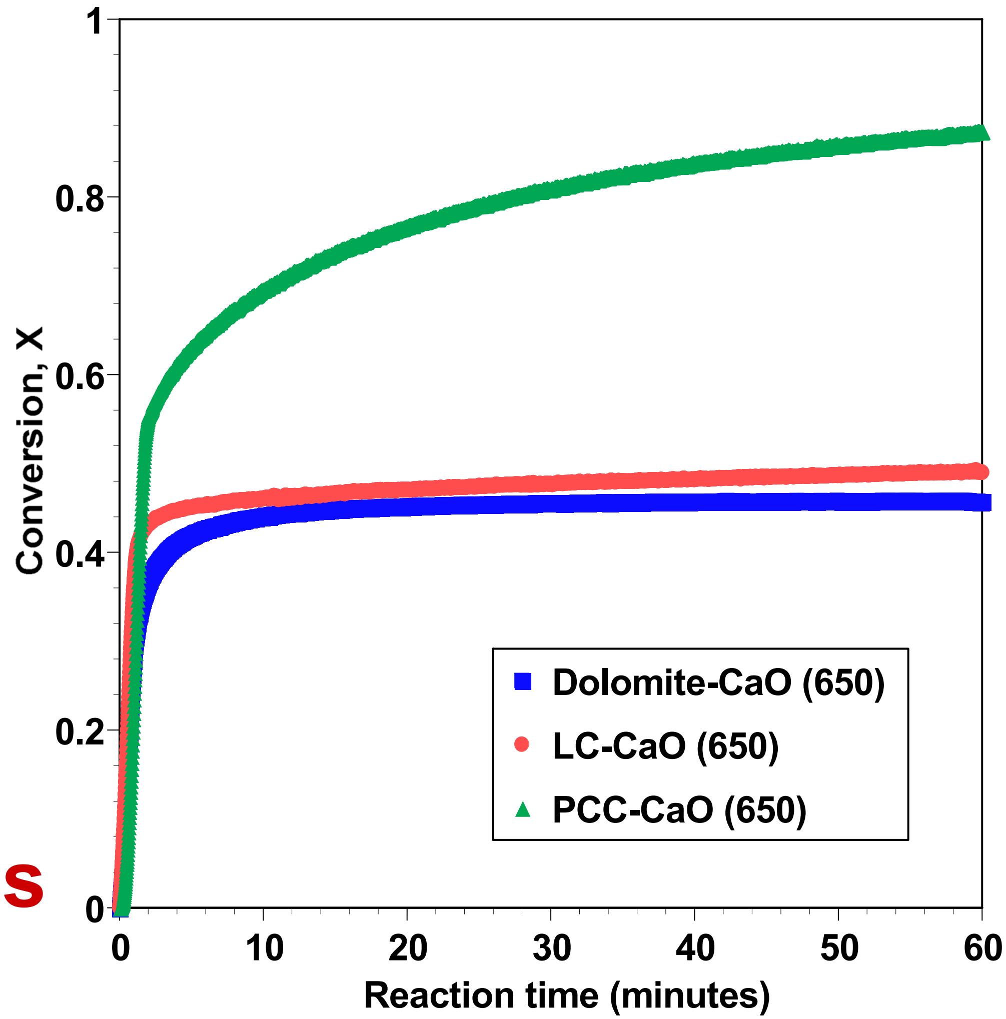
Optimization of Surface area and Zeta potential[1]

Comparison of PSD of PCC with other natural lime based sorbents[2]

[1]Gupta and Fan, (2002); [2]Gupta et al (2004)

Effect of Initial Sorbent Morphology (carbonation of CaO sorbents)

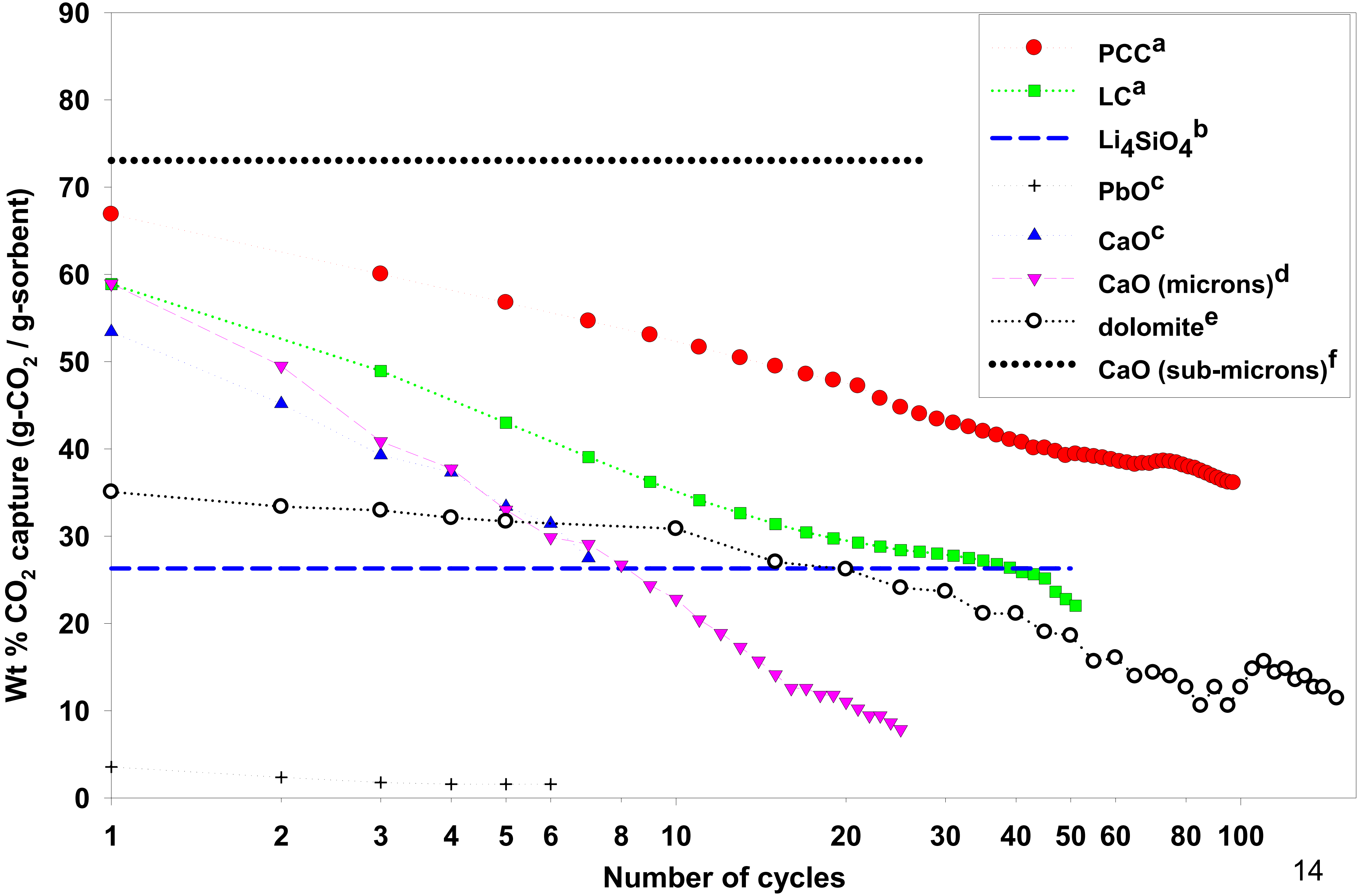
Name	BET SA (m2/g)	PV (cc/g)
LC	1.064	0.003
LC-CaO	17.79	0.078
Dolomite	1.822	0.004
FCD-CaO	29.85	0.08
PCC	36.8	0.11
PCC-CaO	12.79	0.027



- **Two-regime heterogeneous Gas-Solid reaction**
  - ✓ Rapid kinetic regime
  - ✓ Slow product layer diffusion regime

Carbonation in TGA at 700 °C under 100 % CO_2

Comparison of High Temperature Sorbents



([a]current work; [b]Toshiba Corpn., [c]Kato et al, 1999; [d]Barker, 1973; [e]Harrison et al, 2001, [d]Barker, 1974)

Experimental Setup
Combined WGSR and Carbonation

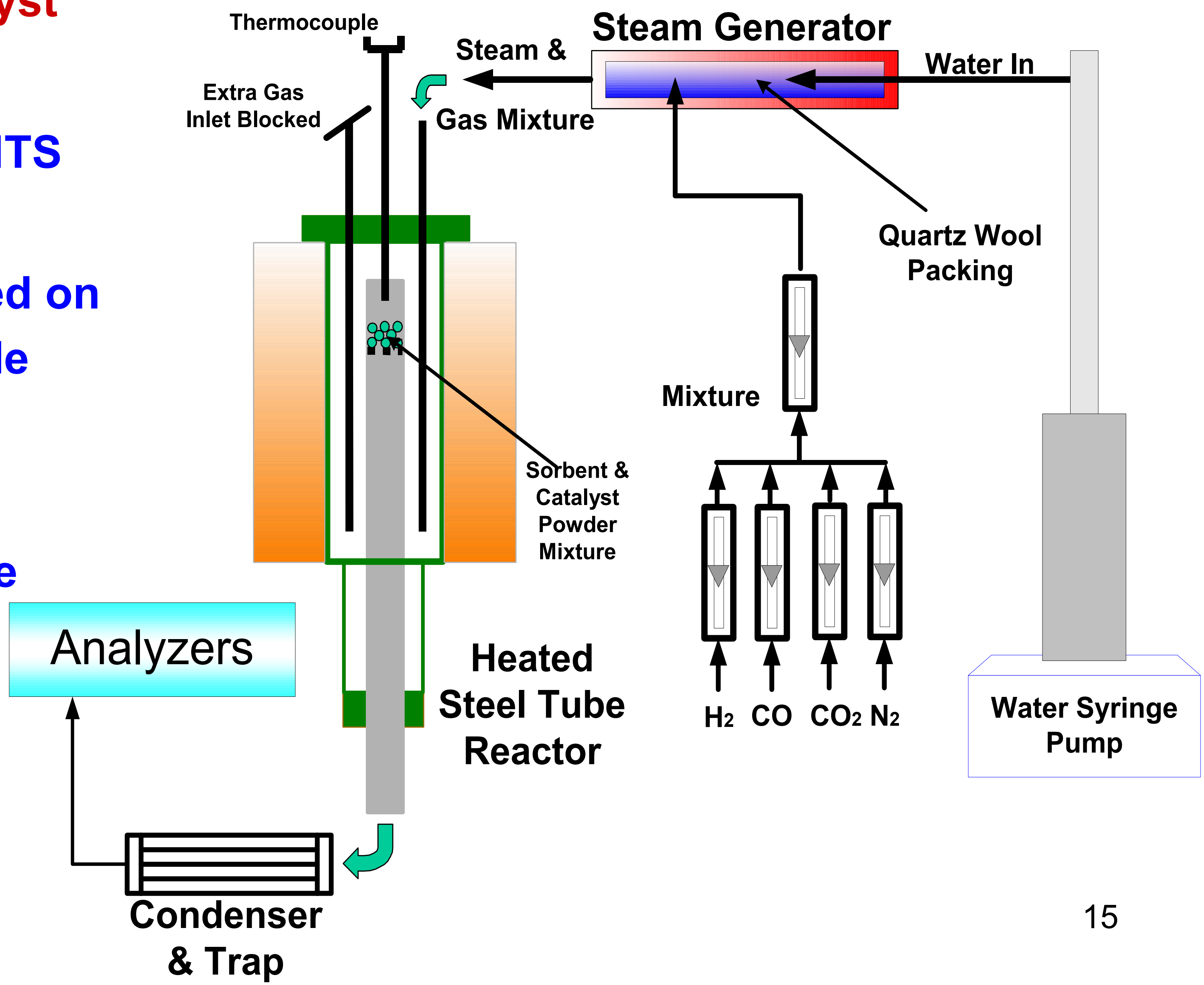
Fixed Bed of catalyst and CaO mixture

- ✓ Süd-Chemie: HTS catalyst
- ✓ Fe_2O_3 supported on chromium oxide

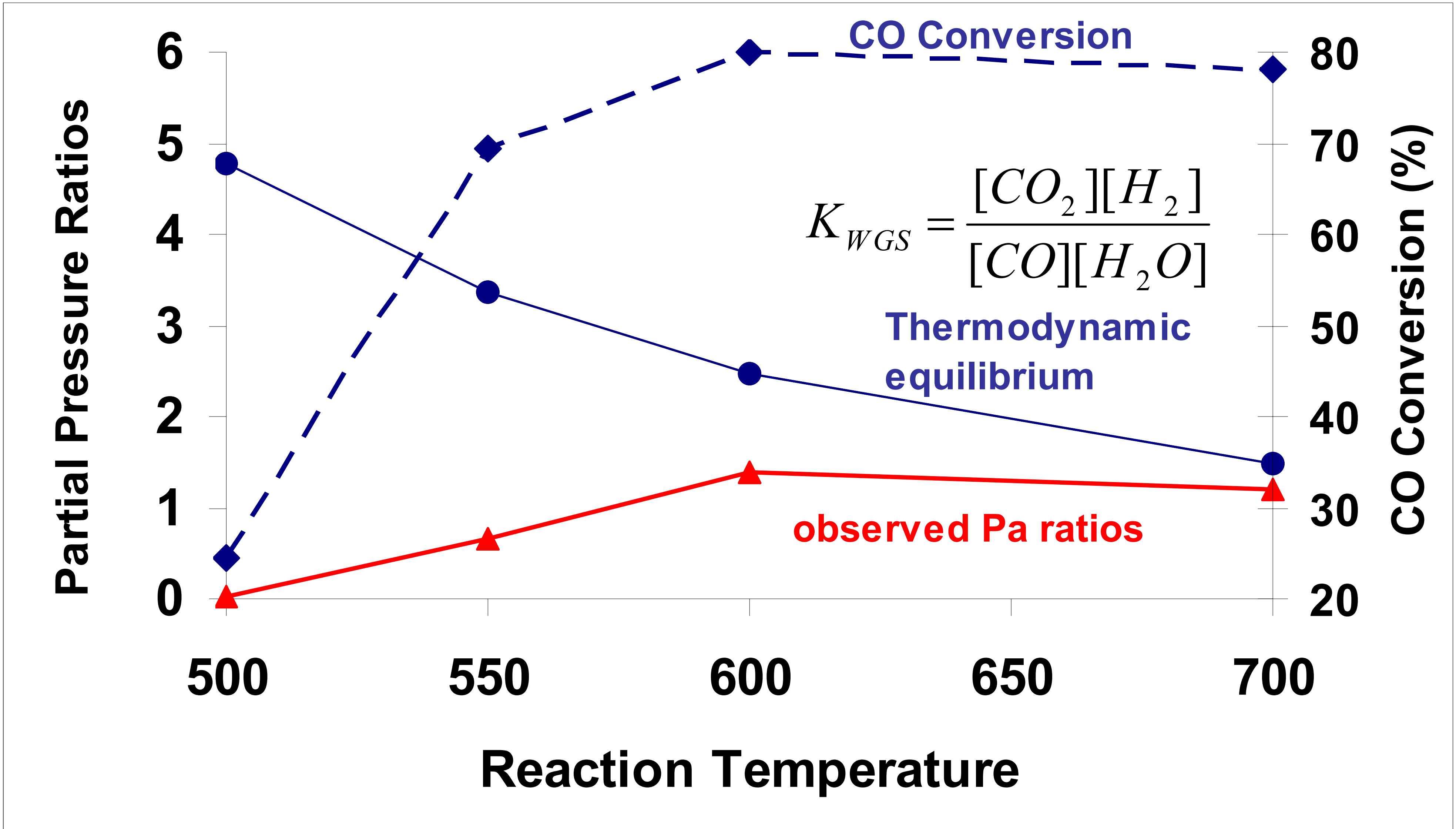
Sorbents

- ✓ PCC (tailored)
- ✓ Linwood hydrate (natural)

- 1500 sccm
- 3 % CO
- Steam/CO = 3
- 600 ^oC

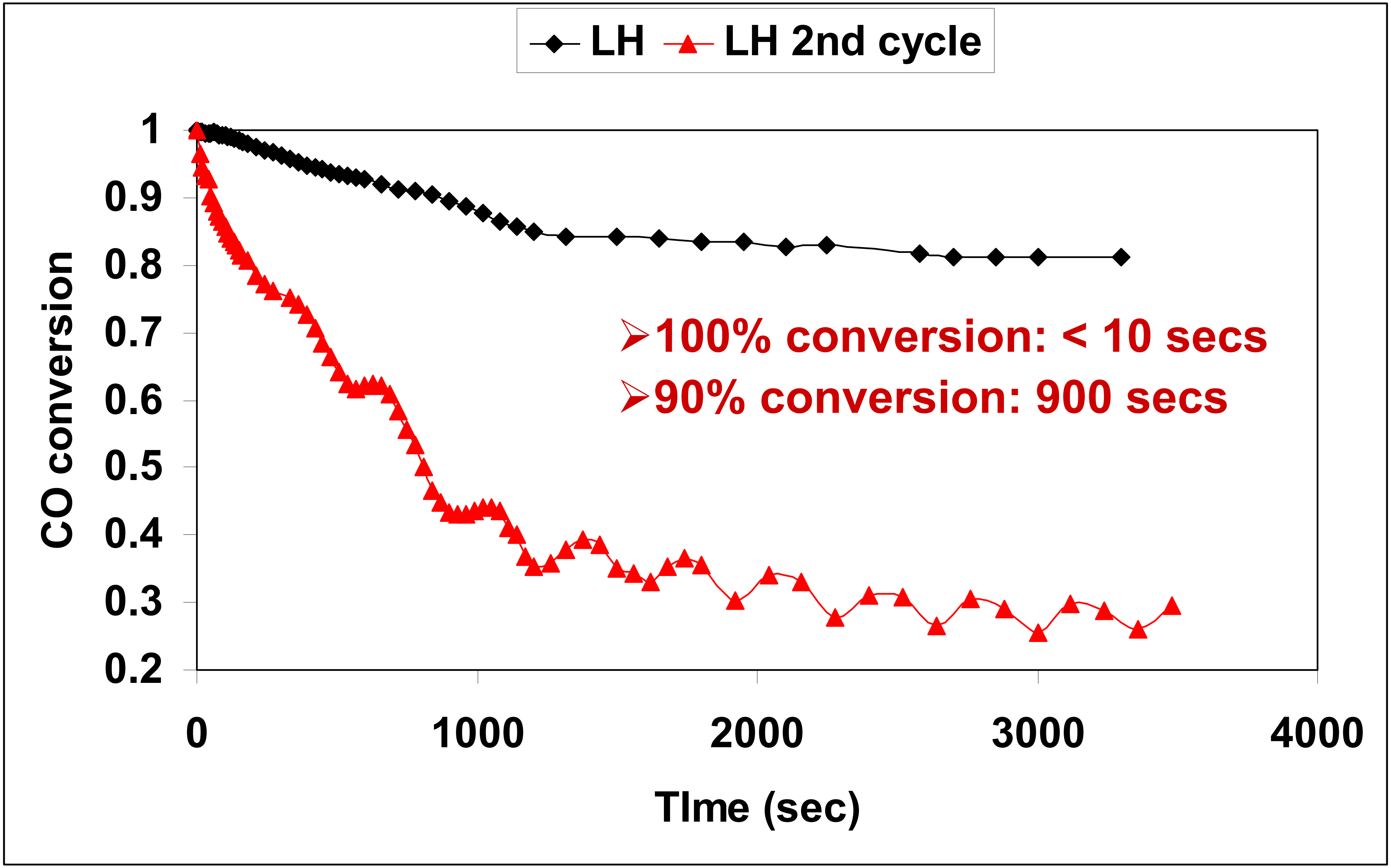


WGS Catalyst Testing w/o Sorbent



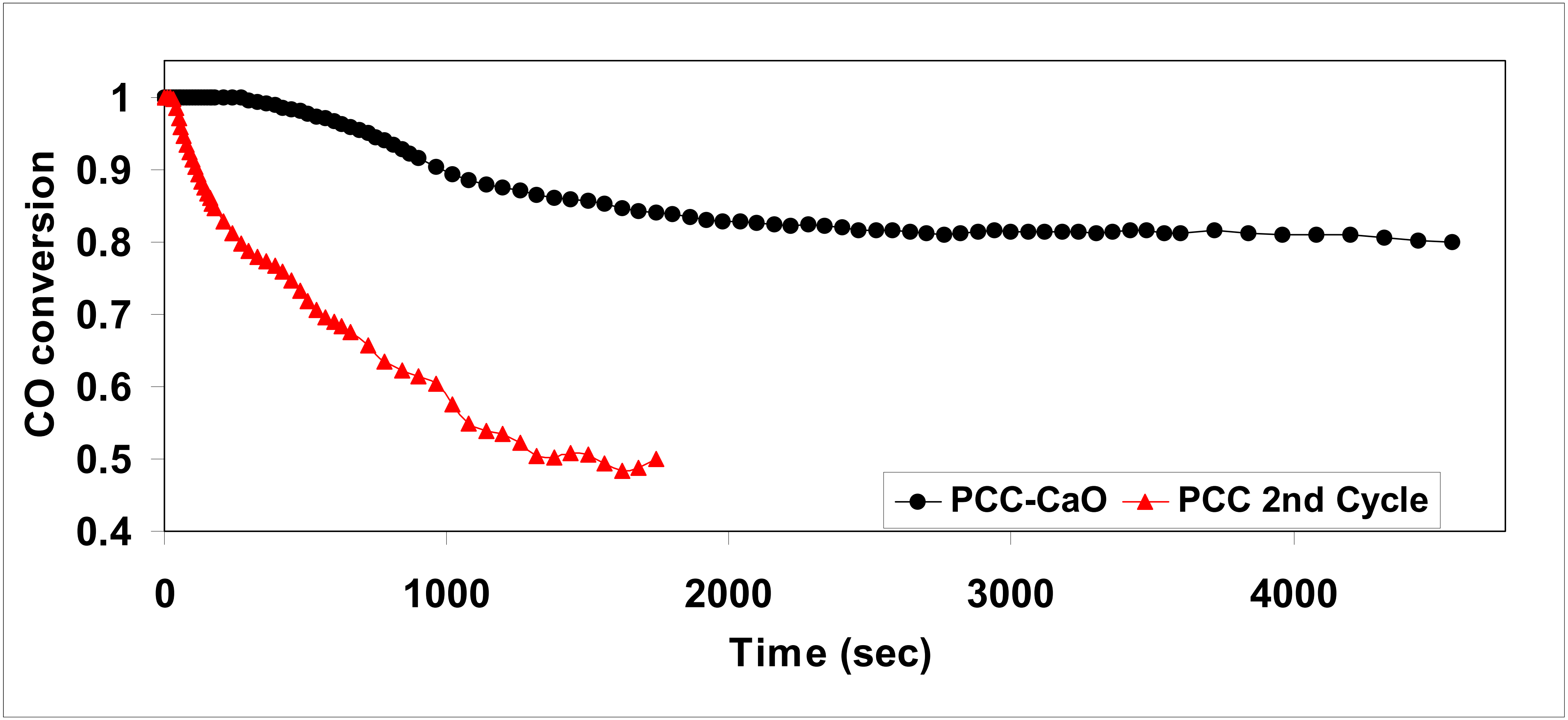
0.5 g HTS catalyst, 3% CO H_2O/CO ratio = 3, Total flow = 1.5 slpm

Performance of Linwood Hydrate



T = 600 °C, 3% CO, 9% H_2O, Total flow = 1.5 slpm

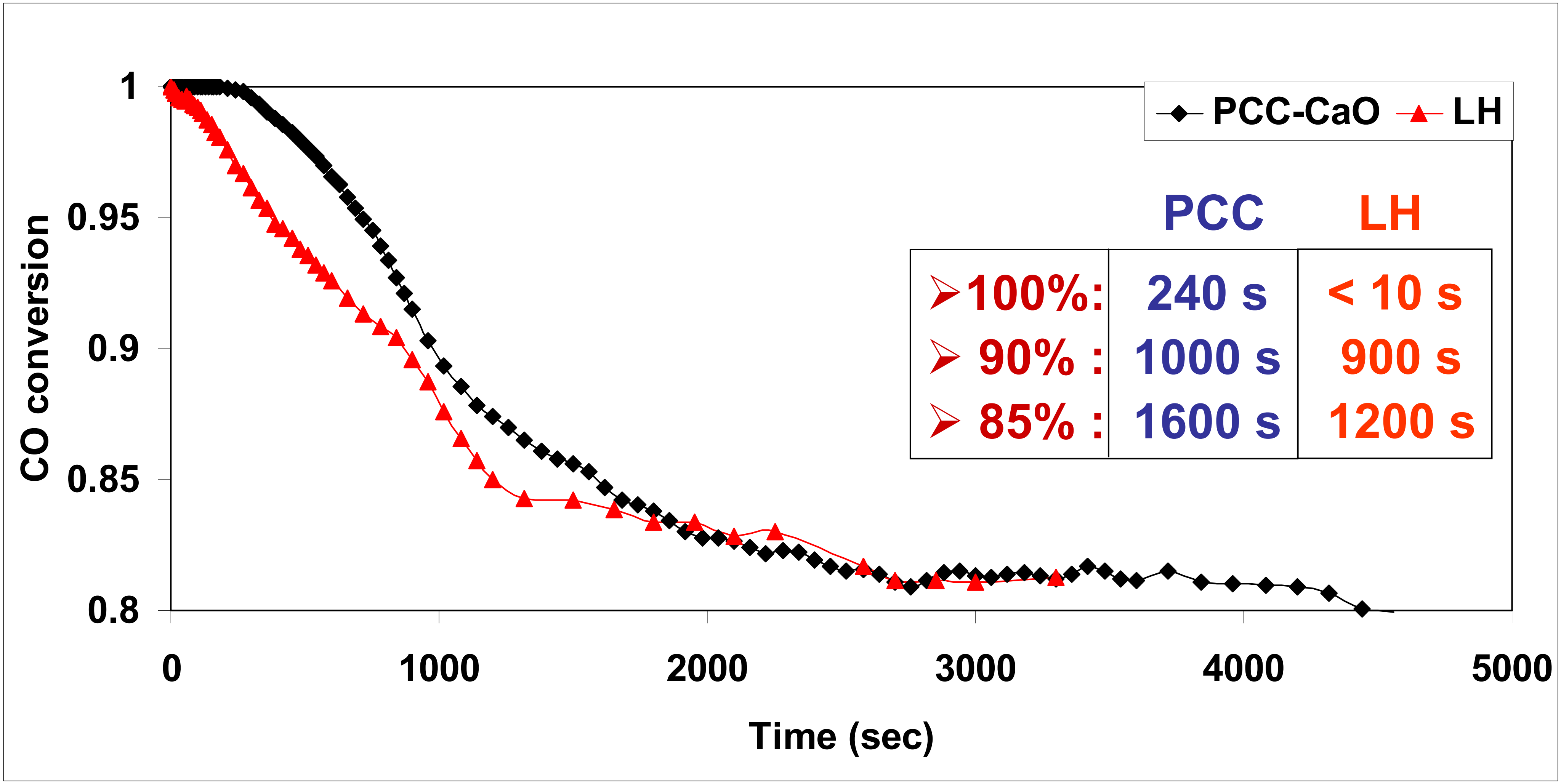
Performance of PCC



- 100% conversion: 240 secs (4 min)
- 90% conversion: 1000 secs (16.5 min)
- Final breakthrough: 2500 secs (42 min)

T = 600 °C, 3% CO, 9% H2O, Total flow = 1.5 slpm

Comparison of PCC and LH

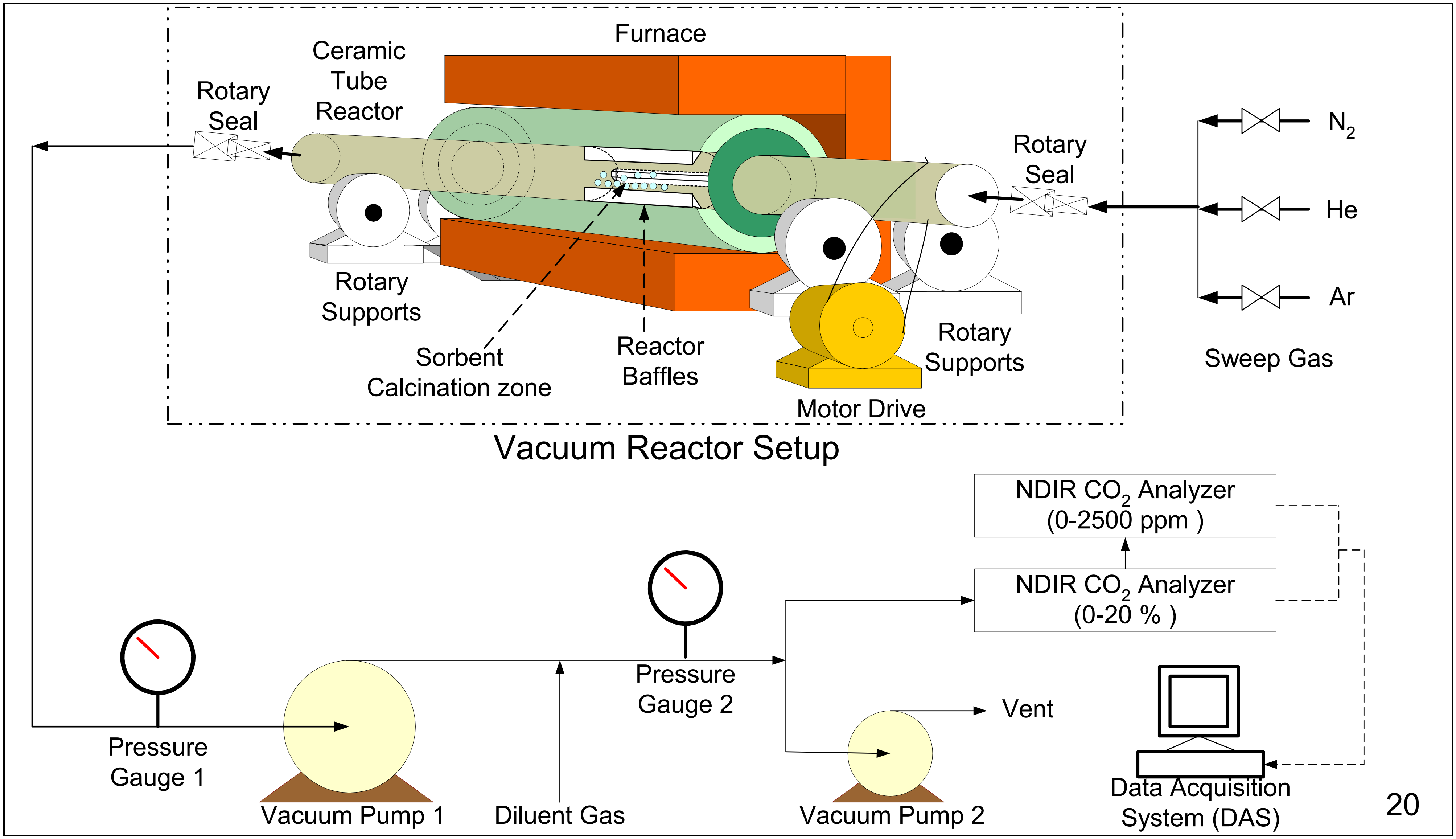


	PCC	LH
➢100%:	240 s	< 10 s
➢ 90% :	1000 s	900 s
➢ 85% :	1600 s	1200 s

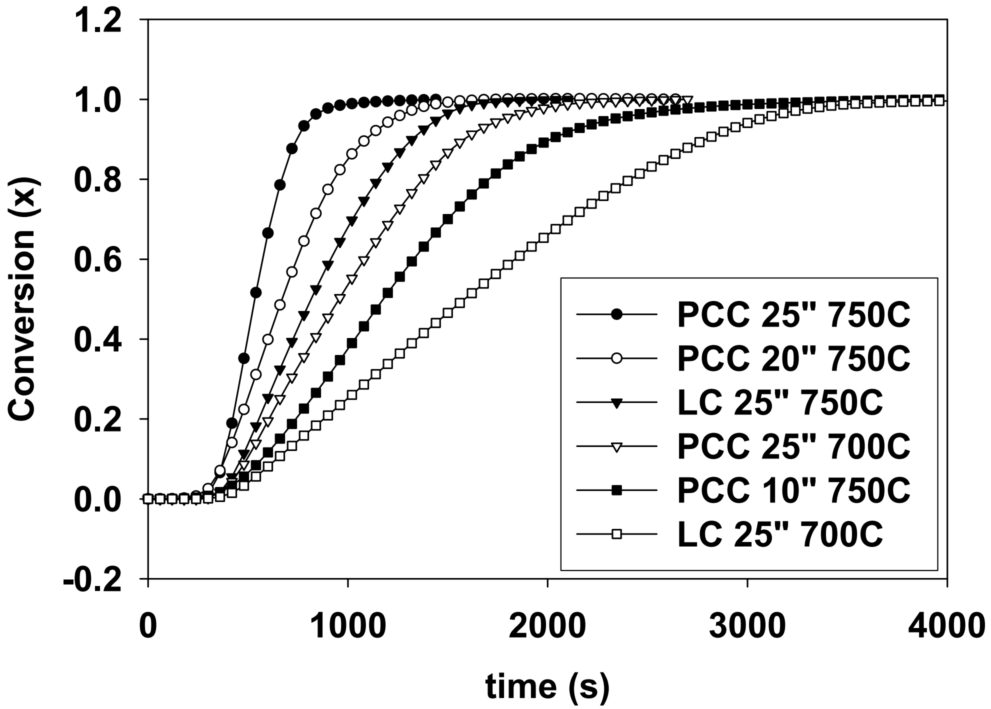
T = 600 °C, 3% CO, 9% H2O, Total flow = 1.5 slpm

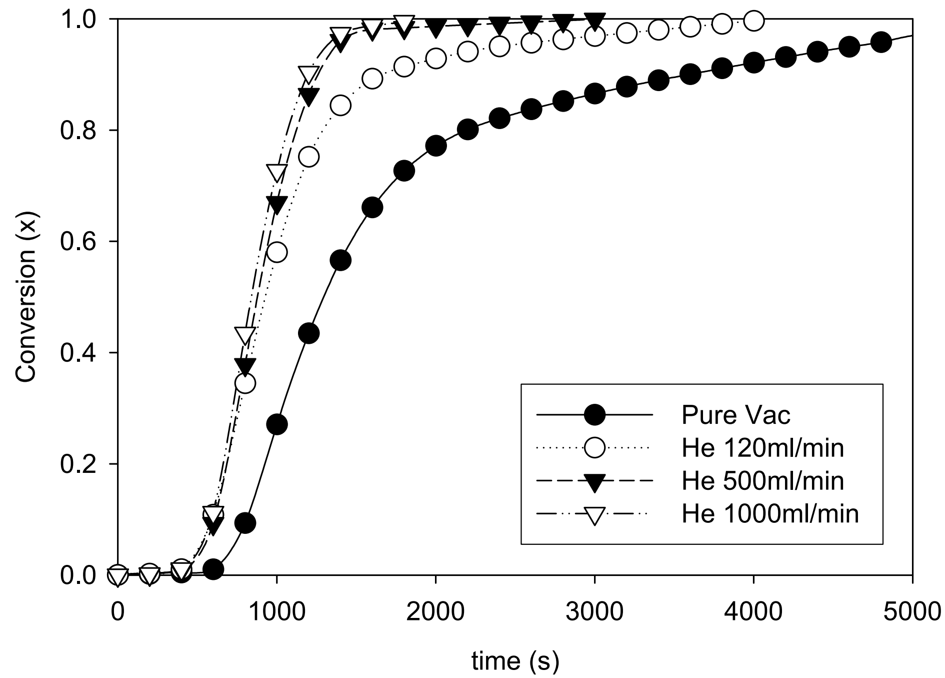
Sub-atmospheric Calcination

Schematic diagram of the calciner reactor setup



Sub-atmospheric Calcination

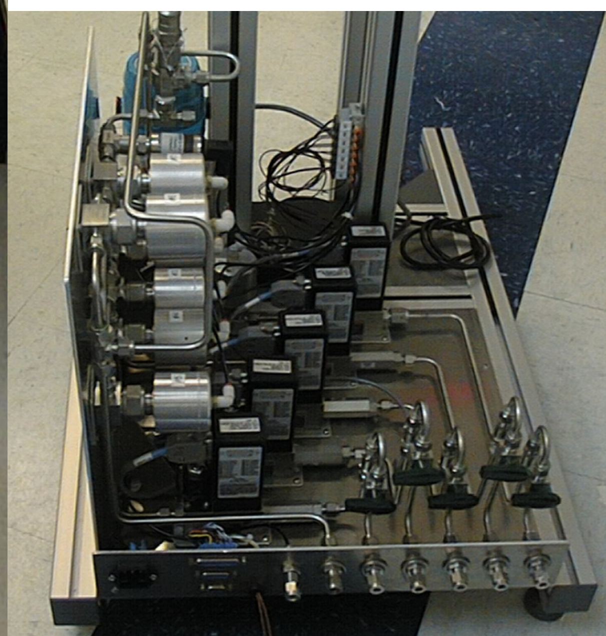




- Effect of vacuum on calcination rate
- Higher vacuum favors the rate
- PCC calcines faster than LC
- Lower calcination temperature favors sorbent morphology

- Effect of diluent gas flow rate
- 0-1000ml/min of He
- Calcination of 10g LC
- 28"Hg vacuum
- T=880 ^{o}C

Future Work (FY 2005)



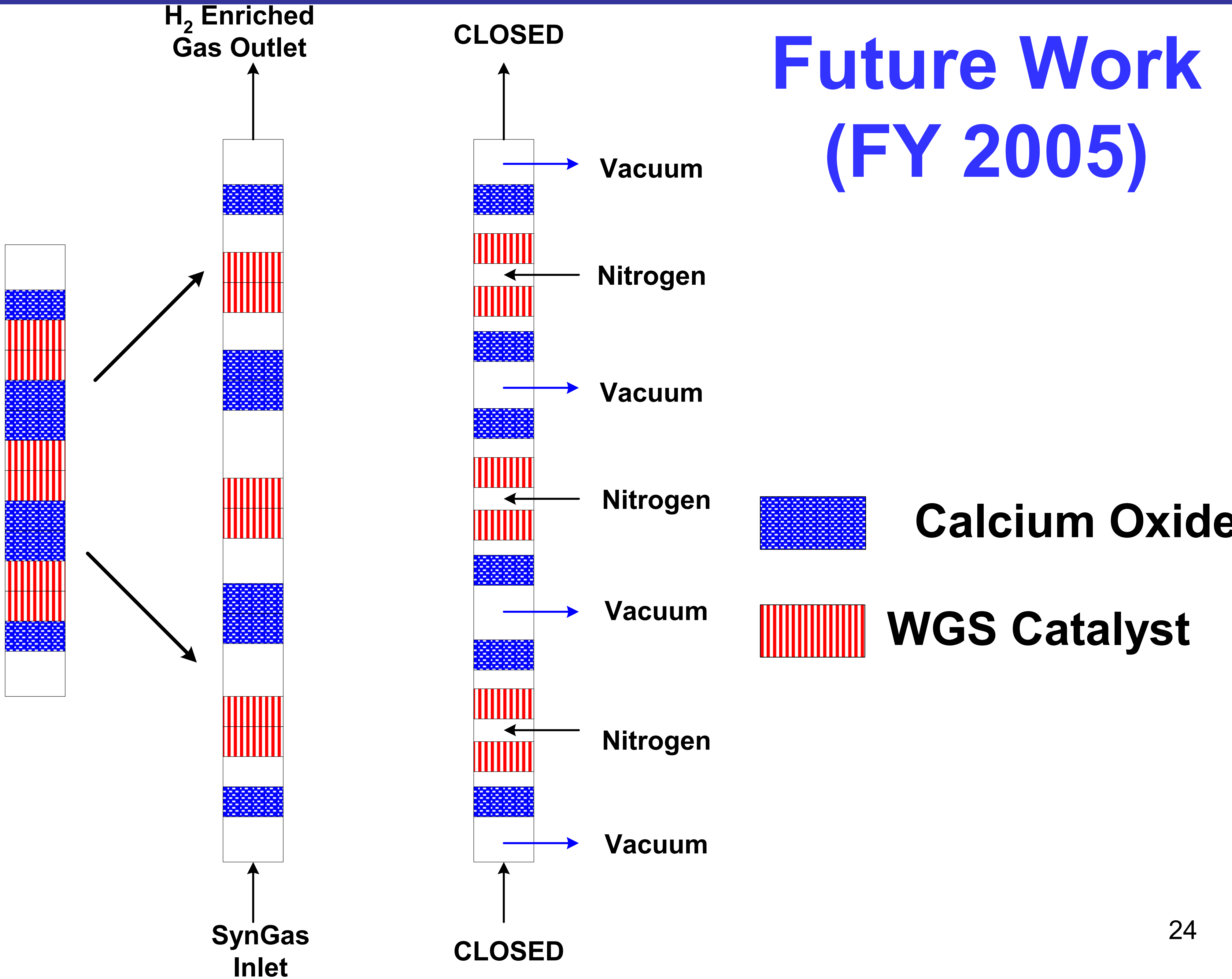
MSB Testing

- Multicyclical Testing that includes:
  - Carbonation
    - Simulated WG mixtures
    - Effect of Pressure
  - Calcination
    - $N_2/H_2O/CO_2$/Vacuum combination
- Effect of H_2S:
  - Competing sulfidation and carbonation
  - Effect of steam to prevent sulfidation
  - Optimization of X_{CO2}/X_{H2S}

Future Work (FY 2005)

- Breakthrough Testing
  - Hydrogen Generation
    - Purity of hydrogen
      - Thermal Conductivity
      - Density
      - Specific Heat
    - CO exit concentration
    - CO_2 exit concentration
- Multicyclic Catalyst Performance
  - Catalyst maintained under inert gas
    - No exposure to CO_2, H_2O

Future Work (FY 2005)



Publications and Presentations

Presentations:

"Enhancing Hydrogen Production With In-Situ CO2 Separation Using CaO/Catalyst Systems" Iyer, M., Gupta, H., Sakadjian, B. and Iyer, M. *AIChE Annual Tech. Meeting*, Austin, TX, 2004.

Gupta, H; Iyer, M.V.; Sakadjian, B.B.; and Fan, L.-S., "The Role of CaO in Maximizing Hydrogen Production from Fossil Fuels" Fuel Cell Seminar, San Antonio, TX, 2004

H. Gupta, M. V. Iyer, B. Sakadjian and L.-S. Fan, "Reaction Enhanced Hydrogen Production from Water Gas Mixtures." 29th International Technical Conference on Coal Utilization & Fuel Systems, April 17-22, 2004, Clearwater, Florida, USA.

Publications:

Gupta, H; Iyer, M.V.; Sakadjian, B.B.; and Fan, L.-S., "The Role of CaO in Maximizing Hydrogen Production from Fossil Fuels" Proceedings from Fuel Cell Seminar, San Antonio, TX, 2004

Hydrogen Safety

Most significant hydrogen hazard associated with this project is

- The experiments involved in this project use a gas mixture consisting of CO, H_2, H_2O, H_2S, CO_2 and N_2.
- High temperatures (100-700^{o}C) and pressure (1-20 bars)
- The most significant hydrogen hazard associated with this project is the combustion/explosion of hydrogen inside and/or outside the reactor. In addition, carbon monoxide could pose a similar safety hazard.

Hydrogen Safety

Our approach to deal with this hazard is

- Minimize gas flow rates and reactor footprint
- Double sash well-ventilated walk-in hood (81 fpm)
- 13 ppmv Hydrogen in the vicinity of reactor
- Manual controls are outside the hood