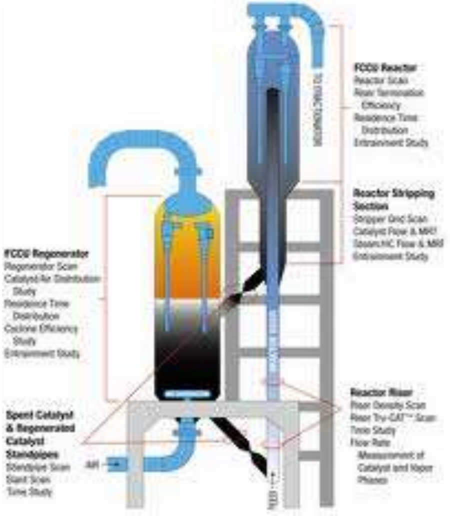
CO_2 Recovery From Power Plants by Adsorption: Issues, Challenges and Approaches

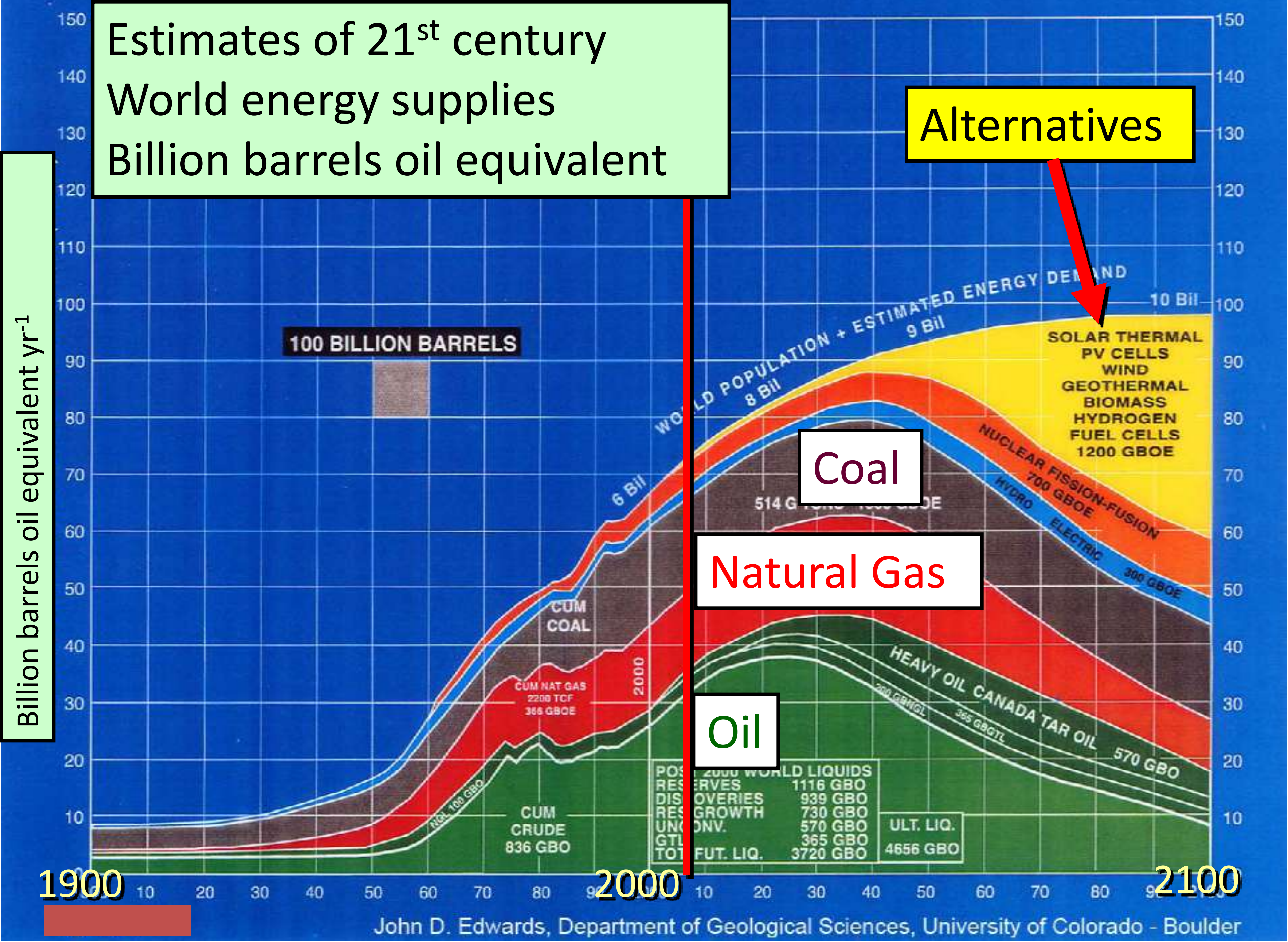
Awareness and Capacity Building in Carbon Capture and Storage: Earth Processes, (ACBCCS-2013)
New Delhi
16th January 2013

Presented
by
Anshu Nanoti

CSIR- INDIAN INSTITUTE OF PETROLEUM,DEHRADUN



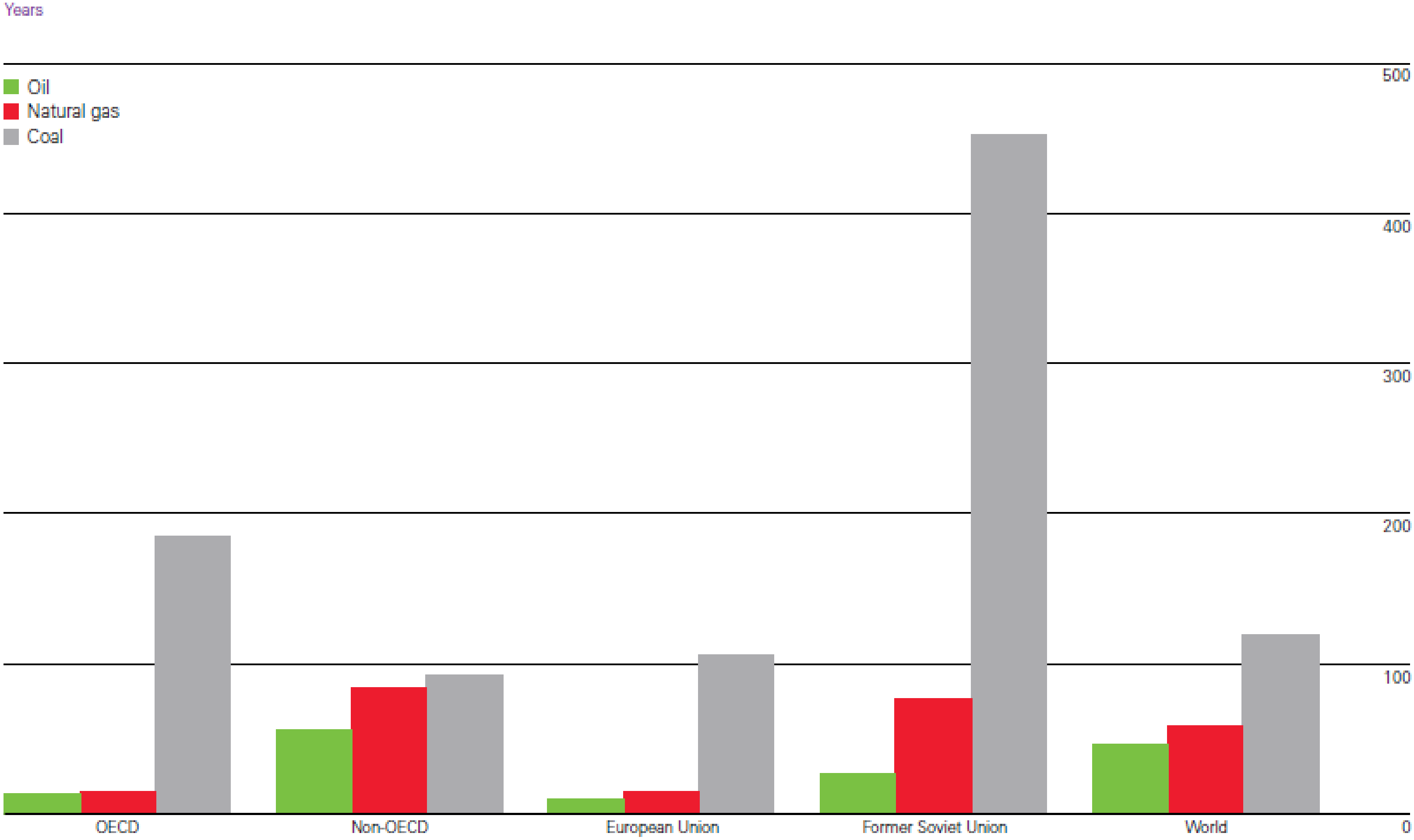
Estimates of 21st century World energy supplies Billion barrels oil equivalent



John D. Edwards, Department of Geological Sciences, University of Colorado - Boulder

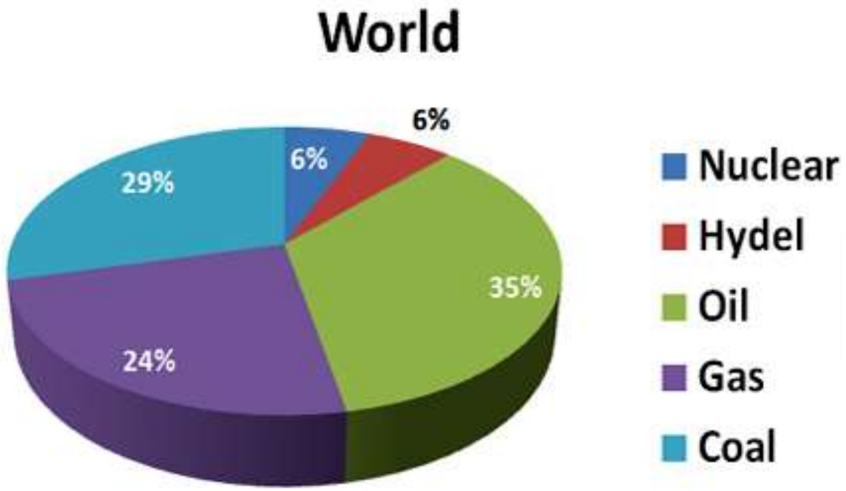
Reserves to Production Ratios (R/P)

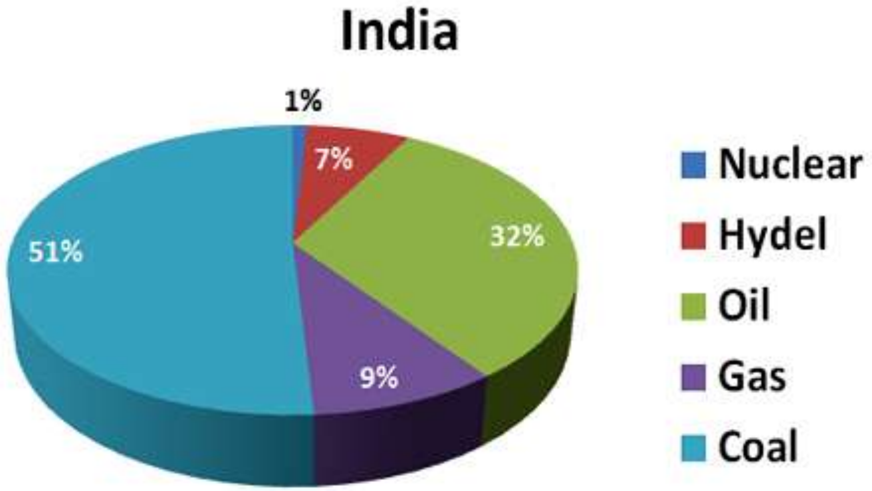
Fossil fuel reserves-to-production (R/P) ratios at end 2010



Coal remains the most abundant fossil fuel by global R/P ratios, though oil and natural gas proved reserves have generally risen over time. Non-OECD countries account for 93.4% of the world's proved oil reserves; 90.9% of natural gas reserves, and 56% of coal reserves. The Middle East holds the largest share of proved oil and natural gas reserves; Europe and Eurasia hold a significant share of the world's natural gas and the largest coal reserves. Asia and North America also hold substantial coal reserves.

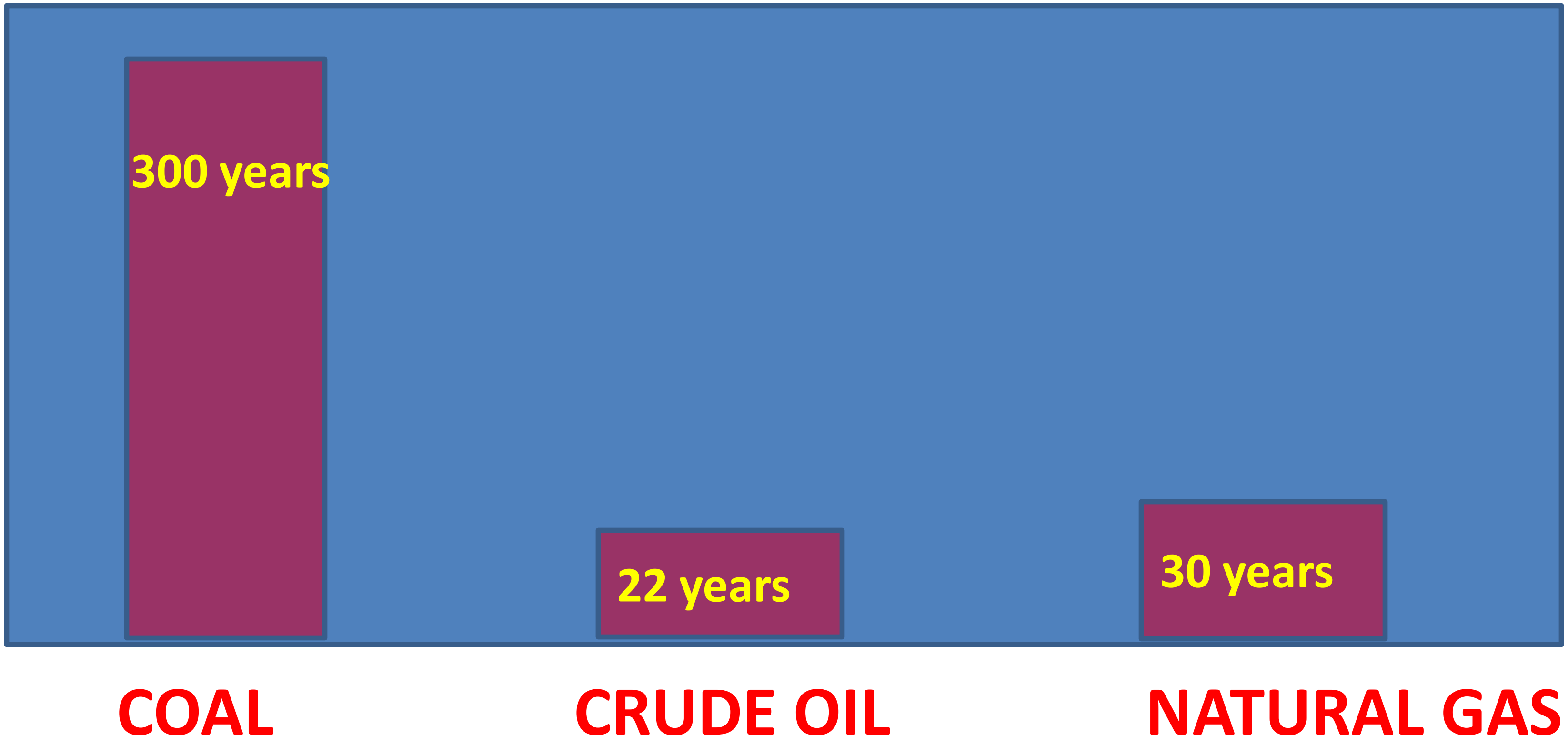
INDIA'S ENERGY BASKET





Fossil Fuel	Reserves	Production	R/P
Coal	92.0 bT	322 mT/A	286.00
Gas	22.8 tcf	752 bcf/A	30.00
Petroleum	5.40 bbl	0.643 mbl/D	15.00

Reserve / Production (R/P)Ratio

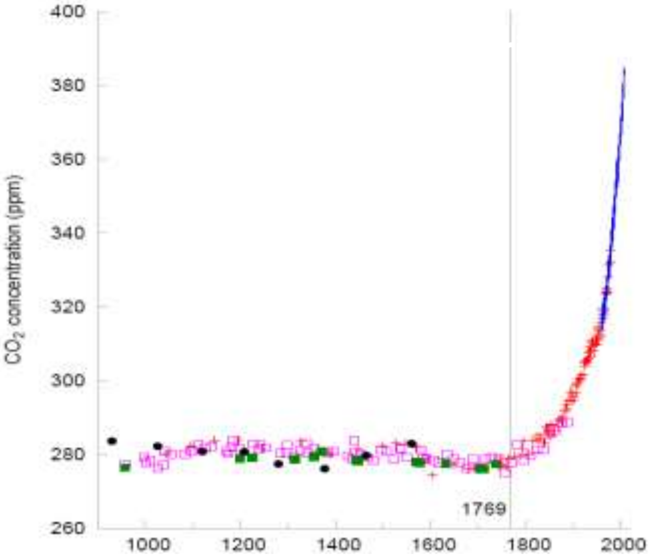


Coal abundance will lead to it being the major Contributor in power generation in the coming decades

Global CO_2 Emissions

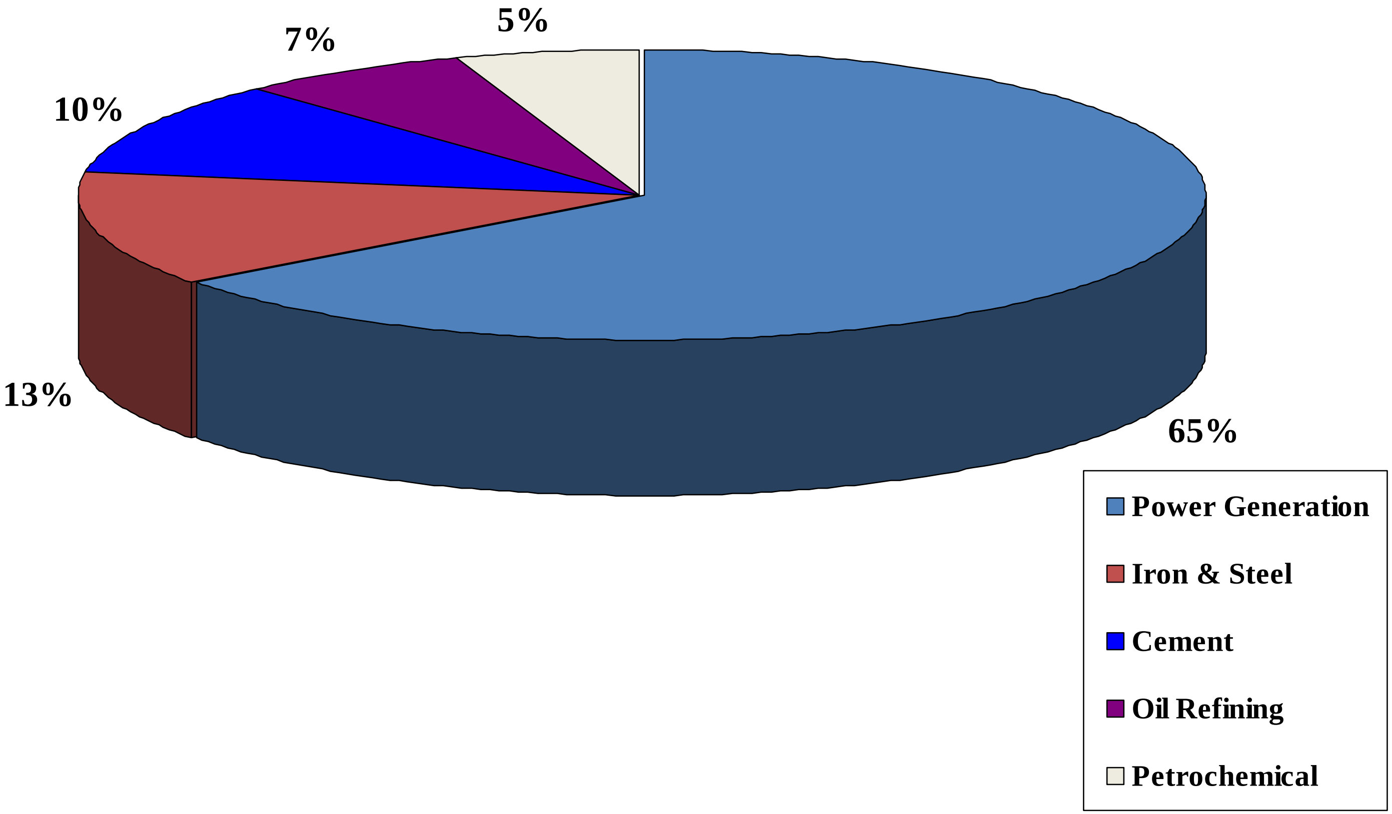
- The World economies emit approximately 30 gigatons of CO_2 (Gt CO_2) to the atmosphere annually

- In the absence of explicit efforts to address climate change and increased demand for energy , CO_2 emission is projected to rise to as much as 9000 Gt over this coming century



- As per UN Framework Convention on Climate Change, cumulative CO_2 emissions need to be held to not more than 2600 $GtCO_2$ to 4600 $GtCO_2$

Sources of CO_2 Emissions



Stabilisation of Atmospheric CO_2 Levels

What are the Options

- **Reduce Energy Use, Improve efficiency of production**

- **Switch to Different Fuels**
  - Natural Gas in Place of coal
  - Renewable Energy
  - Nuclear Power

- **Sequester CO_2**
  - Natural Storage for CO_2
  - Capture and store CO_2

Carbon Capture and Sequestration

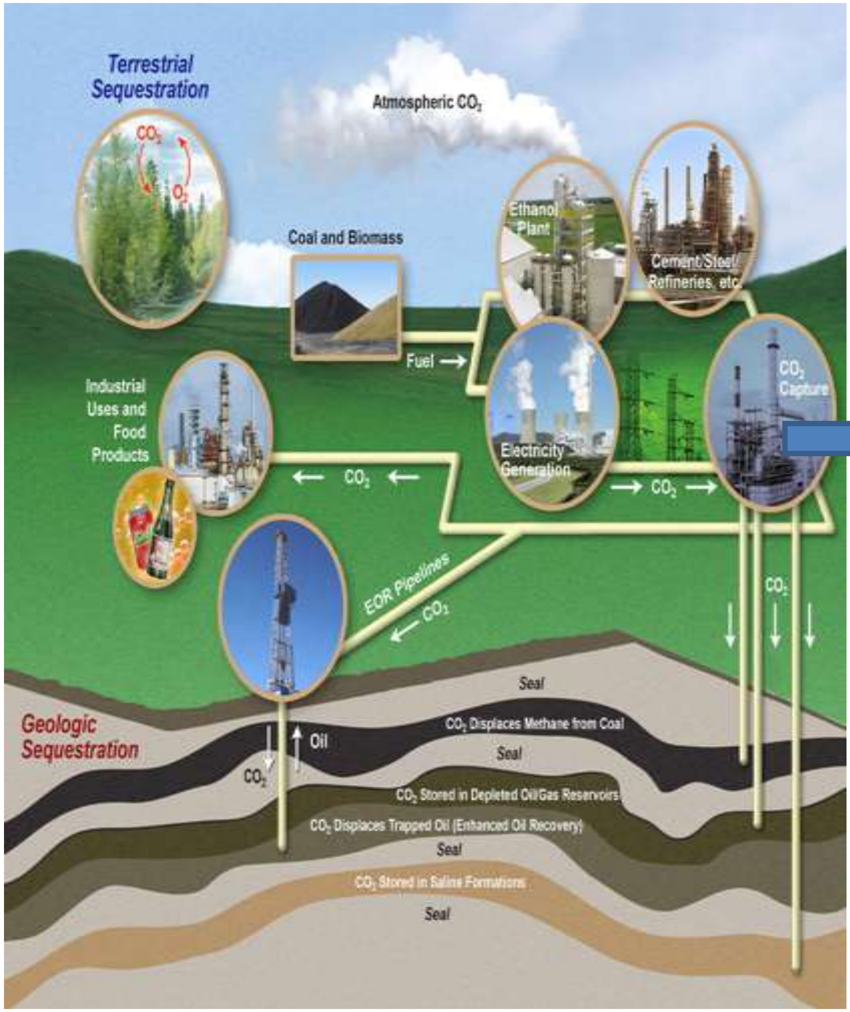
- CCS offers opportunity to meet increasing demand for fossil fuel usage in short to medium term while reducing associated GHG
- CCS complements strategies to meet global warming like
  - Improve energy efficiency
  - Switch to lesser carbon intensive fuels
  - Phase in usage of renewables

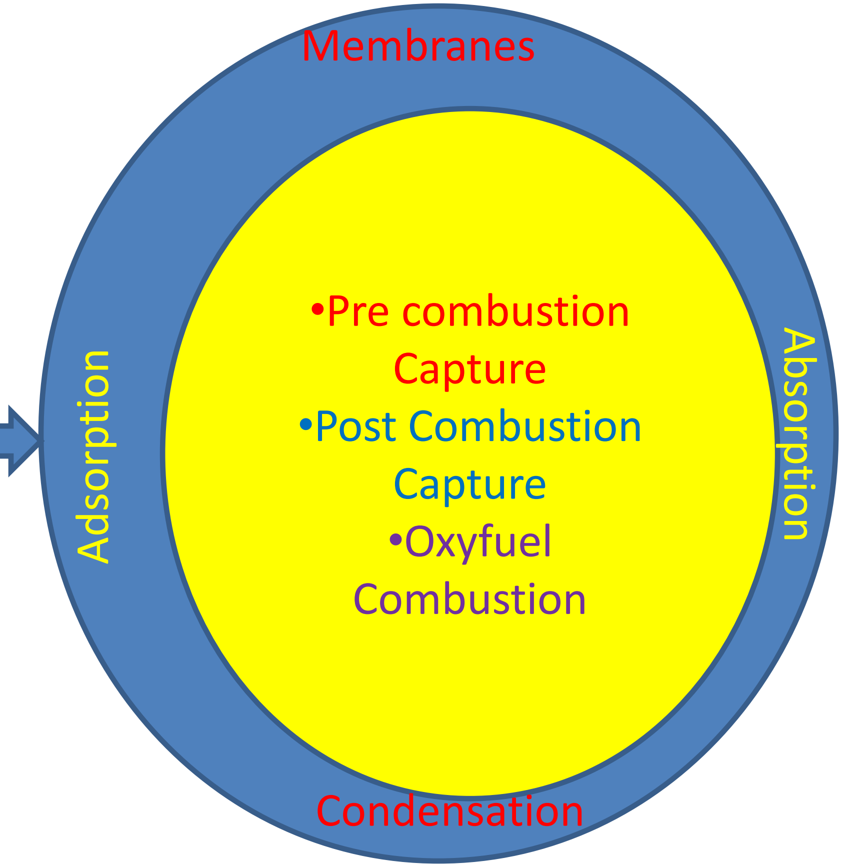
CO_2 Sequestration

CO_2 Sequestration Involves

- Capture
- Transport
- Storage of CO_2 in Geological Formations

Combating Climate Change
Carbon Capture and Sequestration





Membranes

Adsorption

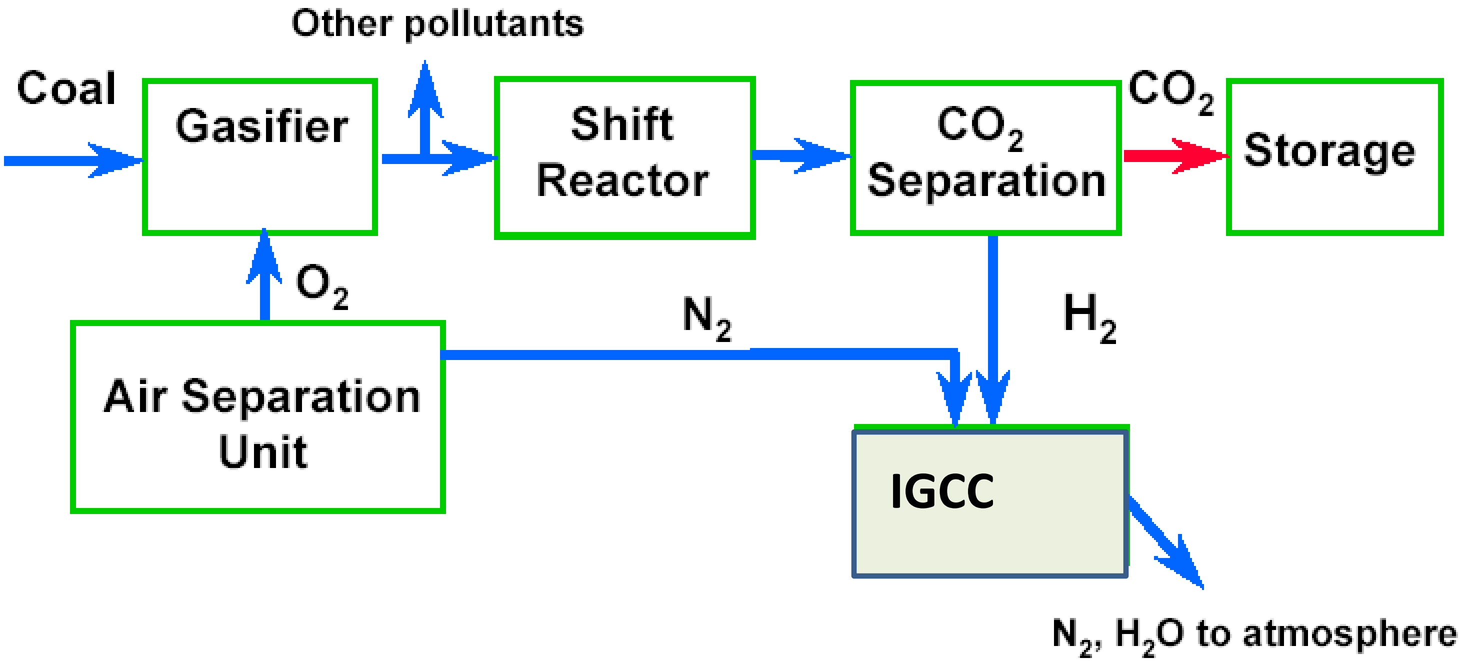
- Pre combustion Capture
- Post Combustion Capture
- Oxyfuel Combustion

Absorption

Condensation

Pre-Combustion CO_2 Capture

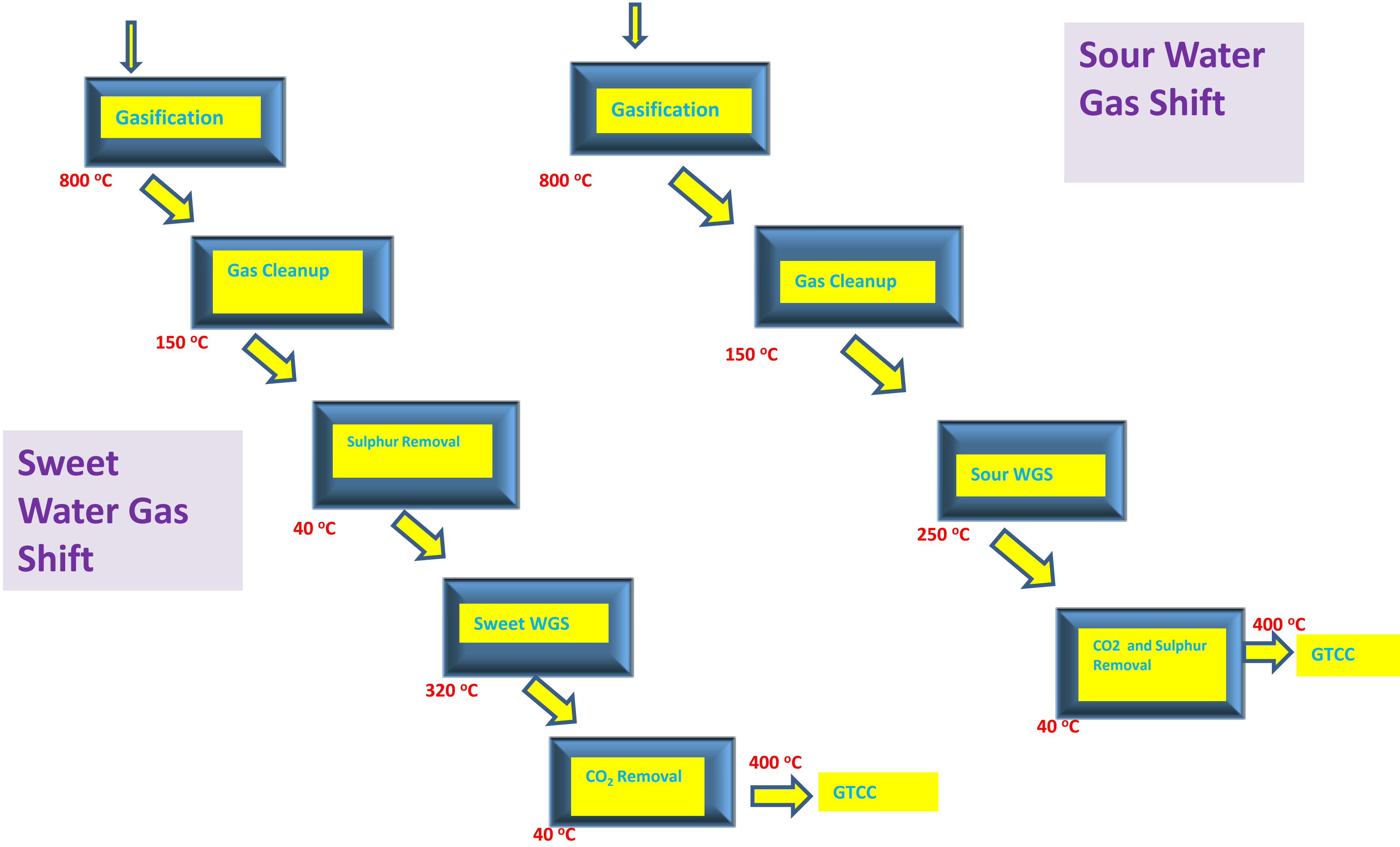
Coal fired power plant



Pre-Combustion CO_2 Capture

- **Advantages:**
- **Generally high CO2 concentration than for post combustion capture**
- **High pressure**
  - **More compact size of the equipment**
  - **High driving force for CO2 capture**
- **90-95% of CO2 emissions can be captured.**
- **Can produce H_2 as transportable energy vector, or liquid fuels from coal - but penalties on efficiency**
- **Disadvantages:**
- **Requires a chemical plant in front of gas turbine**
- **High investment cost of dedicated new-build plant.**
- **High NOx emissions – will require expensive scrubbers.**
- **Efficiency of H_2 burning turbines is lower than conventional turbines.**

Acid Gas Removal in Gasification: Conventional Processes



Sweet Water Gas Shift

Gasification

800 °C

Gas Cleanup

150 °C

Sulphur Removal

40 °C

Sweet WGS

320 °C

CO_2 Removal

40 °C

400 °C

GTCC

Sour Water Gas Shift

Gasification

800 °C

Gas Cleanup

150 °C

Sour WGS

250 °C

CO2 and Sulphur Removal

40 °C

400 °C

GTCC

Acid Gas Removal in Gasification

- Acid gas removal is carried out **at low temperature (40 $_o$C)**

- This involves several steps of **cooling and re-heating** of syn gas in both sour WGS and sweet WGS routes

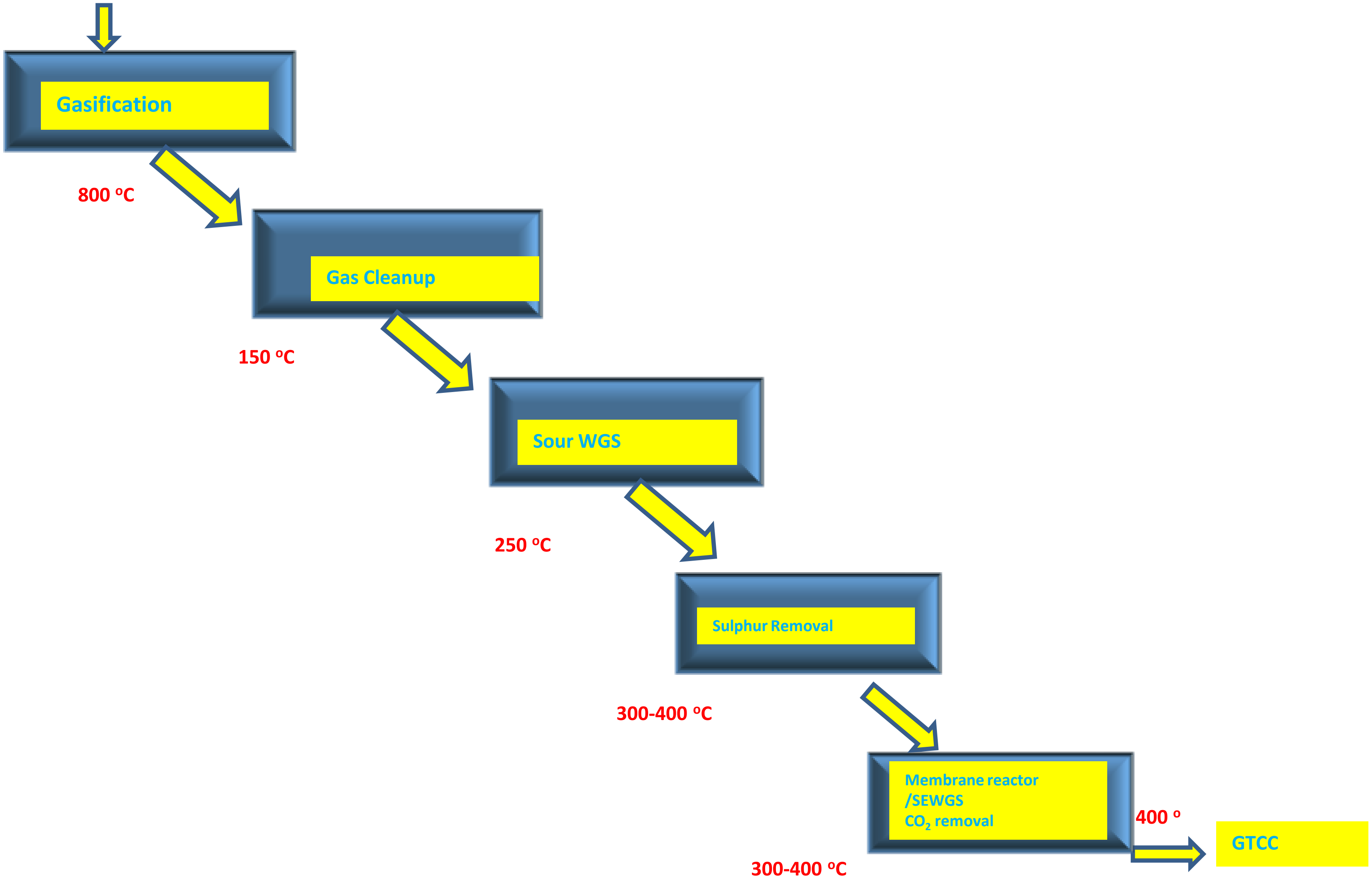
- These **temperature swings** lead to over all thermal **lower efficiency** of the process

- High temp acid gas removal

- Membrane reactors

- Sorption enhanced water gas shift

Acid Gas Removal in Gasification: New Trends



Gasification

800 °C

Gas Cleanup

150 °C

Sour WGS

250 °C

Sulphur Removal

300-400 °C

Membrane reactor
/SEWGS
CO_2 removal

300-400 °C

400 °

GTCC

Expected Benefits

- CO_2 mitigation
- High purity hydrogen production with higher recoveries
- Reduced equipment costs
- High temp. desulphurisation (370-480 C in a 600 MW IGCC plant)

– Reduced plant cost by	$ 269/killowat
– Increase in overall thermal efficiency by	3.6 points
– Reduction in electricity cost by	9.6%
(RTI report 2007)	

R & D Challenges in CO_2 Capture by Adsorption

PRECOMBUSTION

Associated Challenges

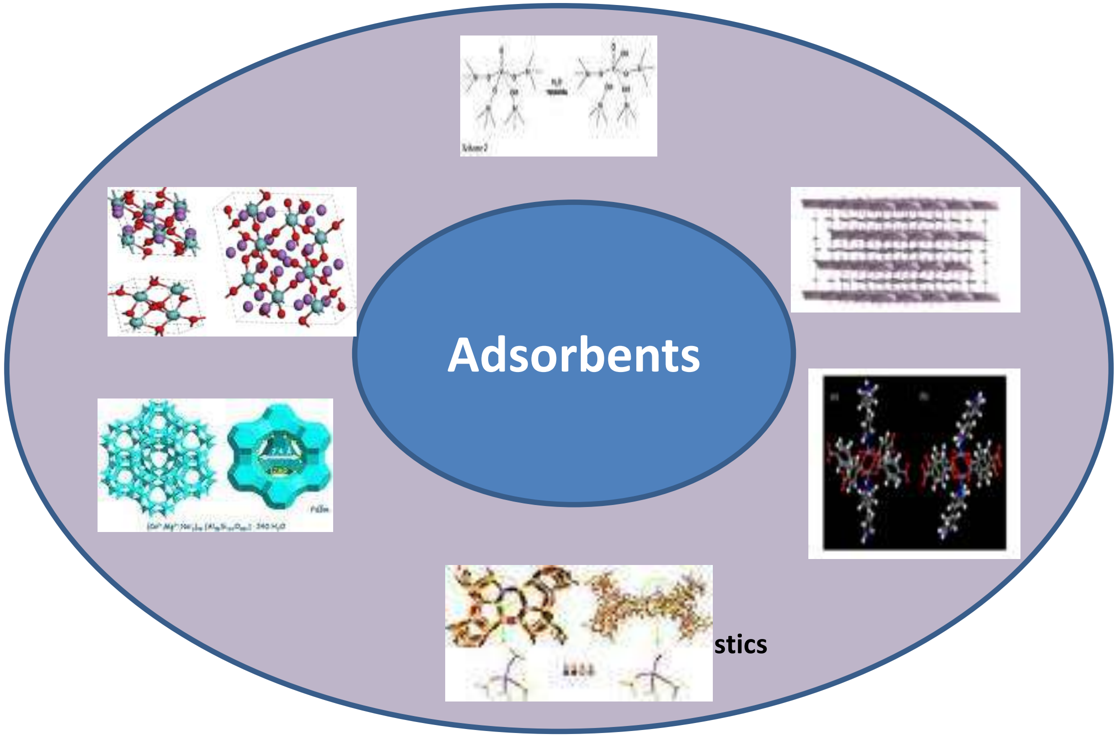
- Gas at high temperature contains both CO2 and H2S

- Large temperature swings necessary in treatment train for CO_2 and H_2S removal ,shift reactions , leads to high energy costs

Enabling R & D

- Develop high temperature CO_2 selective adsorbents
- Develop high temperature H_2S selective adsorbents
- Develop dual - function adsorbents for simultaneous removal of CO_2 and H_2S at high temperature
- Develop adsorbent membranes for selective CO_2 removal in Shift Reactor

For the development of adsorption process
Heart of the process is



Adsorbents

stics

Desirable Characteristics

↓

Good loading capacity
High Selectivity
Ease of Regenerability

Potential Sorbents for High Temperature CO_2 removal

Possible candidates:

– Magnesium Oxide
– Calcium Oxide
- Titanosilicates
- HTLc (k-promoted)
– Lithium Aluminate
– Lithium Ferrite
– Lithium Titanate

Especially promising:

– Lithium Zirconates
– Lithium Silicates
- Eutectic Salt Promoted Lithium Zirconates/Silicates
– Precipitated Calcium Oxide/Calcium Carbonate

Sorbent regeneration by

•Temperature Swing
•Pressure Swing
•Inert Purge

Typical Capacities of Commercial and Developmental CO_2 Selective Adsorbents

Adsorbents	Temperature °C	Loading mol/kg
Activated carbon	250-300	0.1-0.2
5A zeolite	250	0.2
Titanosilicates	24-200	proprietary
HTlc (K promoted)	300-400	0.4-0.7
Double layer hydroxide	375	1.5
Li-Zirconate	500	3.4-4.5
CaO	500	4 to 8

Adsorbents for H_2S Removal

- ZnO
- ZnO-TiO2
- ZnO-TiO2, Zinc Ferrite
- Zinc titanate doped manganese oxide
- CeO2 + La, Cu
- Titanium supported cobalt titanate
  coupled with Zinc aluminate supported Zinc oxide
- ZnO coated monolith

Adsorbents for CO_2 and Sulphur (H_2S, COS) Removal

Adsorbent	Temperature °C	CO2 adsorbed mol/kg	H2S Adsorbed mol/kg	NH3 adsorbed mol/kg	Remarks
13X zeolite	200	0.67	1.85	4.0	H2S loads and unloads reversibly NH3 strongly loads, TSA required for regeneration
HTC	300	0.20	1.79	0.02	H2S regeneration difficult
Mg-Na DS	375	4.70	1.74		H2S regeneration difficult

Use Layered Beds?

Hot Gas Clean up in Clean Coal Technology Development

CSIR Project under Clean Coal Mission Programme

Objectives

To develop high temperature adsorbents for simultaneous removal of CO2 and H2S at high temperature and pressure

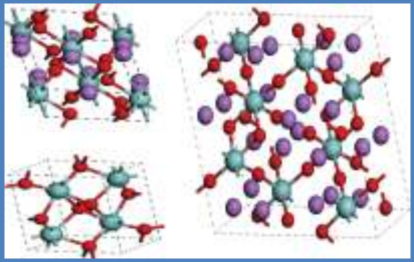
Challenges

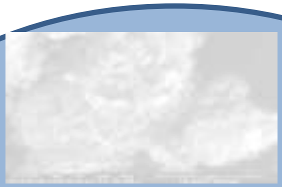
- To develop Selective adsorbent capable of simultaneously removing both CO2 and H2S at elevated temperatures
- Regenerability,cyclic stability
- Thermal stability

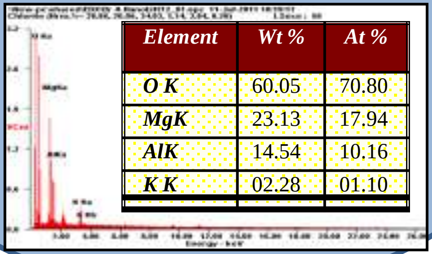
Technology Development for Clean Coal

Adsorbent Synthesis and Screening

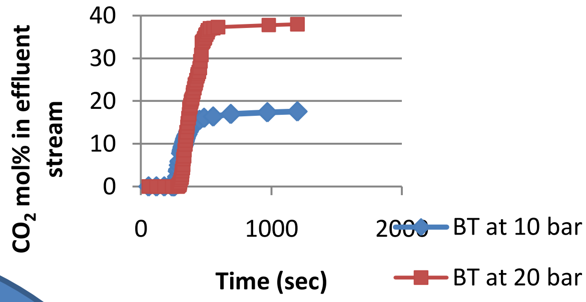
Hydrotalcite, Calcium oxide and mixed oxides are being synthesised and evaluated in high temp







Element	Wt %	At %
O K	60.05	70.80
MgK	23.13	17.94
AlK	14.54	10.16
K K	02.28	01.10



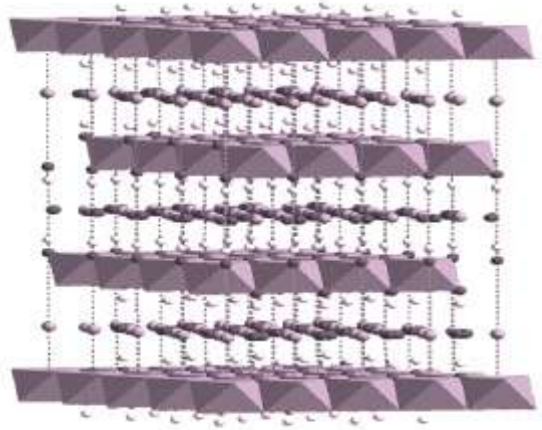
Process Cycle Development

Fixed bed cyclic process is being tested under varying operating conditions

Adsorbent Synthesis

High Temperature Sorbent Development at IIP

Adsorbent development work at IIP is focused on hydrotalcites



- Only hydrotalcites showed appreciable capacity of CO_2 in the targeted temperature window of 300-400 °C
- Hydrotalcites are regenerable at temp. 450-470 °C i.e. temperature swing requirement for regeneration is small
- Hydrotalcites are open to physical and chemical manipulation
  - Numerous combinations of structural cations and interlayer charge-compensating anions possible
- Possibility of CO_2 capacity enhancement by such chemical manipulations
- Possibility of integrating both CO_2 and H_2S sorbing functionality into the structure of hydrotalcites

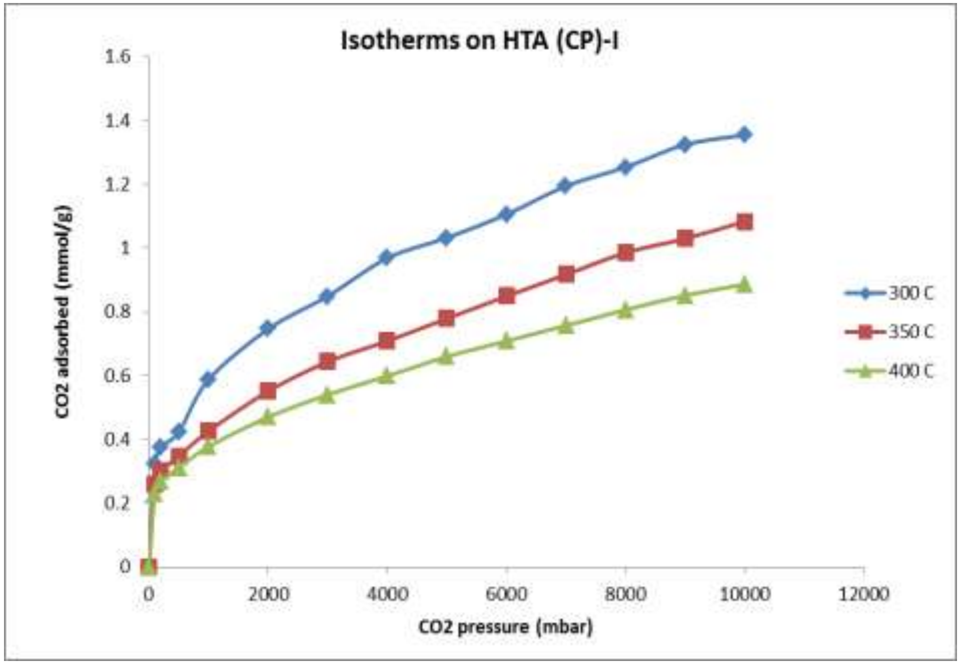
- Other high temperature sorbents such as Lithium Zirconates, Lithium Silicates though have higher CO_2 capacity (4-6 moles/kg) but appreciable uptake occurs at temperature > 450 °C

- These sorbents also require much higher regeneration temperature 650-800 °C

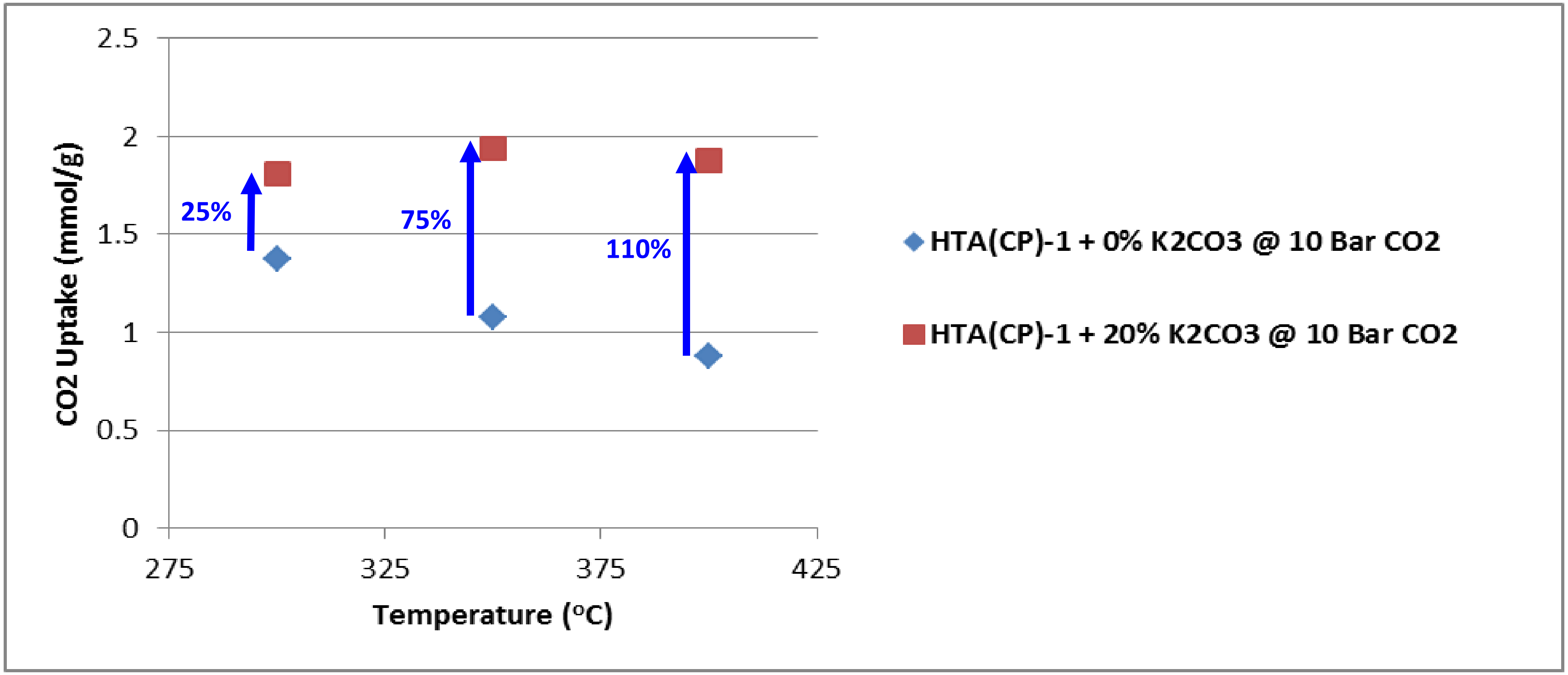
Evaluation of Hydrotalcite Adsorbents

Equilibrium Isotherm Measurements (Temp. 300-400 °C) Using HIDEN Gravimetric Analyzer

HT prepared by Coprecipitation Route

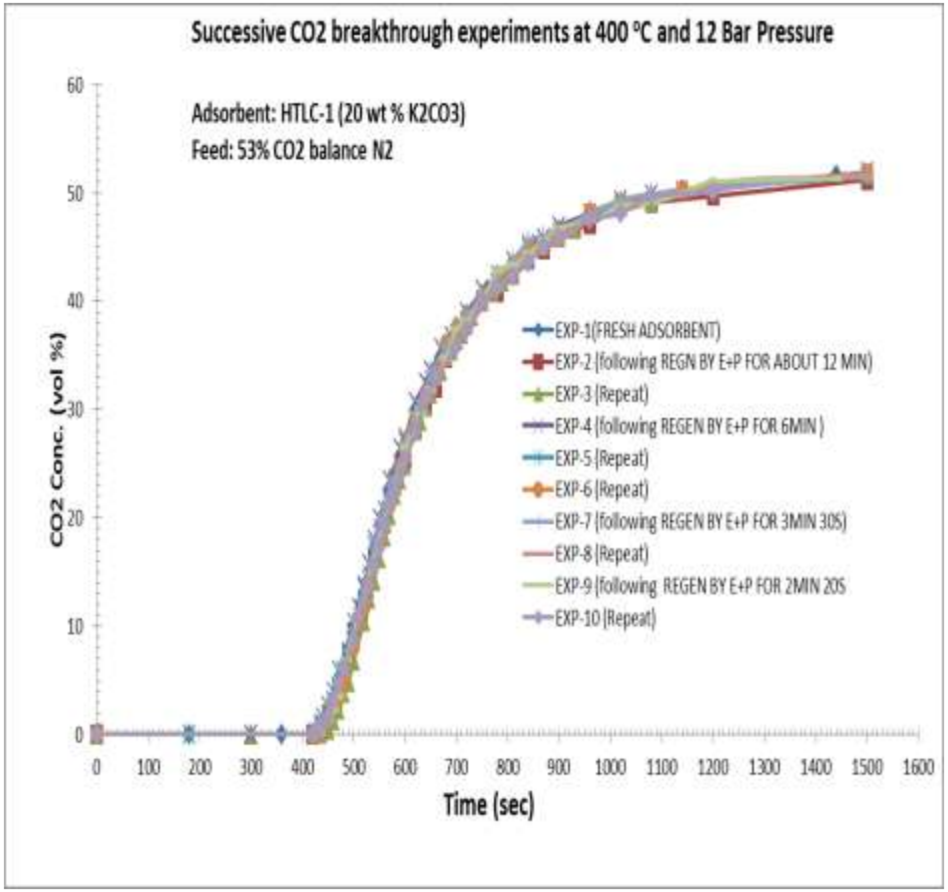


Promotional Effect of K_2CO_3 Impregnation on CO_2 Capacity of a Hydrotalcite Prepared by Co-Precipitation Route



Promotional Effect of K_2CO_3 Impregnation on eqm. CO_2 uptake is Temperature Dependent

Successive CO_2 Breakthrough Experiments at 400 °C and 12 bar Pressure

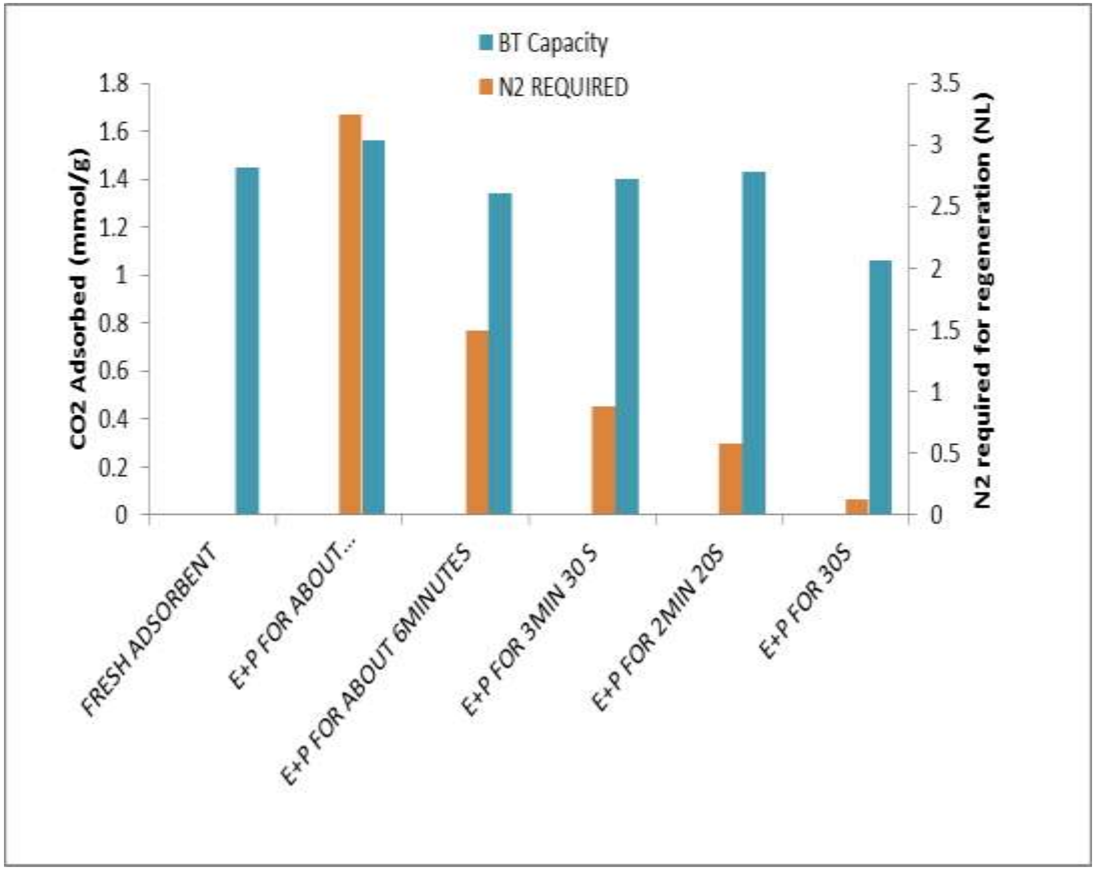


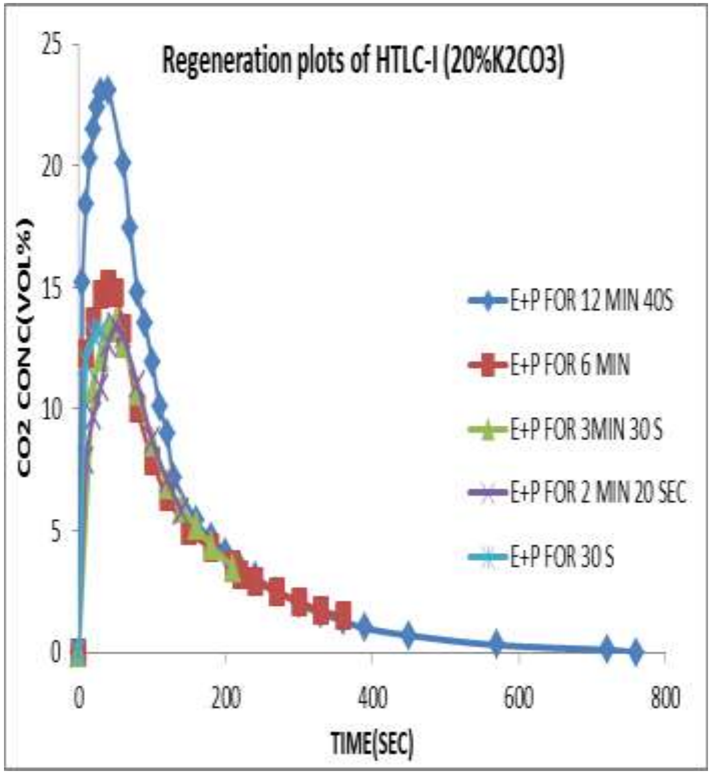
No appreciable deterioration in breakthrough capacity observed over repeated sorption-desorption cycles

- Single Column Adsorber
- Microprocessor based
- Max. Temp: 500
- Flexibility to evaluate different PSA.VSA cycles

Regeneration Studies

Optimization of Inert Purge Requirement for Adsorbent Regeneration



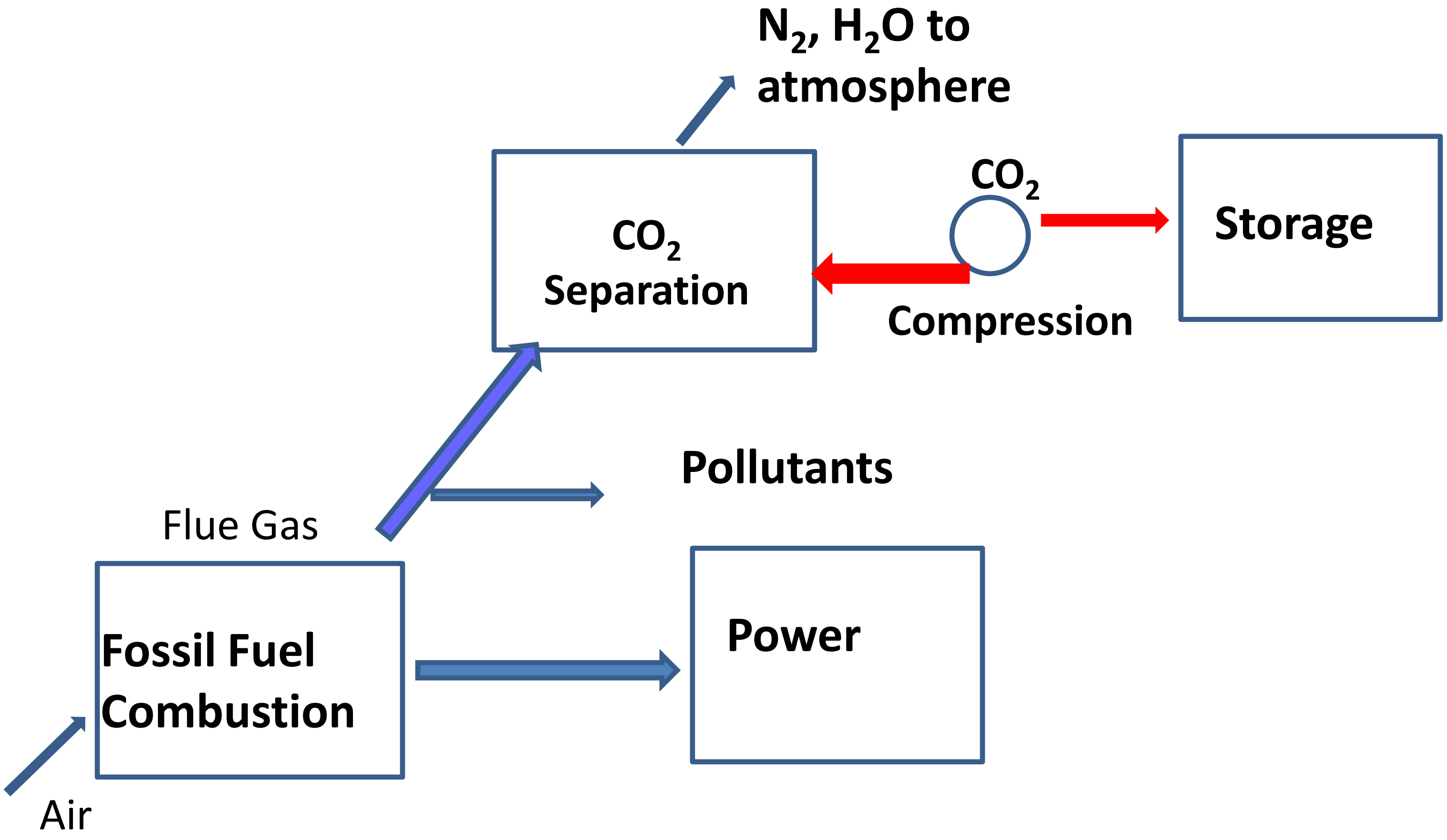


Significant reduction in regenerant requirement was observed with small drop in breakthrough capacity

Round Up

- CO_2 capacity of IIP sorbents are comparable to the best reported values for similar class of high temperature sorbents (Ref: FP-7 EU CAESAR Prog.)
- A correlation exists between equilibrium CO_2 capacity with surface area of hydrotalcite based sorbents
- A temperature dependent promotional effect of K_2CO_3 impregnation on CO_2 uptake has been observed
- Highest CO_2 uptake in the temperature range 350-400 ^oC for the promoted adsorbent
- Adsorbents are regenerable under inert purge with or without evacuation at ~450 ^oC
- This indicates a small temperature swing of 50-100 ^oC will be required for adsorbent regeneration
- No appreciable loss in breakthrough capacity was observed over multiple cycles of adsorption-regeneration

Post Combustion Capture



N_2, H_2O to atmosphere

CO_2 Separation

CO_2

Storage

Compression

Pollutants

Flue Gas

Fossil Fuel Combustion

Power

Air

CONVENTIONAL POWER PLANT

R & D Challenges in CO_2 Capture by Adsorption

POST COMBUSTION

Associated Challenges

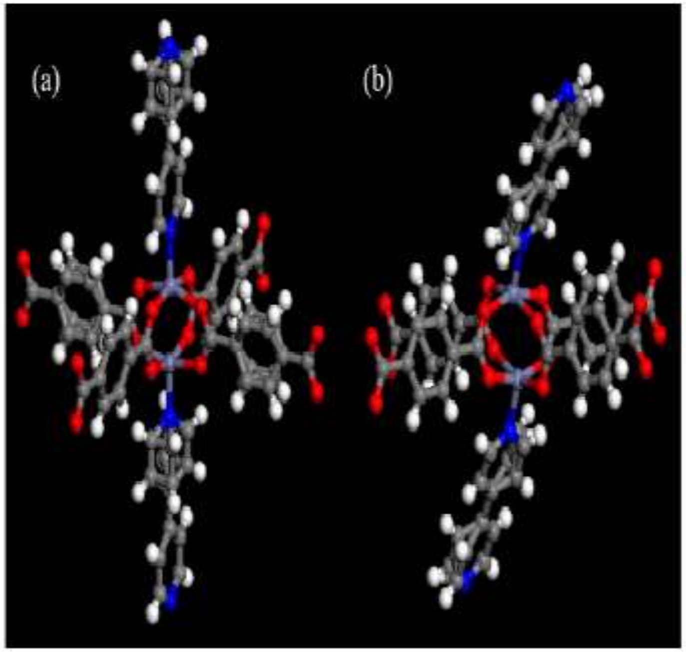
- Low capacity of available adsorbents
- Moisture in flue gas
- SOx, NOx contaminants
- Low flue gas pressure,low CO_2 partial pressure
- Very large flue gas flows

Enabling R & D

- -Improve adsorbent capacity >20 wt%
- Develop very large Surface area (>5000m^2/gm)adsorbents such as MOF
- Improve moisture , SOx and NOx tolerance of such MOFs
- Process intensification :
  Use structured adsorbents
- Process intensification :
  Use RPSA
- Develop improved process cycles to reduce power costs to < 0.1Kwhr/Kg CO_2 removed

Metal Organic Framework Adsorbent

- MOF are new class of adsorbent material with strong potential for CO2 adsorption
- Generally consisting of two building elements: inorganic coupling units and organic linkers
- Highly porous with large surface area
- Pore size and functionality can be tailored

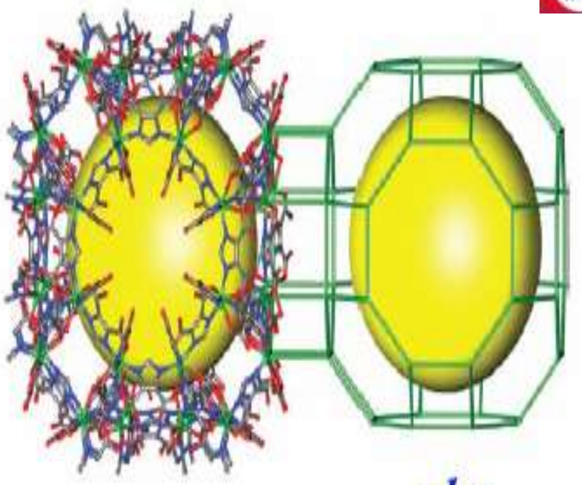


***P**roperties to exploit*

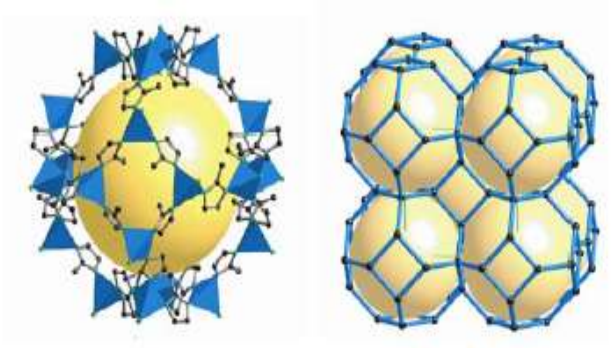
<u>similarities to molecular sieves</u>:
- synthesis conditions
- good yields
- crystalline
-tunable hydrophil(phob)icity and acid(basic)ity

ty

<u>differences from molecular sieves</u>
- lower temp stability (up to 450 oC reported)
- much higher SA/ PV
- more unobstructed gas diffusion
- much more diverse chemistry
- many more metals/ metal clusters available
-organic linkers can contain functionality



rho

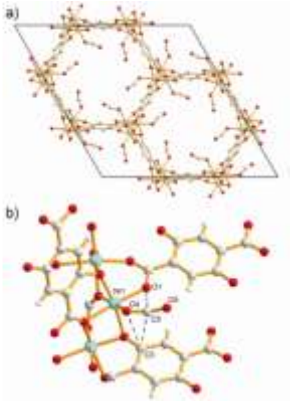


sod

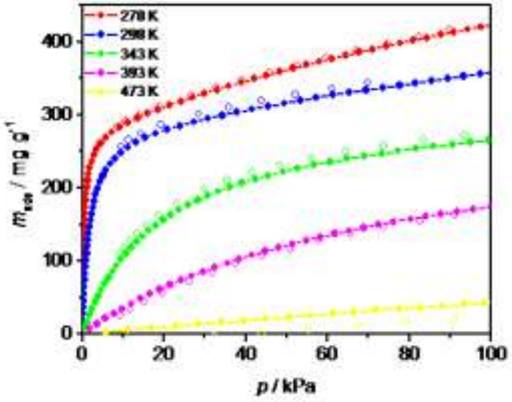
8 from Yaghi, et al. PNAS 2006, 103, 10186

Objective and Scope of Work

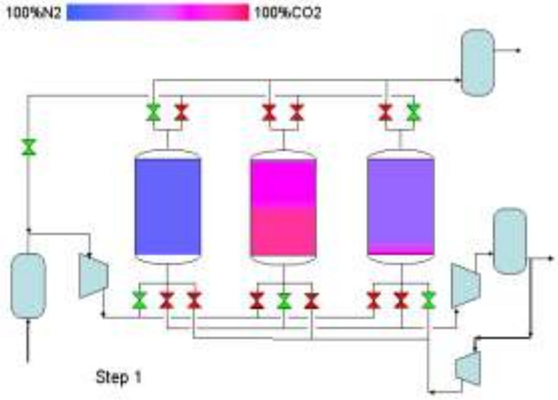
To evaluate performance of MOF for capture of CO_2 from flue gas



MOF Adsorbent Synthesis



Adsorbent screening & evaluation



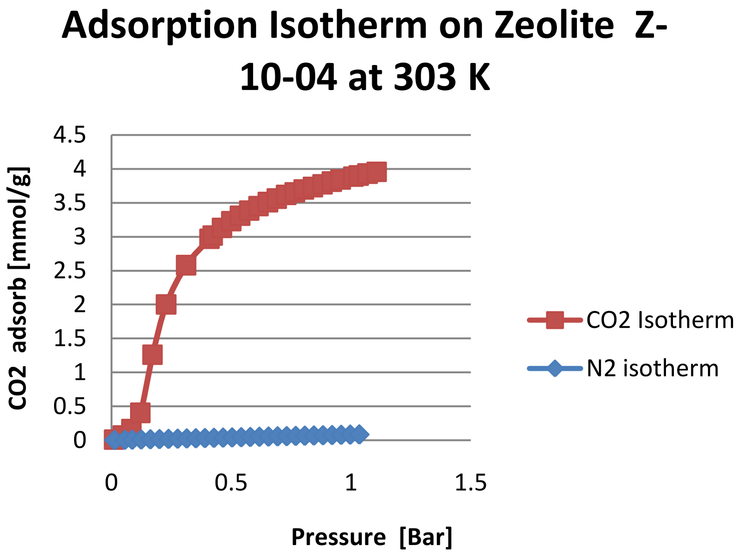
Process Optimisation ,Simulation modelling

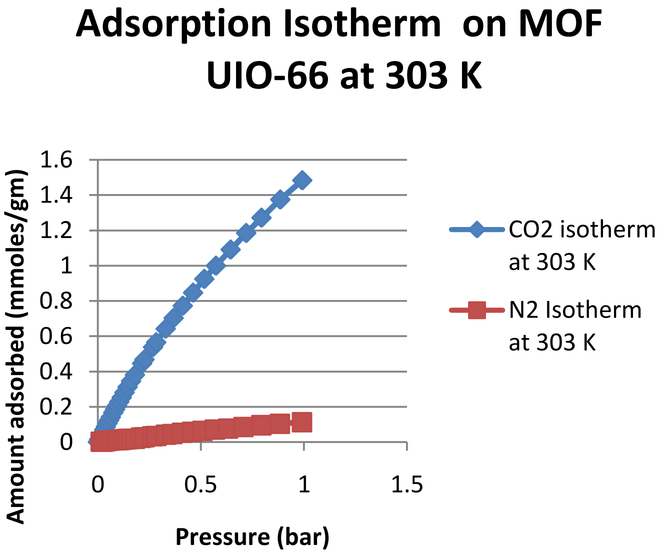
Adsorbent Screening & Evaluation

Adsorbents were screened on the basis of

- Isotherms
- Breakthrough Measurements in Single Column Microadsorber Unit
- Desorption Breakthrough Measurements
- Breakthrough Measurements in Presence of Moisture
- Single Column PSA Studies

Comparison of Equilibrium Isotherm Data





Adsorbent Selectivity for CO2-N2 at I bar

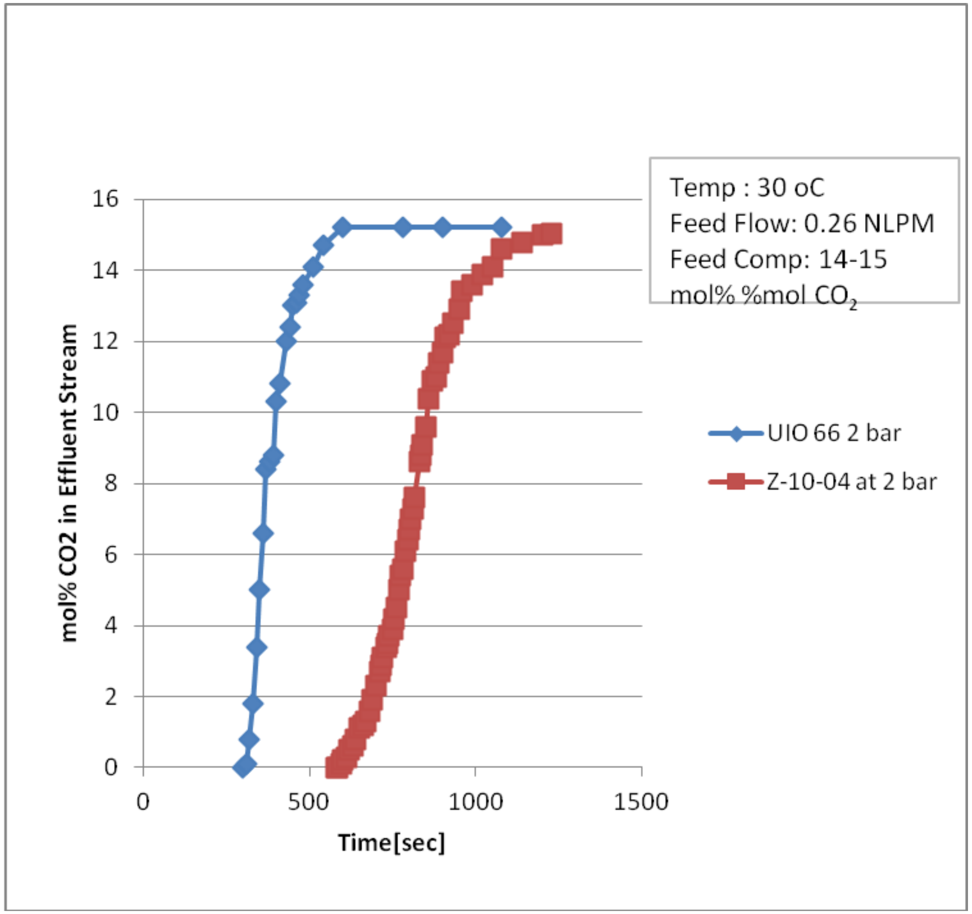
Zeolite Z-10-04	MOF- UIO-66
40.0	13.2

MOF Capacity for CO_2 is lower than zeolite in the pressure range of interest

Deciding Factor will be regenerability !

Breakthrough Measurements

Comparison of CO_2 breakthrough of MOF and Zeolite



Temp : 30 oC
Feed Flow: 0.26 NLPM
Feed Comp: 14-15 mol% %mol CO_2

Feed Comp: 15 mol% CO_2 **in N_2**

Temp: 303 K

Feed Flow Rate: 0. 26 NLPM

Adsorber Col dia: 1.1 cm

Adsorbent loading: 5 gms

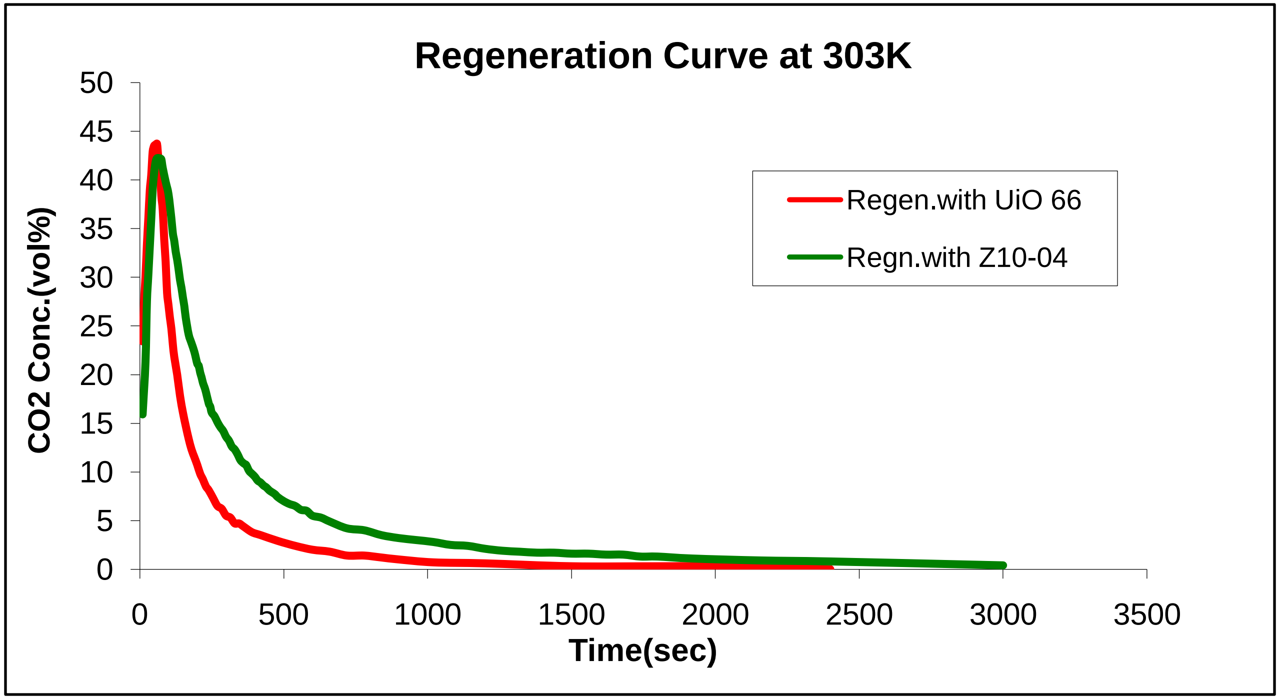
Sharper Breakthrough curves with MOF

Better adsorption kinetics are indicated

Could impact adsorbent regenerability

Regeneration Studies

Comparison of Regeneration Curves



Better Regenerability of MOF is Demonstrated

VSA Cycle Studies

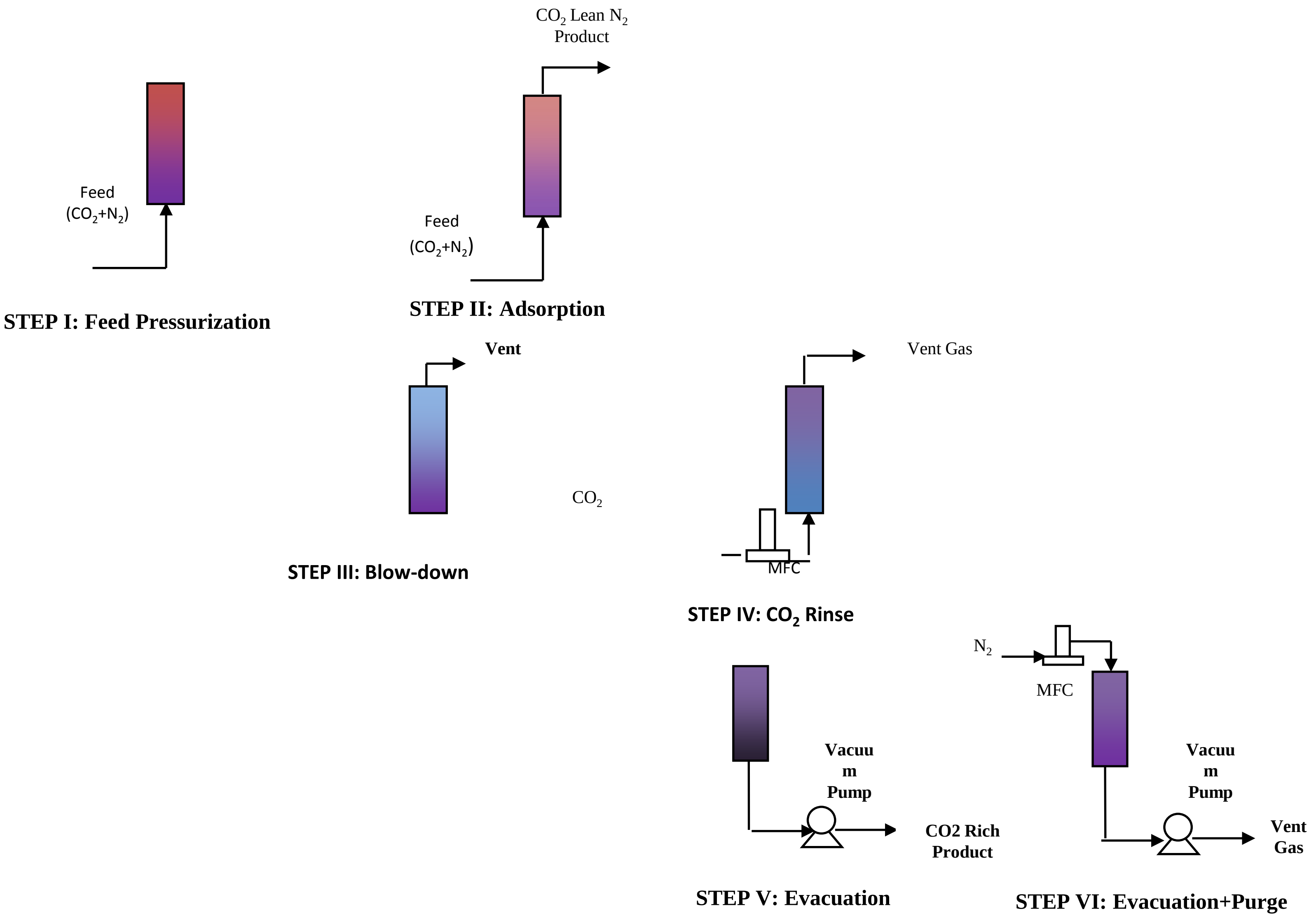
Single Column VSA Cycle Studies

- Six step VSA Cycle was used in the single column microadsorber
  - Feed pressurisation
  - Adsorption
  - Blowdown
  - Cocurrent CO2 rinse
  - Countercurrent Nitrogen purge
  - Countercurrent Evacuation with Nitrogen purge

•Feed 15% CO2 in nitrogen
•Feed flow :0.26 NLPM
•Pressure , high: 1.5 bar
•Pressure ,low: 0.1 bar
•Temperature :55C

- Pure nitrogen was used as countercurrent purge
- Pure CO2 was used as cocurrent rinse

Single Column PVSA Cycle Steps



Feed (CO_2+N_2)

STEP I: Feed Pressurization

CO_2 Lean N_2 Product

Feed (CO_2+N_2)

STEP II: Adsorption

Vent

STEP III: Blow-down

Vent Gas

CO_2

MFC

STEP IV: CO_2 Rinse

Vacuum Pump

CO2 Rich Product

STEP V: Evacuation

N_2

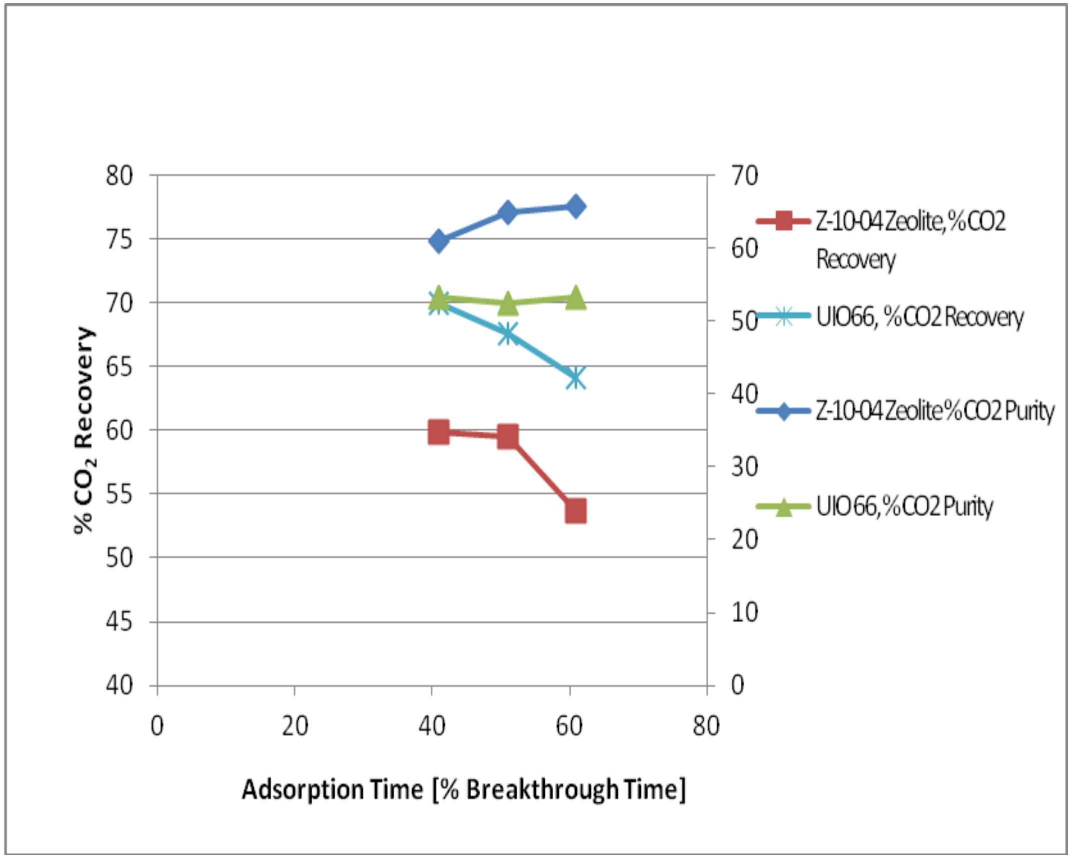
MFC

Vacuum Pump

Vent Gas

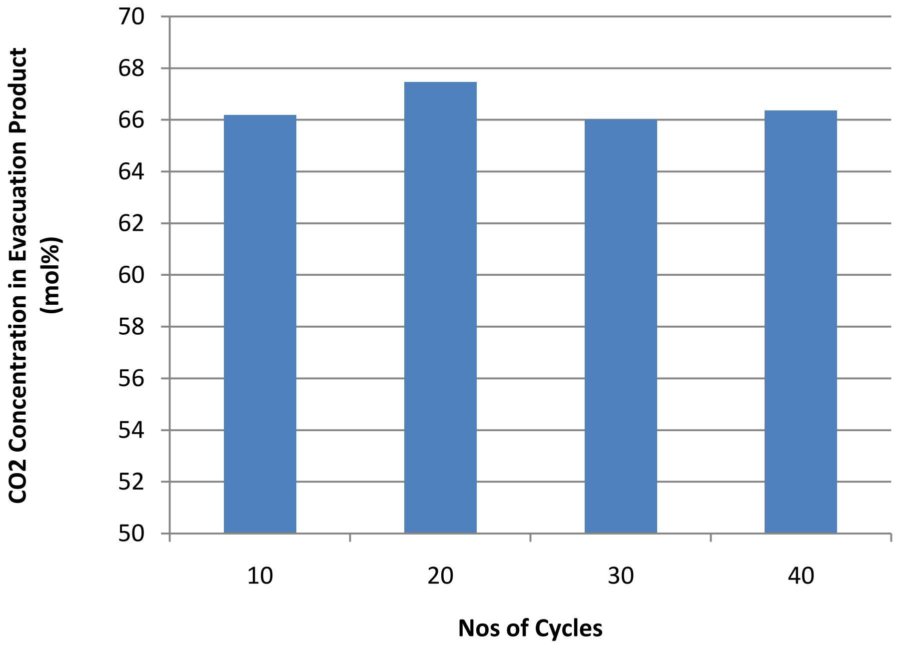
STEP VI: Evacuation+Purge

Effect of Adsorption Cycle Time on Performance



At minimum cycle time CO2 purities are higher with zeolite but recoveries are lower

Cyclic Stability of MOF for CO_2 Recovery



- CO_2 concentrations in product remain constant up to 40 PSA cycles studied
- No deterioration in the adsorbent performance observed
- UIO -66 shows good cyclicity over a large number of PSA cycles

Conclusion

- MOF UIO-66 has been compared with a commercial zeolite for CO_2 separation from mixtures with N_2.
- The MOF shows lower capacities and selectivities than the zeolite for this separation
- CO_2 purities observed in single column PSA studies are higher with zeolite
- The regenerability with MOF appears better leading to higher CO_2 recoveries
- Long term cycle stability is observed with MOF
- Minimal Loss in capacity is observed with MOF but this capacity loss appears to get stabilised

THANK YOU