Lowering Carbon Footprint through CO_2 Capture and Sequestration: A Refinery Perspective

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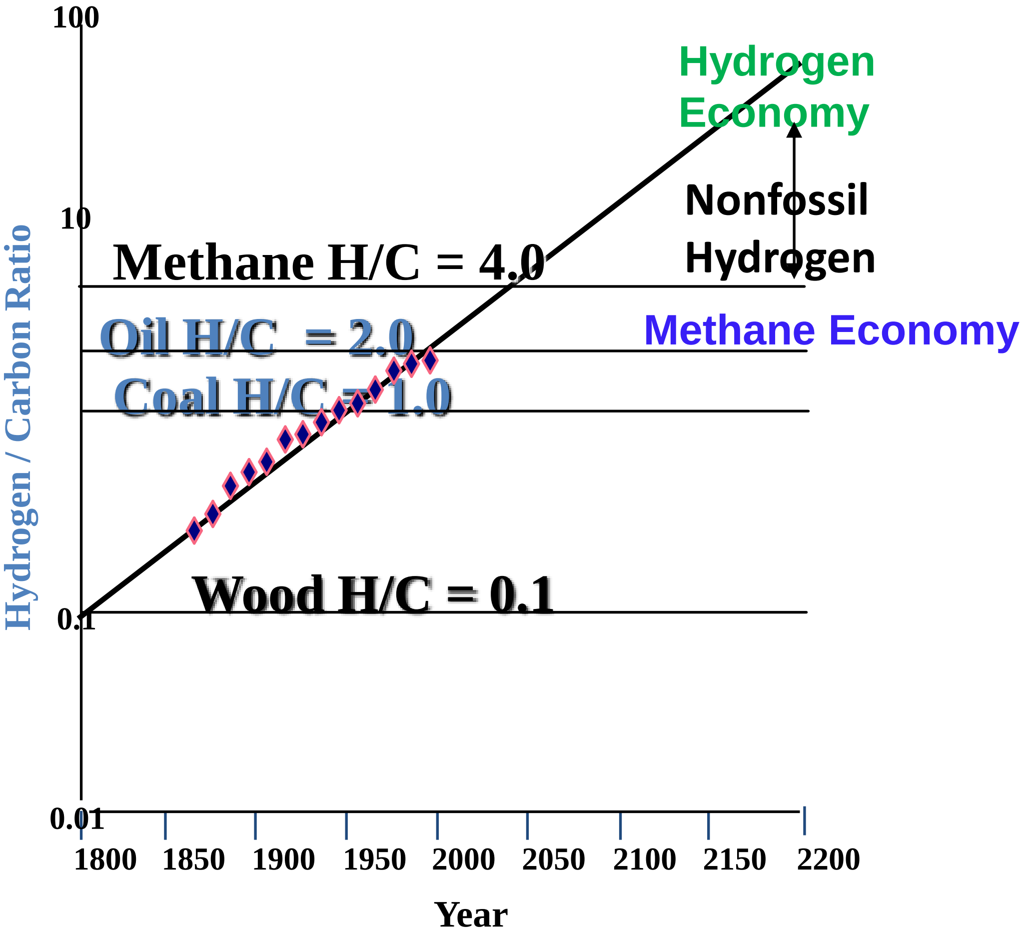
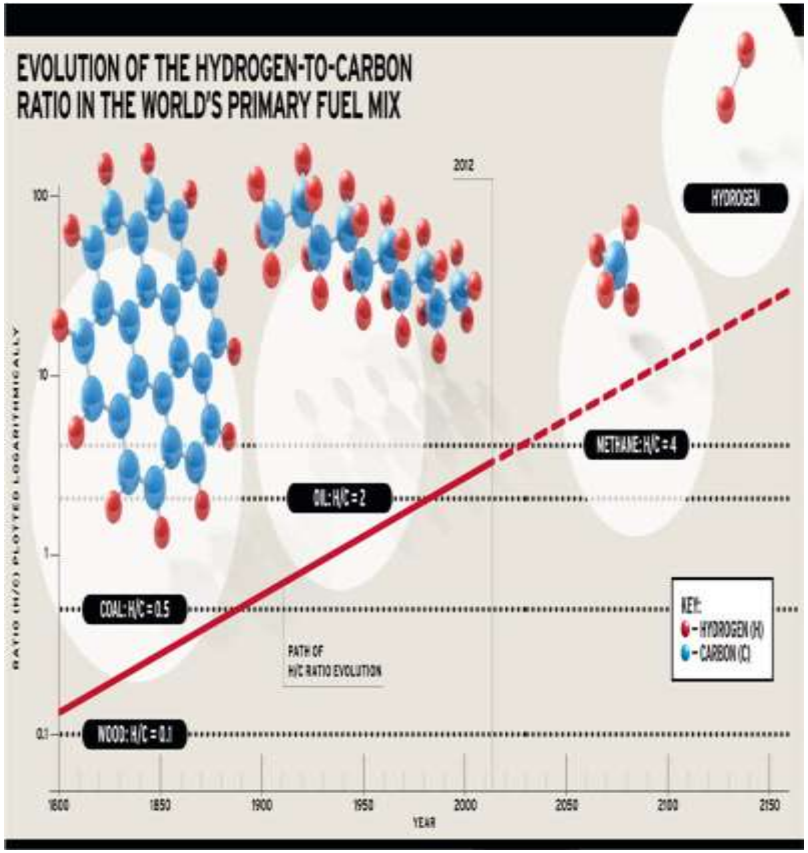
PRESENTATION OVERVIEW

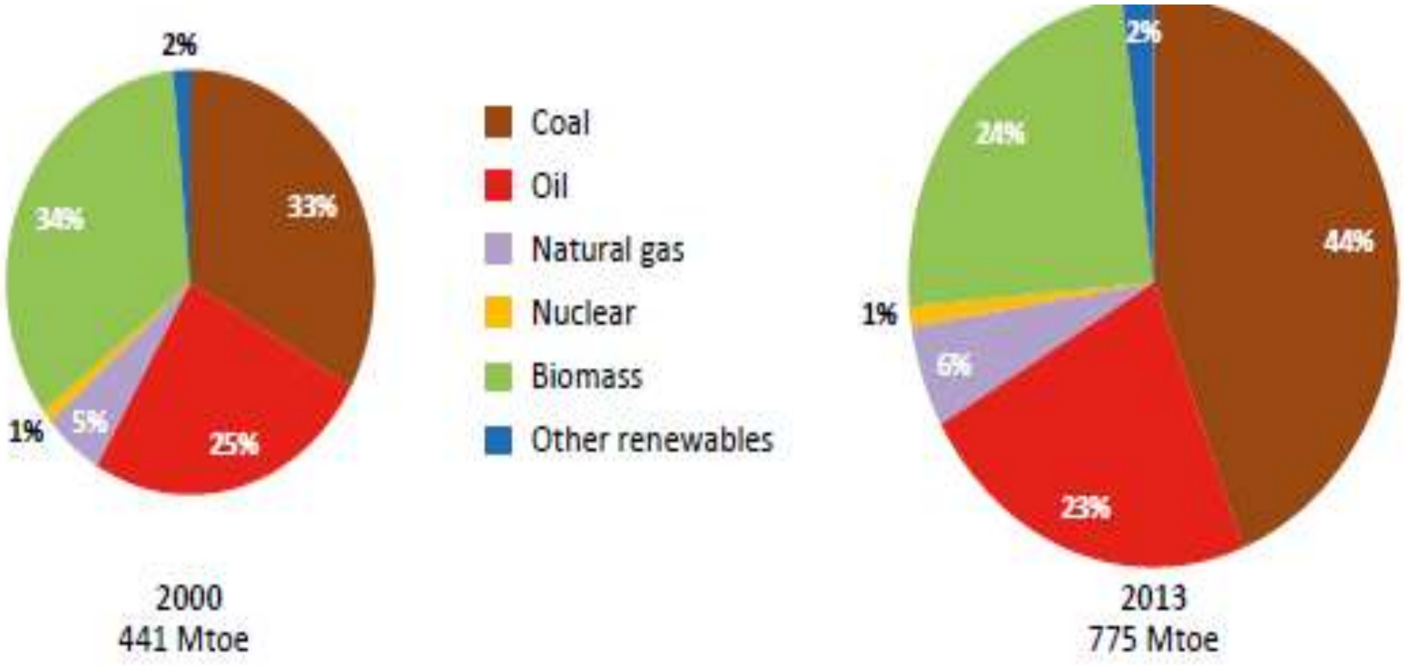
- **Energy Scenario and Global Warming**
- **Petroleum Refinery at a Glance**
- **Potential Sources of CO_2 Emission in Oil Industry**
- **Approaches to Capture CO_2**
- **CO_2 Capture Technologies**
- **CO_2 Capture by Pressure Swing Adsorption Using MOF**

Trend in H/C in Global Energy Consumption





Primary Energy Demand in India by Fuel



(Energy Outlook 2015)

As per IEEJ 2018 Primary Energy demand : 851 Mtoe

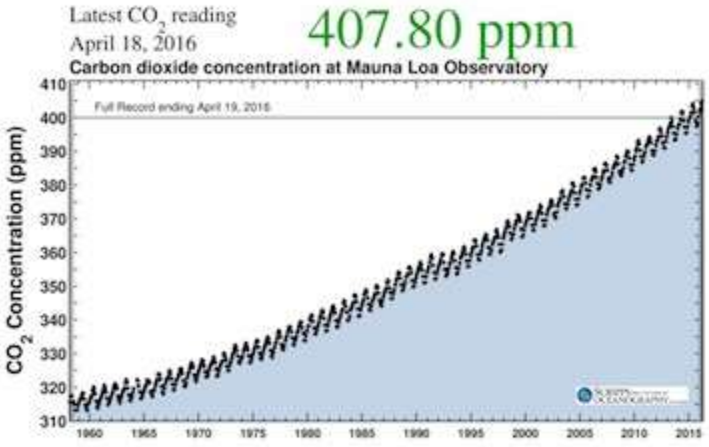
Consequences of Increasing Energy Demand

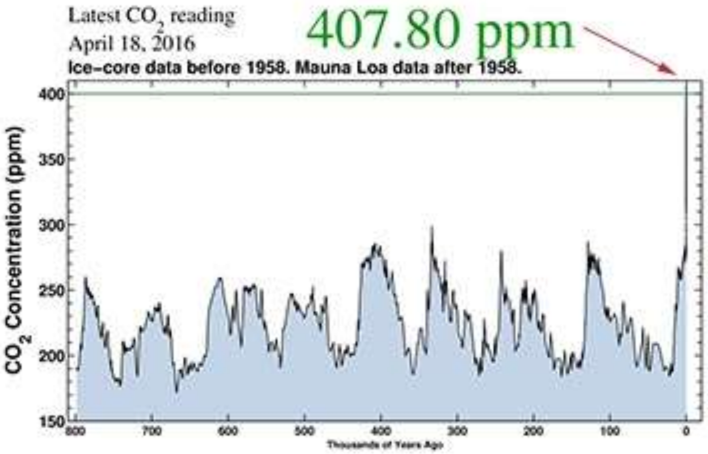
- Burning fossil fuels released CO_2 which leads to global warming
- Gathering wood for fuel result in deforestation
- Increase use of transportation fuel leading to smog and affecting the quality of air
- Mining of coal causes air and water pollution

Net result

Global warming

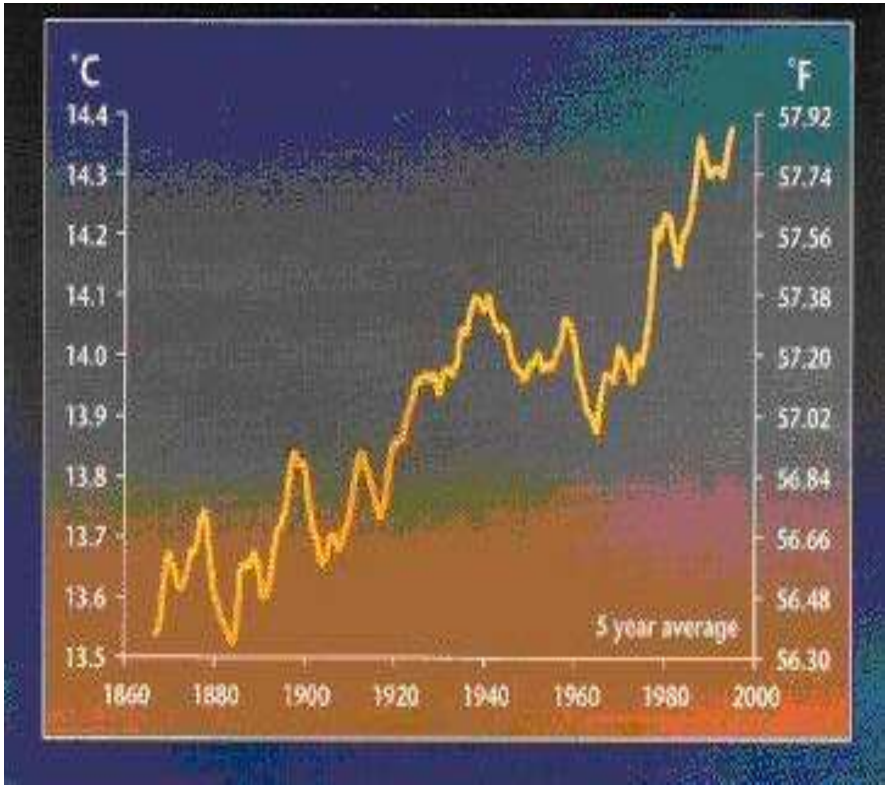
Climate change





Climate Change
Predicting Global Temperature Increases

Average global temperatures have risen 0.6°C in the past 100 years.



Source: IPCC Report on Climate Change, 2007

The Time of India: Global warming to claim 33% of ice volume in Hindu Kush Himalayan region: Expert

IANS | Dec 4, 2017, 08.19 PM IST

The Guardian

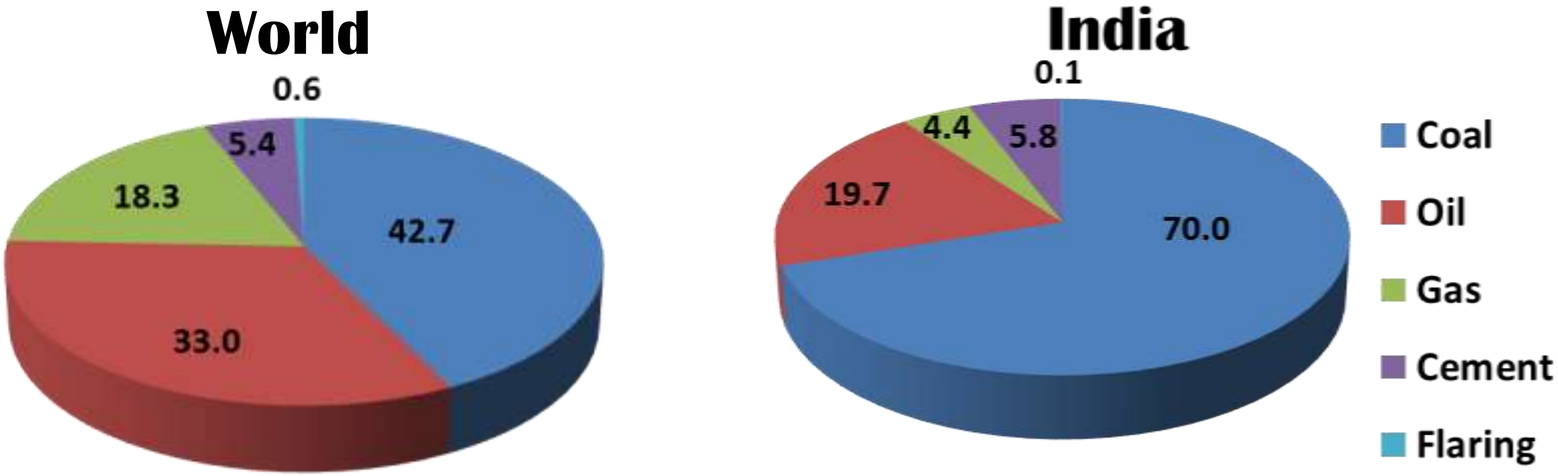
Glacier loss is accelerating because of global warming

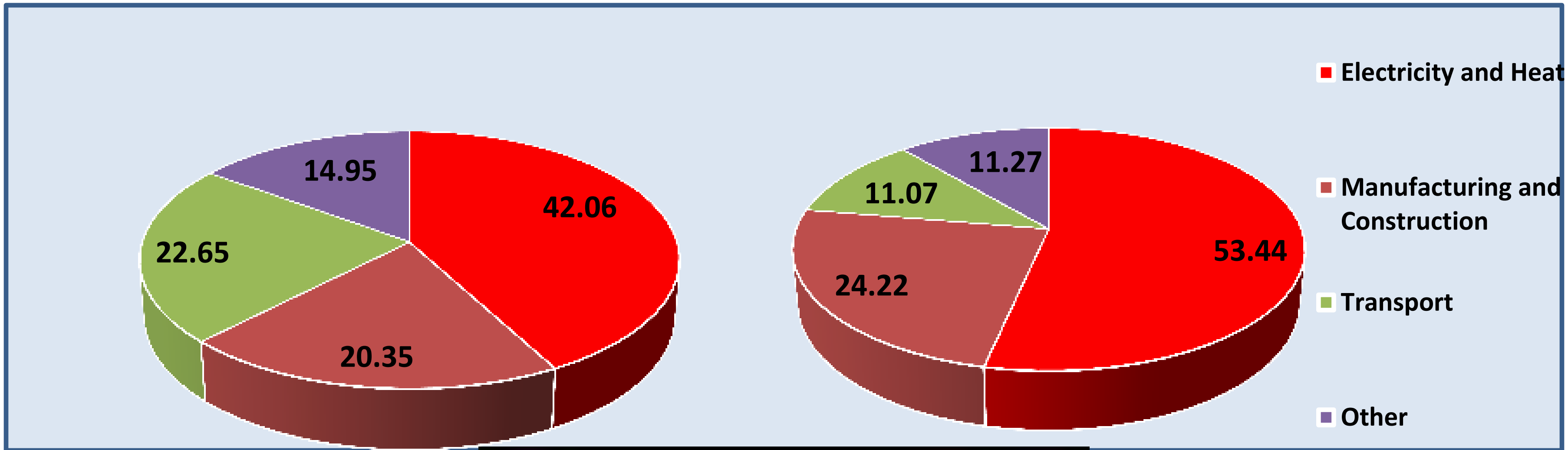
LOS ANGELES: The polar bear populations are declining fast as they are unable to catch enough prey to meet their energy needs due to climate change, a study has found.

The Guardian

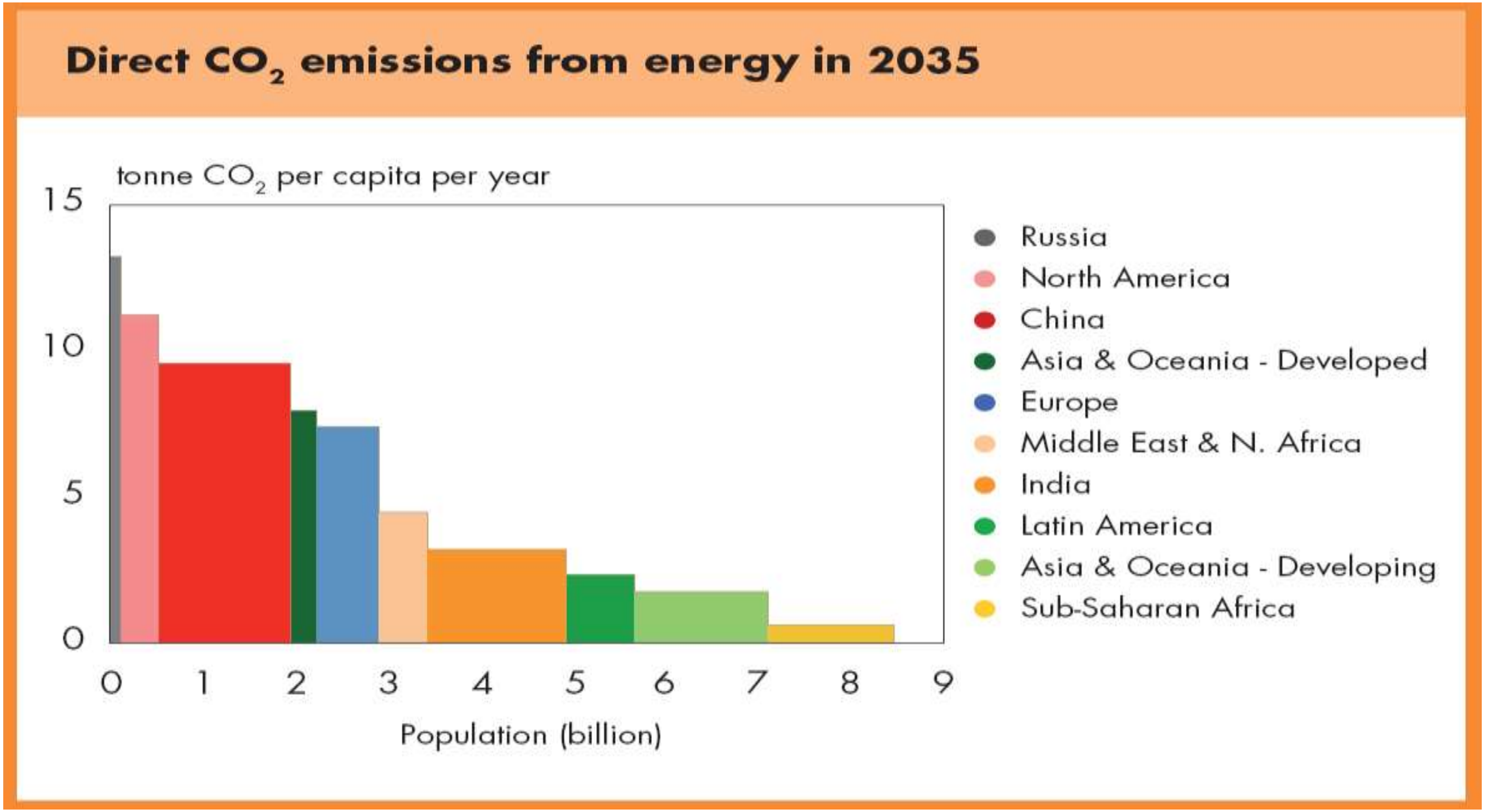
Suicides of nearly 60,000 Indian farmers linked to climate change, study claims

Fuel and Sector wise CO_2 Emissions (%) (2011-12)





Projected CO_2 Emissions per Capita / Year: 2035

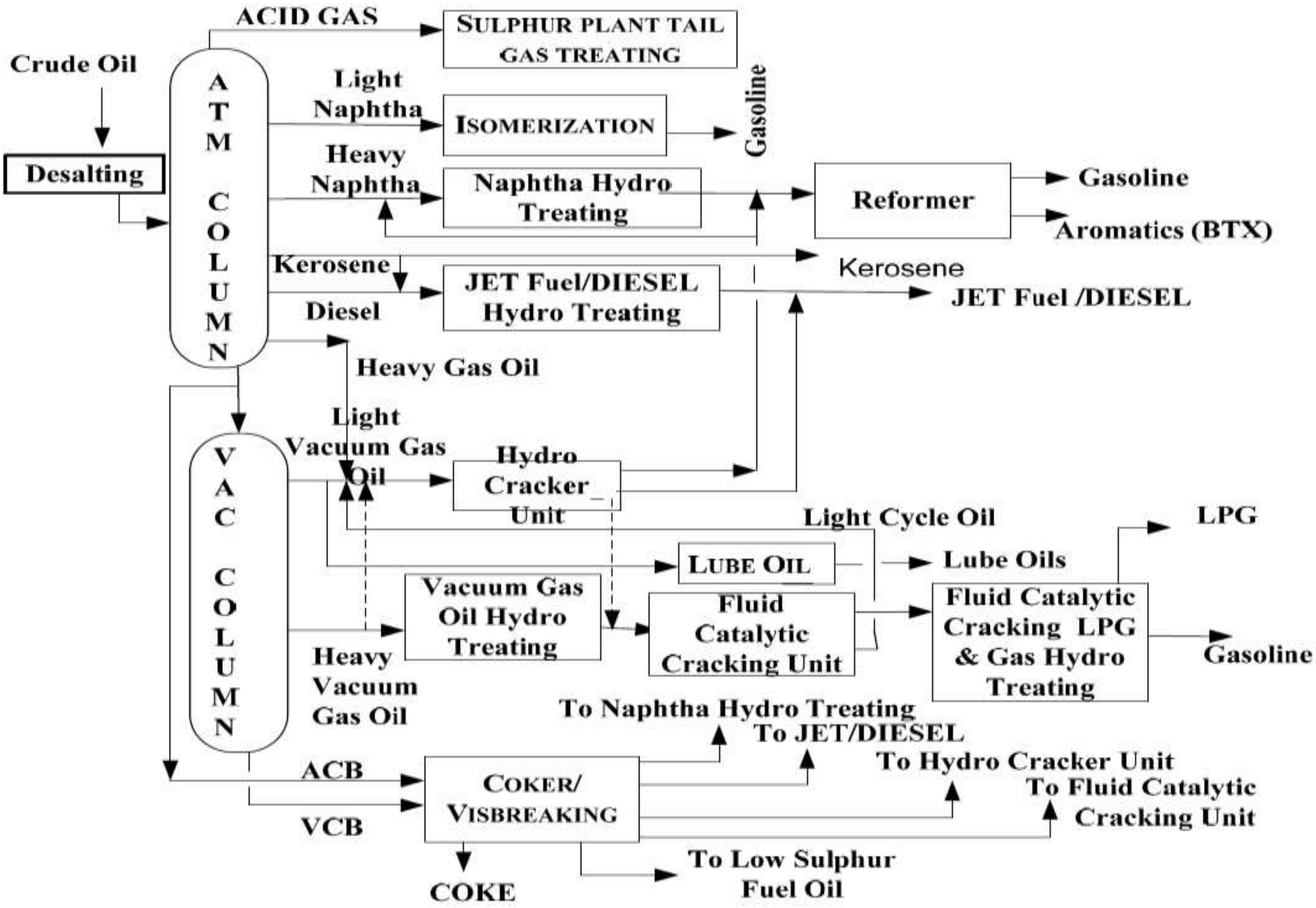


Major CO_2 Emission Sources

S. No.	Stationary Source	Mobile source	Natural Source
1	Fossil fuel-based electric power plants	Cars, and sports utility vehicles	Plants, Animals
2	Independent power producers	Trucks and buses	Plants and animal decay
3	Manufacturing plants in industry [a]	Aircrafts	Ocean/Land Exchange
4	Commercial and residential buildings	Trains and ships	Land emission/leakage
5	Flares of gas at fields	Construction vehicles	Volcano
6	Military and government facilities	Military vehicles & devices	Earthquake

Emissions from Refineries at a Glance

Refinery Flow Diagram



Crude Oil

Desalting

ATM COLUMN

ACID GAS

SULPHUR PLANT TAIL GAS TREATING

Light Naphtha

ISOMERIZATION

Gasoline

Heavy Naphtha

Naphtha Hydro Treating

Reformer

Gasoline

Aromatics (BTX)

Kerosene

Kerosene

Diesel

JET Fuel/DIESEL Hydro Treating

JET Fuel /DIESEL

Heavy Gas Oil

VAC COLUMN

Light Vacuum Gas Oil

Hydro Cracker Unit

Light Cycle Oil

LUBE OIL

Lube Oils

LPG

Vacuum Gas Oil Hydro Treating

Fluid Catalytic Cracking Unit

Fluid Catalytic Cracking LPG & Gas Hydro Treating

Gasoline

Heavy Vacuum Gas Oil

To Naphtha Hydro Treating

To JET/DIESEL

To Hydro Cracker Unit

To Fluid Catalytic Cracking Unit

ACB

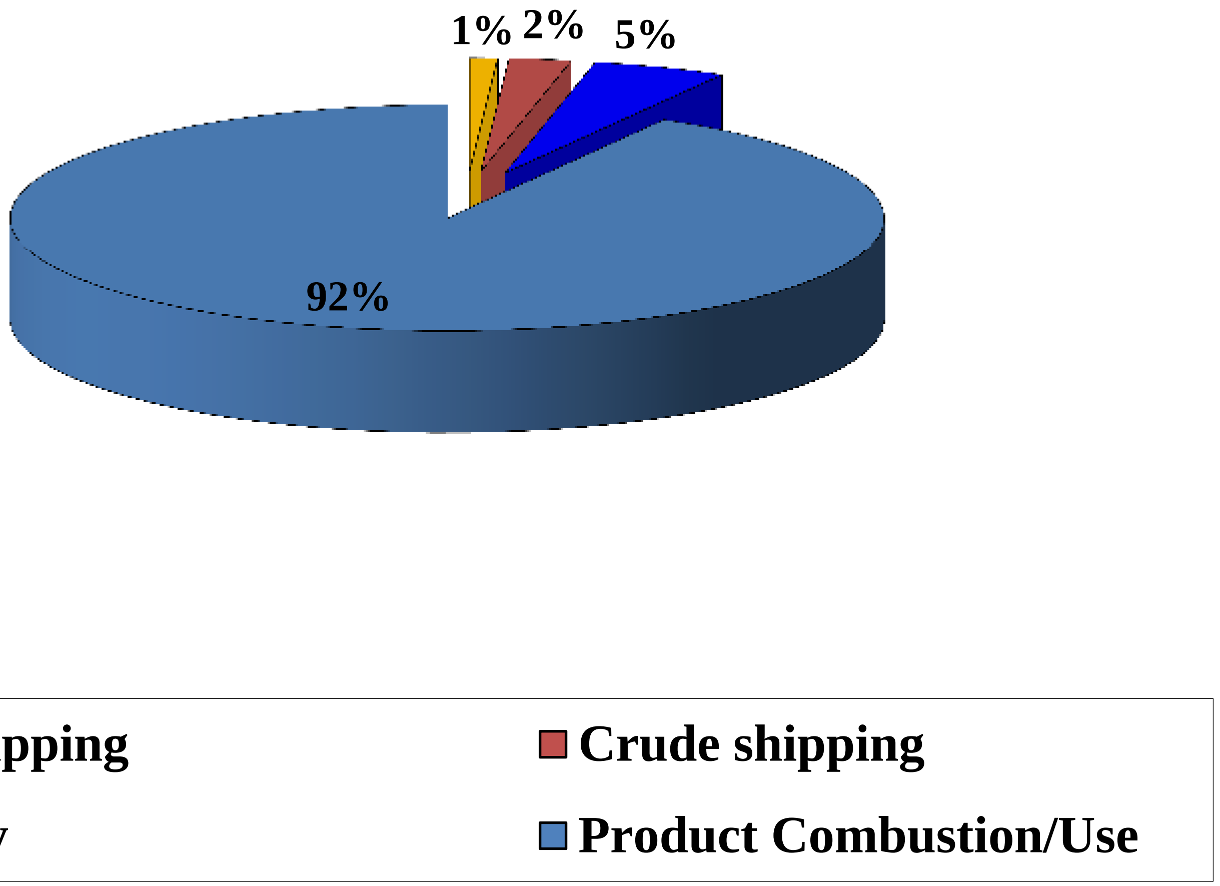
VCB

COKER/ VISBREAKING

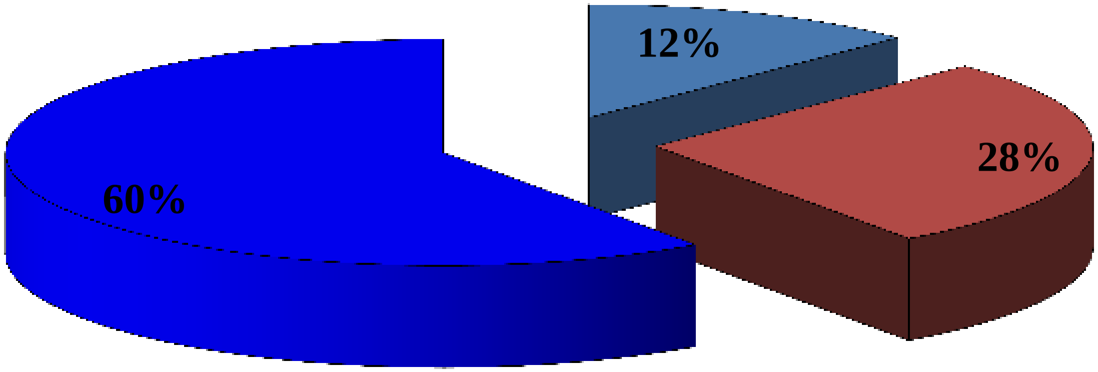
COKE

To Low Sulphur Fuel Oil

Typical break down of CO_2 Emissions from Cradle to Grave for Oil Industry



Typical Break Down of CO_2 Emissions – Refiner's Perspective



CO_2 Emissions from Oil Refinery

CO_2 emissions from a refinery are affected by

- The complexity of refinery (No. of Different processes)
- Quality of crudes and other raw materials used
- Fuel type be burned (Fuel oil, NG, light naphtha)
- Quality of product slate delivered (e.g. low sulfur fuels)

CO_2 Emission Sources In Refinery

Combustion Sources :direct

- Boilers, Process heaters, Turbines, Engines, Flares, Catalytic and thermal oxidizers, Coke calcining kilns, Incinerators

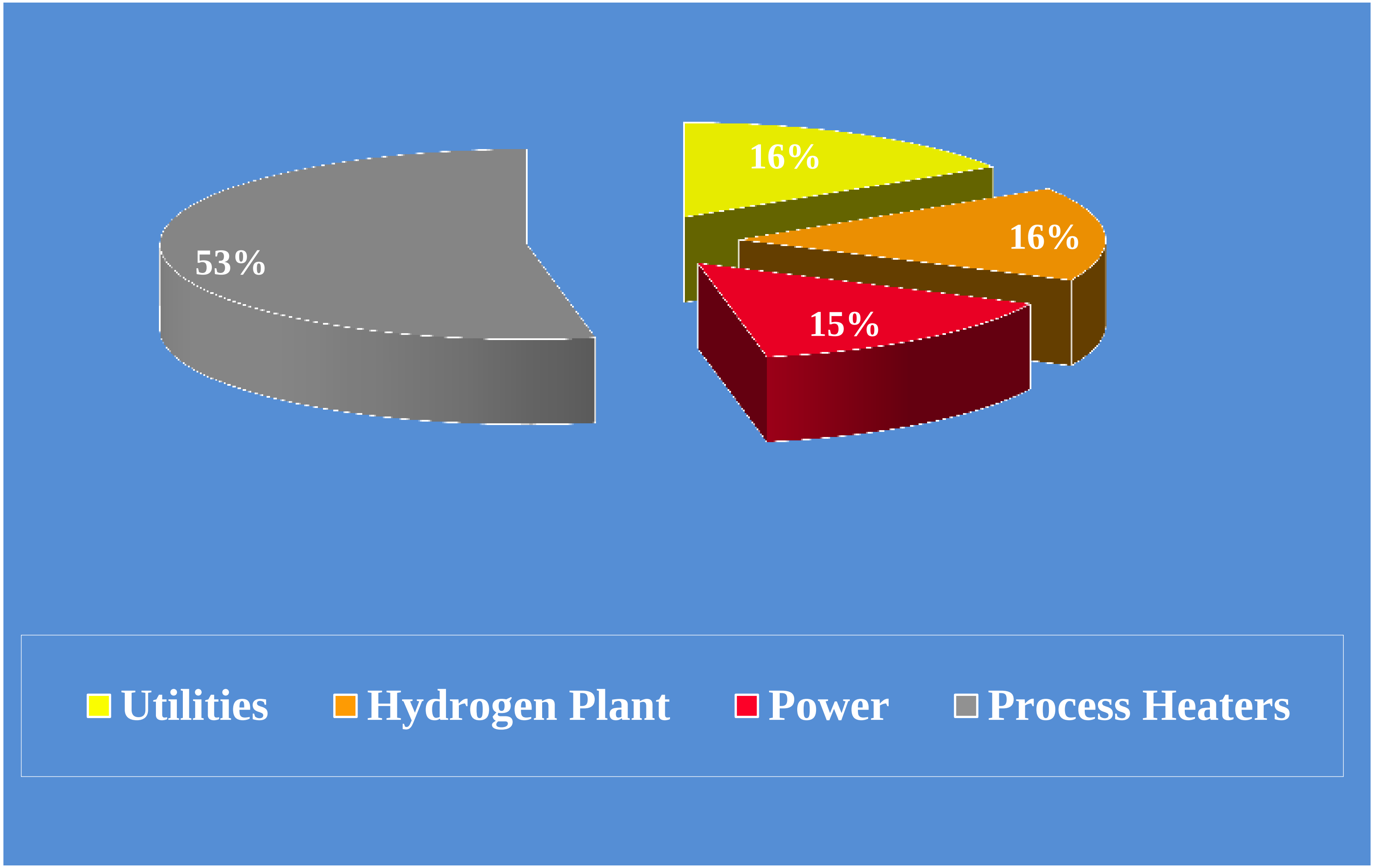
Combustion Sources - Indirect

- Electricity imports Process heat/steam imports

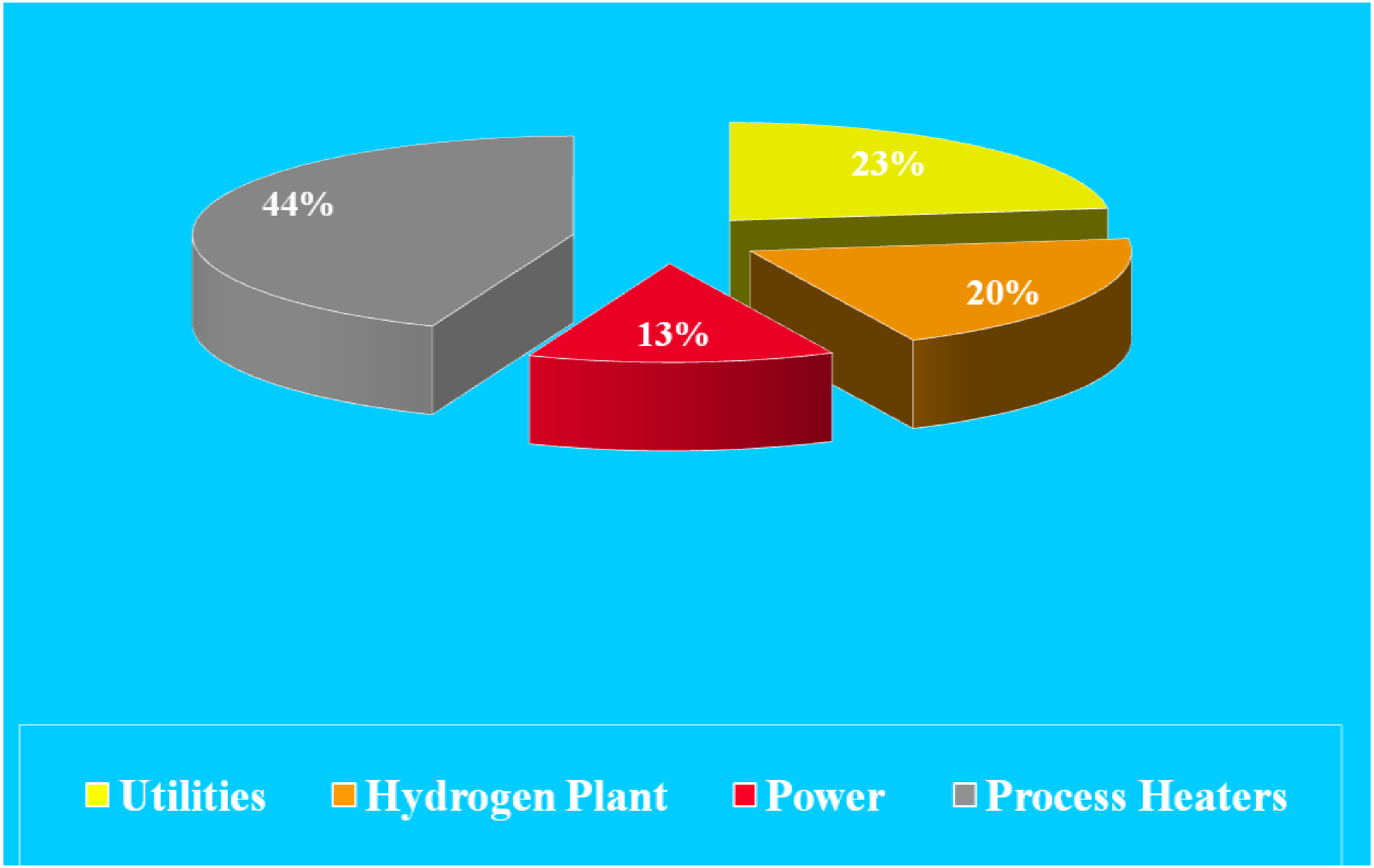
Vented Sources – Process Vents

- Catalytic cracking, Catalytic reforming, Catalyst regeneration, Thermal cracking, Flexi-coking, Delayed coking, Steam methane reforming (hydrogen plants)

HCK Based Refinery CO_2 Emissions Profile



FCC Based Refinery CO_2 Emissions Profile



CO_2 Emission In Refinery

- Increased use of hydrogen has resulted in to increased emissions of CO_2
- Hydrotreating unit producing a 50 ppm sulphur diesel oil consumes 4 to 7 kg of hydrogen per ton of diesel
- Each ton of hydrogen produced from NG will release 10 ton of CO_2
- Innovative technologies to reduce hydrogen consumption and CO_2 emissions needed.
- The main sources of CO_2 emissions in the refinery are combustion sources, and processes like hydrogen production, catalytic cracking etc
- CO_2 emissions from a refinery vary from 0.2 to 0.5 tons CO_2/ ton of crude which is very high

CO_2 Reduction Management in a Refinery

The Basic strategy should cover the following areas:

- The fuel system
- Energy efficiency (pinch studies)
- Hydrogen (pinch/management studies)
- The Catalytic Cracker (where applicable)
- Advanced processing options
- Process/utility/plant integration

The above said areas are complex and interacting systems so heuristic approach is required

Approaches to Capture CO_2

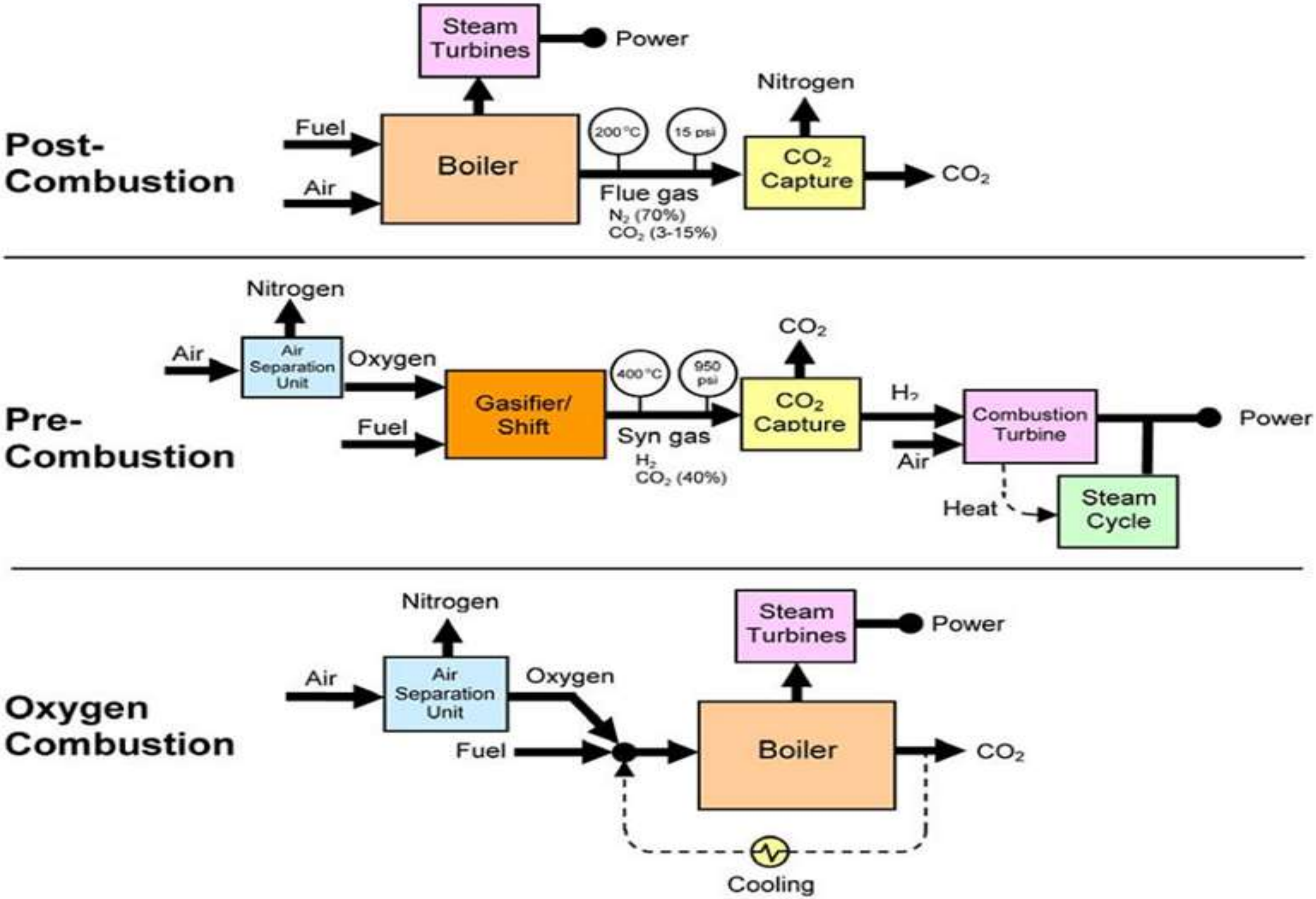
CO_2 Capture in Power Generation

- **Post combustion Capture**: **Remove CO_2 after the coal/NG combustion process**

- **Pre combustion capture: Remove CO2 during or just after the gasification process where H_2+ CO_2/CO is formed**

- **Oxy-fuel combustion : Use highly enriched oxygen for coal combustion. No issue of separation of CO2 from nitrogen containing flue gas arises**

CO_2 Capture Technologies



CO_2 Capture Technologies

Separation Technologies For CO_2 Removal

- **ABSORPTION**- Solvent (Physical, Chemical) as Separating Agent
  Separation is based on solubility
- **ADSORPTION**- Microporous Solid (Adsorbent) as separating agent
  Separation based on Surface forces, size, diffusion
- **MEMBRANES**- Solid/liquid film as separating agent
  Separation based on solubility, diffusivity, size difference in transport through films

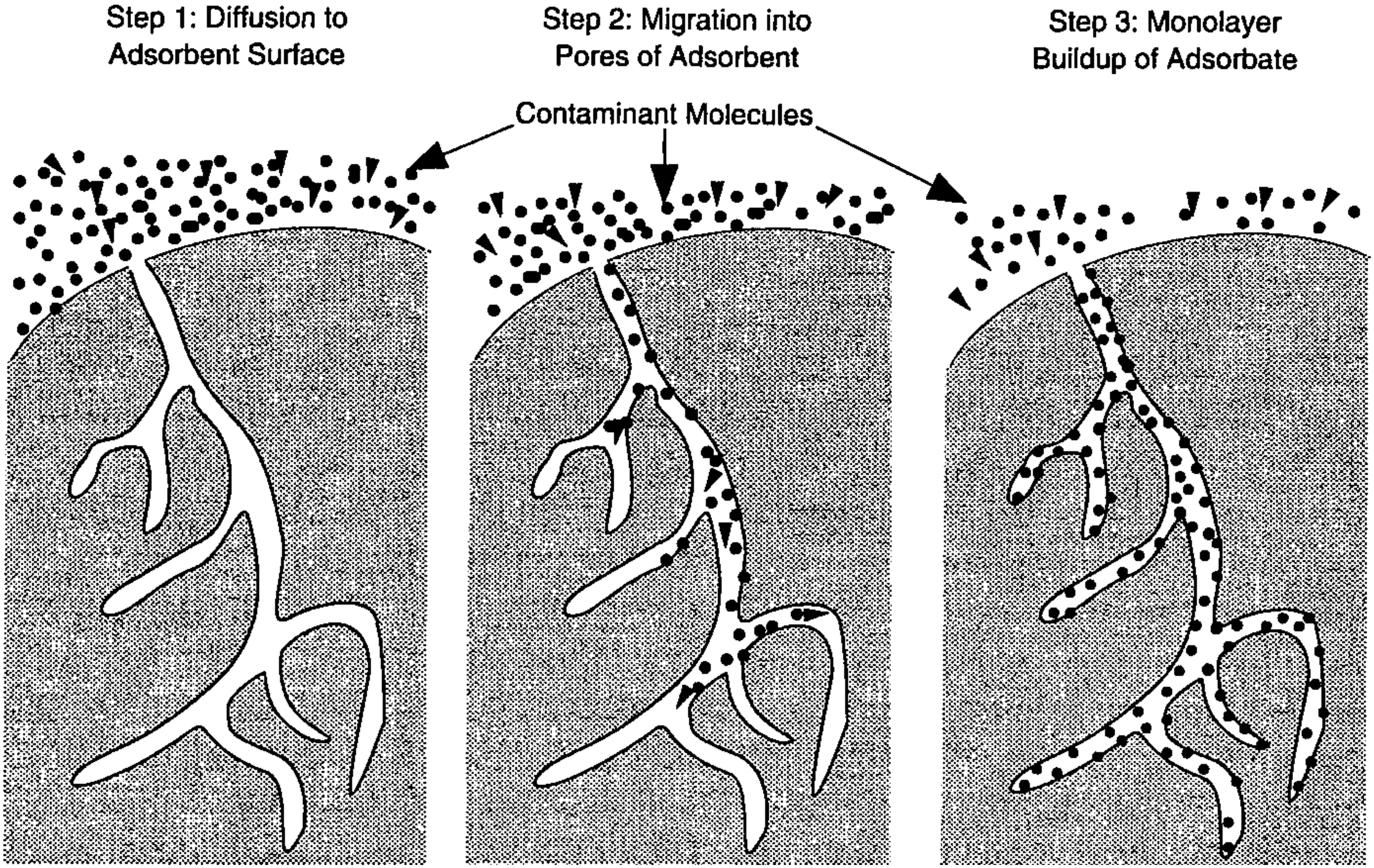
Principles of Adsorptive Separations

- **Adsorptive separations use microporous solids as separating agents. This is called an adsorbent**
- **These selectively take up “adsorb” components from feed mixture**
- **Component(s) adsorbed is called adsorbate**
- **Adsorptive purifications involve adsorbate concentration <10%**
- **Adsorptive bulk separations involve adsorbate concentrations>10%**

Principles of Adsorptive Separations

- **Adsorption is a two step process**
- **First step is the ADSORPTION STAGE with feed contacting the adsorbent generally in granular form**
- **Continued contact of feed with adsorbent leads to saturation of adsorbent**
- **So Second Step is REGENERATION stage with use of a desorbent and /or change of conditions like temp/pressure to remove adsorbed species from the adsorbent**

Adsorption Mechanism



Choosing An Adsorbent

- Capacity
- Selectivity
- Adsorption kinetics
- Regenerability
- Compatibility
- Cost

Adsorbent Capacity

- Amount of adsorbent taken up by the adsorbent per unit mass or volume

  Depends on

  -Fluid phase concentration
  -Temperature
  -Initial condition of adsorbent
    Strengths of surface forces
    Relative polarity of surfaces
  - Amount of surface area available: :Micro porosity
  -Accessibility to this area :Distribution of Macro/Meso/Micro Pores

Adsorbent capacity data gathered at

- Constant temperature
- Varying adsorbate concentration

↓

Isotherms

(loading v/s concentration at constant temp.)

Significance of Adsorption Capacity

Critical :

Decides Adsorbent Inventory

It fixes the volume of adsorber vessel

Both are generally significant if not dominant

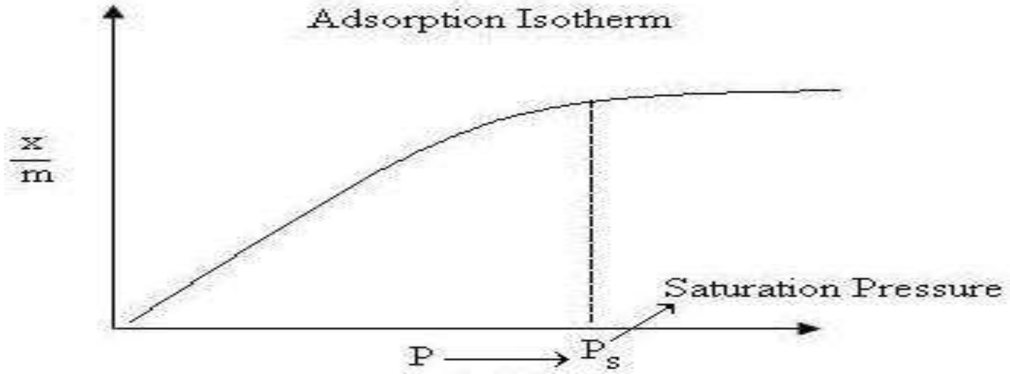
- Typically 1 Milli Mol/Gm Capacity Of Adsorbent Desirable

Adsorption Isotherms

$$\text{Adsorbate} + \text{Adsorbent} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

$$A + B \rightleftharpoons AB$$

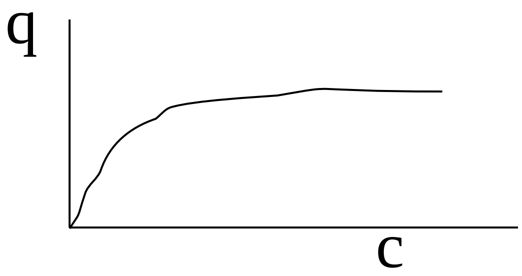
According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored.



Adsorption Capacity

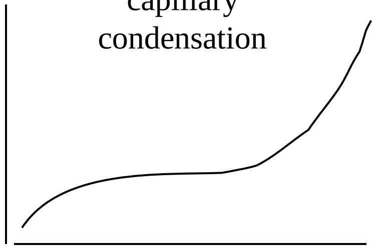
- FOR A PARTICULAR ADSORBENT-ADSORBATE SYSTEM CAPACITY VARIES WITH TEMP, CONCENTRATION AND RELATIONSHIP IS GIVEN IN A ISOTHERM (Constant T) , ISOSTERES(Constant Loading)

TYPE I Monolayer formation

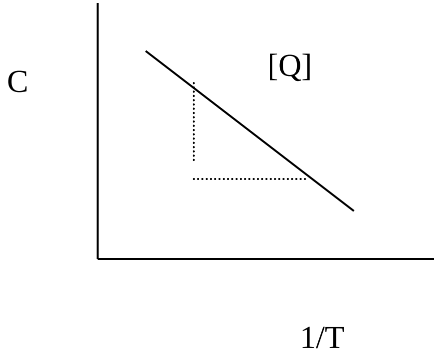


Use this to find out loading at different adsorbate conc influid

TYPE II ISOTHERM capillary condensation



ISOSTERE



Use this to find out Heat of Adsorption

Adsorbent Selectivity

- Quantified by $\alpha_{ij}=(y_i/y_j)/(x_i/x_j)$

  An alternative expression that is roughly equivalent is :

  $\alpha_{ij}{'}=K_i / K_j$

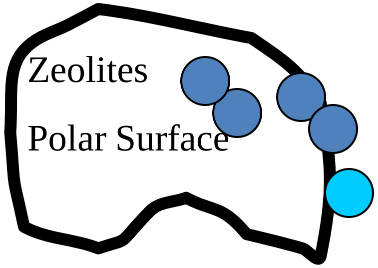
- Two types :Equilibrium Selectivity and Kinetic Selectivity

- Equilibrium Selectivity :Depends on nature of surface forces between adsorbent and adsorbate components

- Kinetic Selectivity : Depends on difference in rates of adsorption of adsorbate components

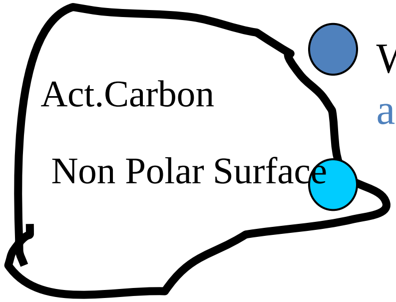
Adsorbent Selectivity

- Equilibrium selectivity



Water : Polar molecule . Surface forces VDW+Polar-Polar . Water gets adsorbed

Methane : Non Polar molecule . Surface forces VDW only . Methane may get weakly adsorbed

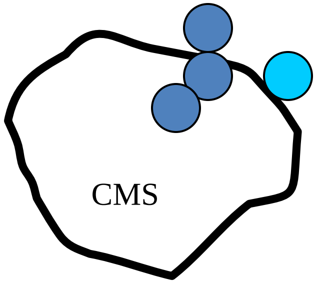


Water, Polar molecule Surface forces only VDW Weakly adsorbed

Methane Non polar molecule, Surface forces only VDW .strogly adsorbed

Adsorbent Selectivity

- KINETIC SELECTIVITY



Kinetic diam of O_2 is 3.46 A , slightly less than pore diam of CMS adsorbent

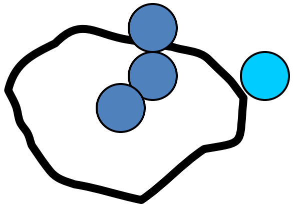
O_2 diffuses into CMS faster than N_2 which has slightly larger diam. of 3.64A

O_2 gets adsorbed and N_2 is rejected

Commercially used in producing N_2 from air in high purity by PSA

Adsorbent Selectivity

- SIZE EXCLUSION



•Kinetic diam of n-paraffin 4.8 A , slightly less than pore diam of 5A adsorbent

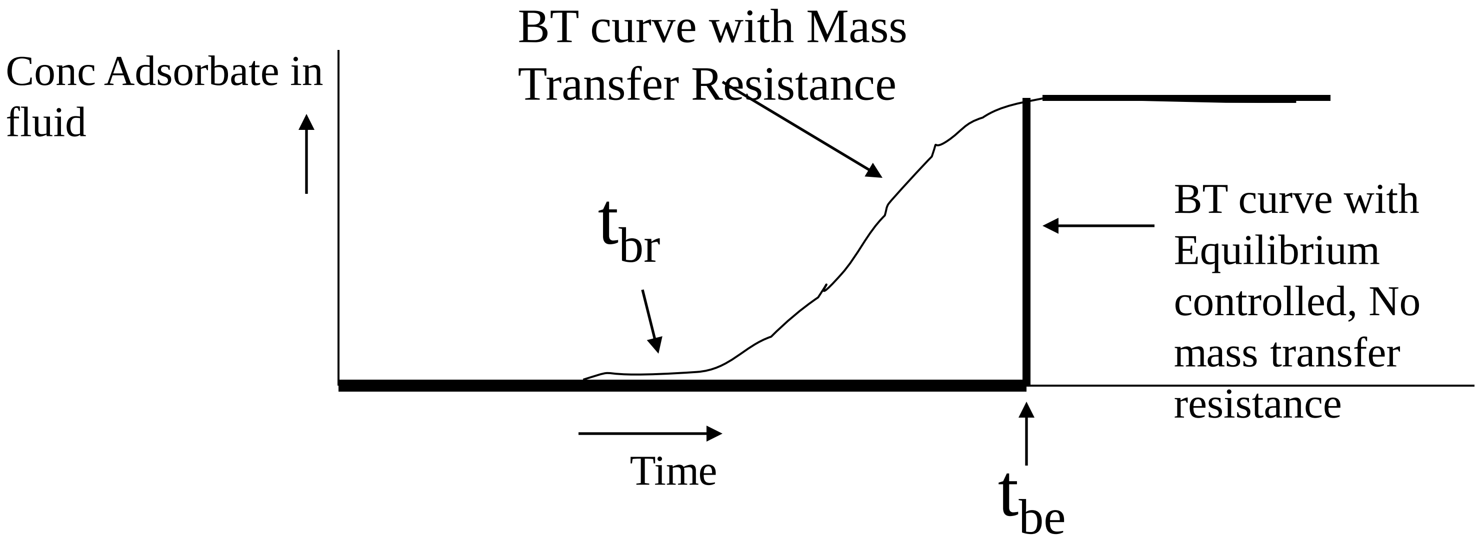
•n-Paraffin diffuses into zeolite but iso-paraffins ,naphthenes and aromatics of kinetic diams 5.2 to 6.0 A are not allowed to enter

•Commercially used in producing /separating n-paraffins from hydrocarbon streams **(MOLEX, ISOSIV)**

Adsorption Kinetics

- Intraparticle diffusional resistances control adsorption rate
- Fast kinetics leads to sharp breakthrough curve. Maximum utilisation of adsorbent when there is no intraparticle mass transfer resistance
- Slow kinetics leads to distended breakthrough curve with adsorbate early leakage

Effect of Mass Transfer Resistance on Breakthrough



Adsorbent Regenerability

- Both capacity and kinetics may be favourable but regenerability has to be easily achieved and sustained over repeated cycles (Does it have a “HEEL”)
- Adsorbent regeneration may be by Temp Swing, Pressure Swing ,displacement or purge
- For PSA/TSA Examine isotherm data under changed conditions of temperature and pressure

Regeneration Methods

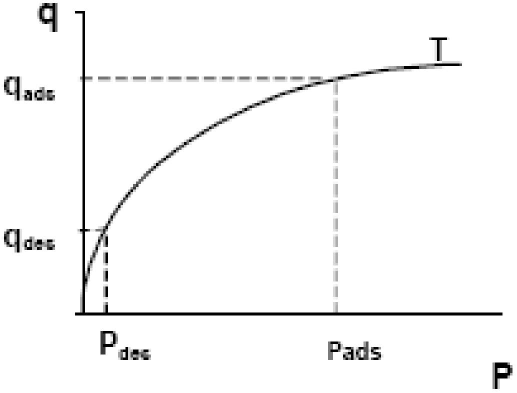
- THERMAL SWING
  - Suitable for liq/gas
  - Good for strong adsorbed
  - Large heat requirement
  - Rapid cycling not possible,bed cooling may be necessary

- PRESSURE SWING
  - Good for weak adsorbed
  - Rapid cycling possible
  - Suitable for gas
  - Mech energy requirement
  - Low purity of strong adsorptive

- DISPLACEMENT DESORPTION
  - Good for strongly adsorbed
  - Avoids heat
  - Addtl separation step necessary
- PURGE
  - Constant T,P operation
  - Large volume requirement

CO_2 Capture by Pressure Swing Adsorption

- **PSA Widely Attractive Technology For Gas Separations :**
- **H_2 recovery**
- **O_2, N_2 Production**
- **CO_2 Removal, Etc**
- **PSA Capitalises On Dependance Of Adsorption Equilibrium On Pressure**



Separation Achieved Through Selective Concentration Of Component(s) On Solid Adsorbent At High Pressure.
Desorption Follows When Pressure Is Lowered
Commercial PSA Designed To Repeat Cycle Of Pressurisation-Adsorption And Depressurisation-Desorption To Provide Continuous Gas Separation

Commercial PSA Separations

- **HYDROGEN RECOVERY / PURIFICATION**
- **AIR SEPARATION FOR OXYGEN/NITROGEN PRODUCTION**
- **N-ALKANE SEPARATION**
- **AIR DRYING**
- **CO_2 REMOVAL**
- **HELIUM RECOVERY / PURIFICATION**
- **CO RECOVERY**
- **SOLVENT /GASOLINE VAPOR RECOVERY**
- **OLEFIN/ PARAFFIN SEPARATION**
- **NITROGEN-METHANE SEPARATION**

CO_2 Capture by PSA :Some Issues

- **Current capacities of H_2 PSA are 6 MMCMD**
- **Flue gas from typical 210MW power plant will be 36 MMCMD**
- **Presence of SO_X may deactivate adsorbent. Wet FGD would be required. This would also cool the flue gas, beneficial for PSA**
- **Effect of NOx,Fly ash and O_2 on adsorption must be considered**
- **Adsorbent must work in presence of moisture**
- **Conventional PSA cycles produce the weak adsorptive (in this case N2) in high purity**
- **For CO2 recovery , new cycles are required to be designed and studied to produce the strong adsorptive CO2 in high purity**
- **Either PSA or VSA will have to be decided depending on choice of adsorbent, operating pressure and regeneration presssure keeping in mind that flue gas will be at almost ambient pressure**

CO_2 Capture by PSA Recent Trends

- **Novel adsorbents for adsorbing CO_2 at high temperatures and in presence of moisture under development**

- **These include Mesoporous materials, hydrotalcites etc**

- **New cycles being developed for recovery of strong adsorptive in high purity**

- **These include strong adsorptive purge, stripping reflux, dual reflux**

Economics of CO_2 Capture Technologies

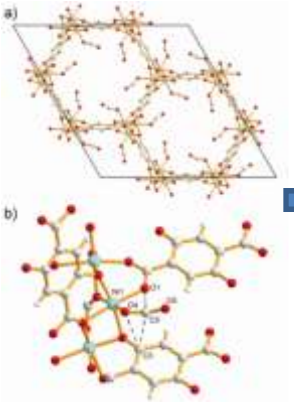
Cost of CO_2 Capture Using Chemical Absorption, PSA/VSA And Gas Separation Membranes

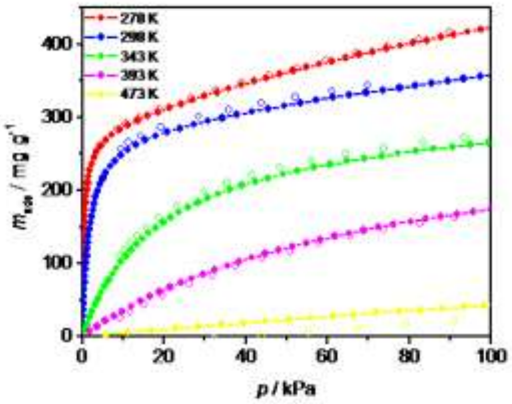
	Chemical absorption		Physical adsorption		Gas membrane separation	
Status of technology	Base line commercial	State-of-the art commercial	Base line technology	Emerging	Base line technology	Emerging
	MEA solvent	KSI solvent	PSA	VSA	PPO membrane	Co-block membrane
CO_2 recovery rate(%)	90	90	90	75	90	90
CO_2 purity(%)	>98	>98	44	48	43	62
Energy Penalty(%)	36	21	47	28	52	45
Capture cost US$/tonne CO2 avoided	47	34	61	40	78	64

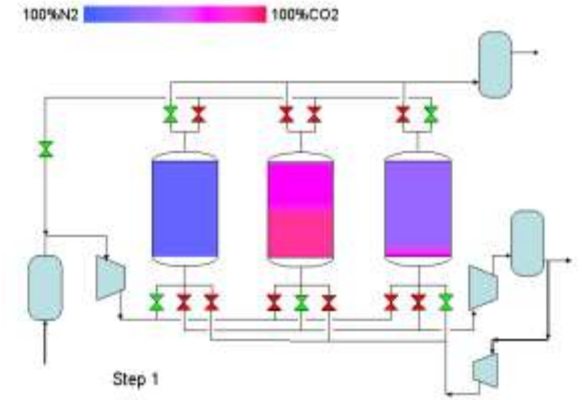
CO_2 Capture by Pressure Swing Adsorption Using MOF

Objective and Scope of Work

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







MOF Adsorbent Synthesis

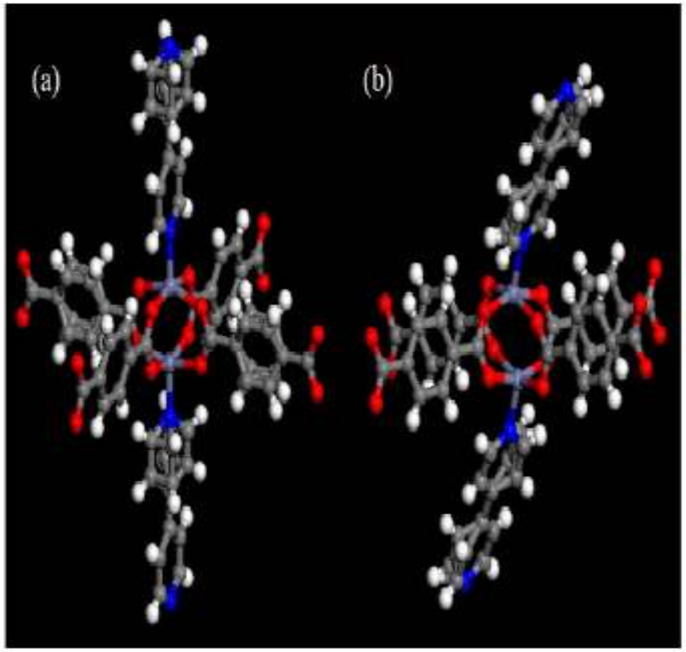
Adsorbent screening & evaluation

Process Optimisation ,Simulation modelling

MOF Adsorbent Preparation and Formulation

Synthesis of Metal Organic Framework Adsorbent

- MOF are new class of adsorbent material with strong potential for CO_2 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



Properties to exploit

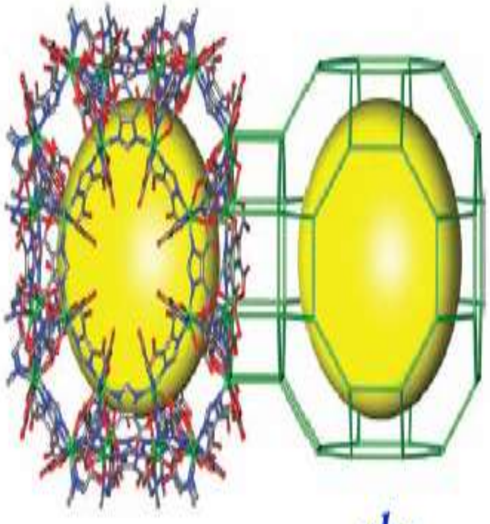
<u>similarities to molecular sieves</u>:

- 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



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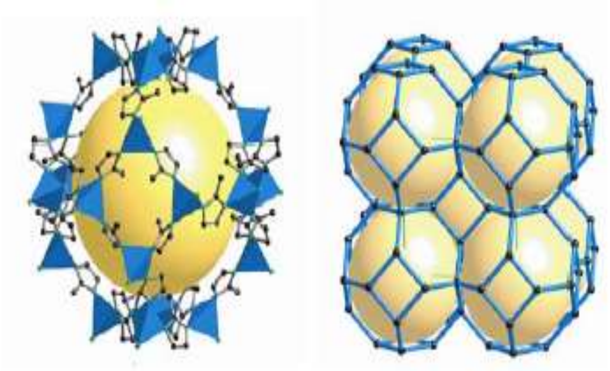


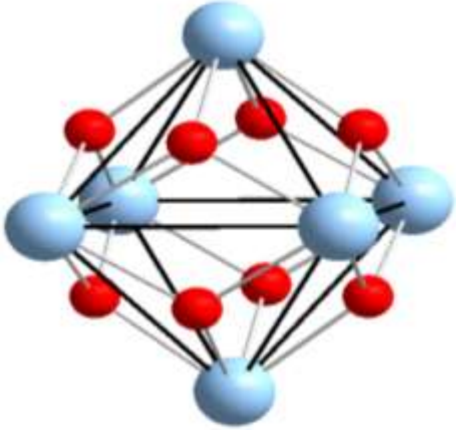
sod

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

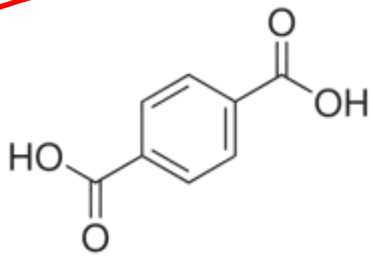
The UIO family

- ❑ UiO MOFs comprise a series of 3D isostructural materials build up of zirconium oxide clusters which are connected with different dicarboxylic acids.

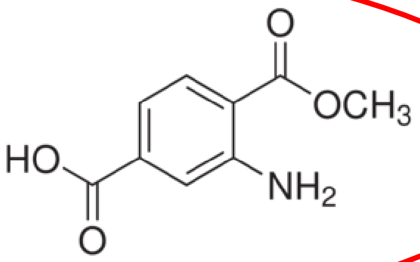
- ❑ The core of the cluster is built up of 6 zirconium atoms forming a regular octahedron and 8 oxygen atoms capping the 8 faces of the Zr_6 octahedron (Zr_6O_8). The octahedrons faces are capped by 4 μ_3-O and 4 μ_3-OH groups.



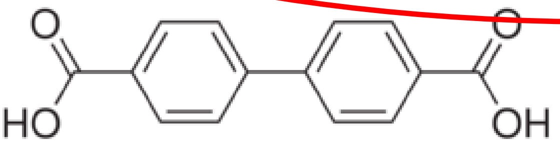
$Zr_6O_4(OH)_4$ cluster



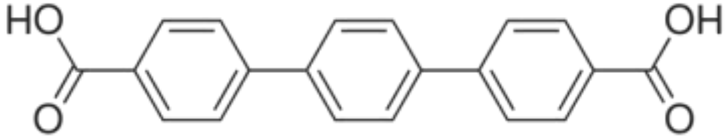
UiO-66



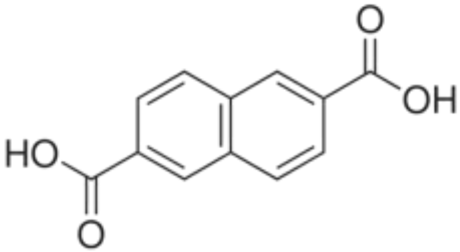
UiO-66-NH_2



UiO-67



UiO-68

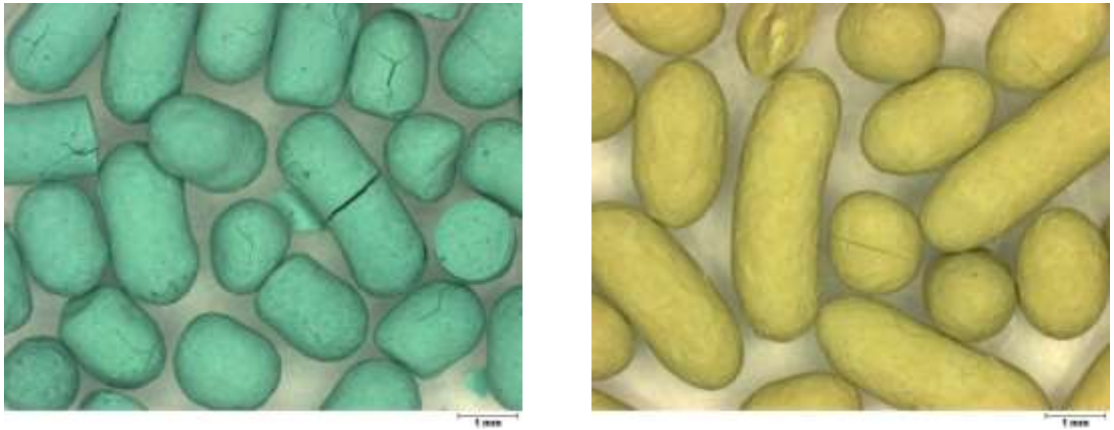


UiO-69

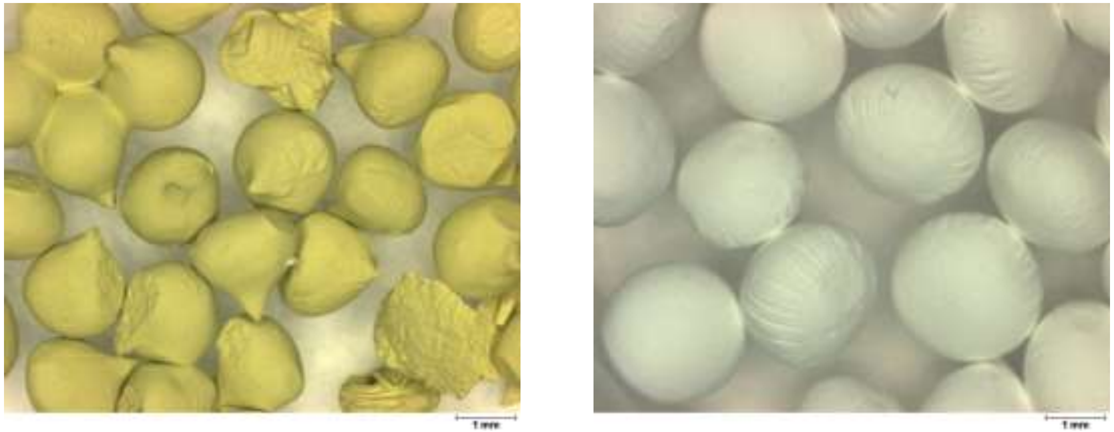
JH Cavka *et al*, *JACS*, **2008**

Adsorbent Formulation

Any process will require formulated adsorbents!



Pictures of UiO-Ni and CPO-27-Ni made by extrusion method.



Particles of MCM-41 (left) and CPO-27-Ni (right) made by the ”droplet” method.

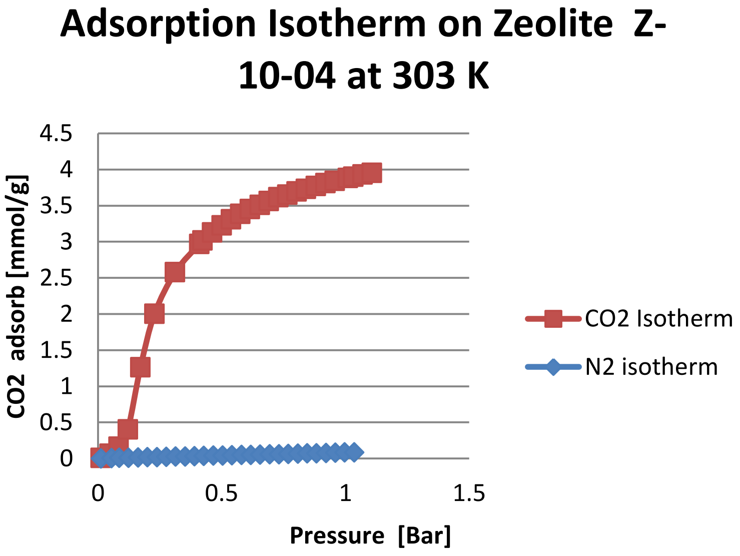
Adsorbent Screening & Evaluation

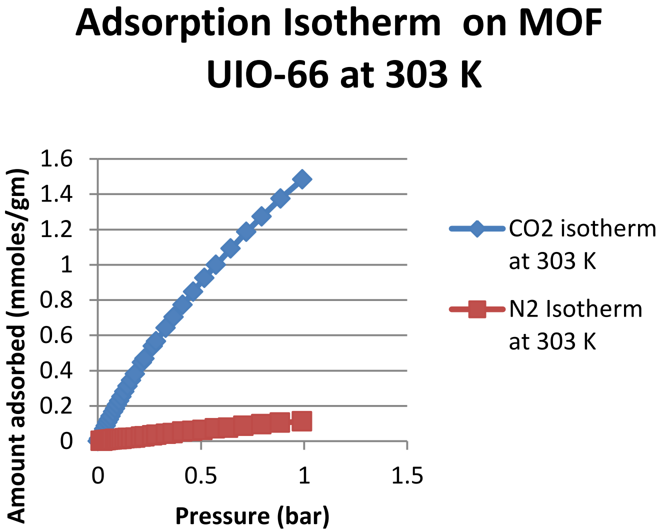
Adsorbent Evaluation

Adsorbent evaluation was carried out on the basis of

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

Comparison of Equilibrium Isotherm Data





Adsorbent Selectivity for CO_2-N_2 at 1 bar

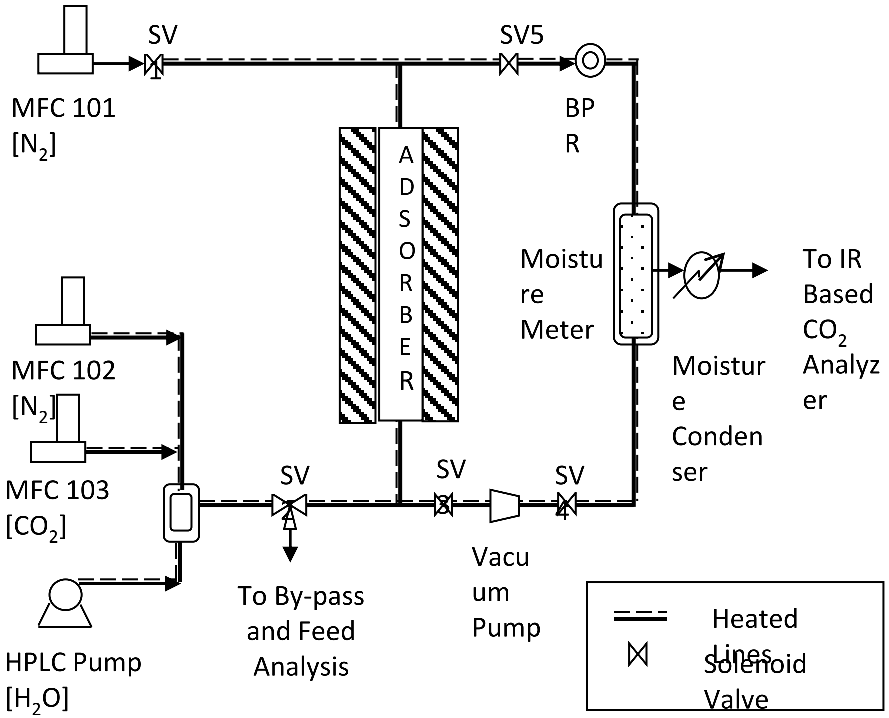
Zeolite Z-10-04	**40.0**
MOF- UIO-66	**13.2**

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

Deciding Factor will be regenerability !

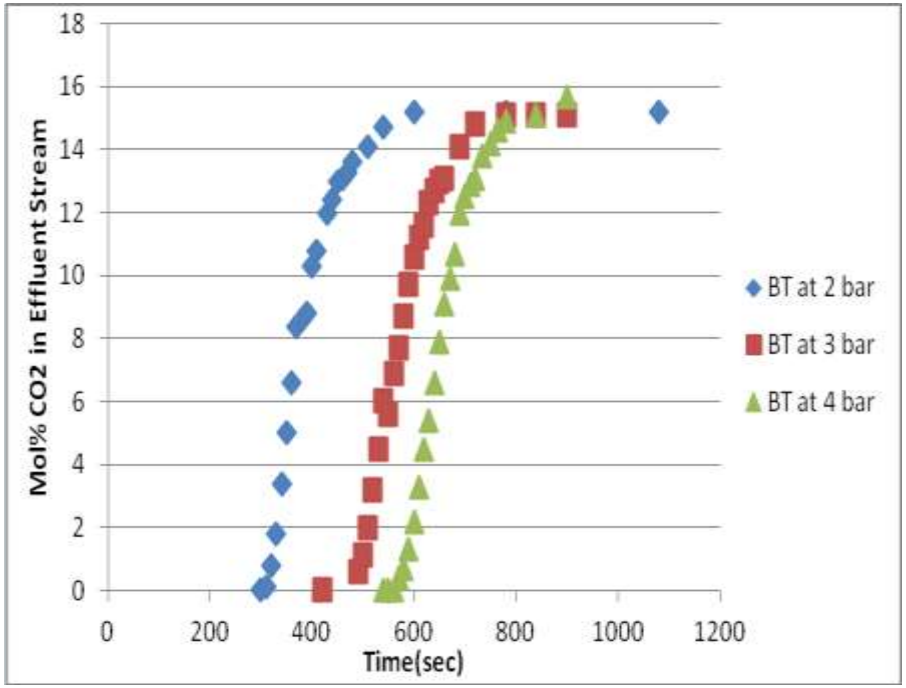
Breakthrough Measurements

Experimental Set up



- Minimum adsorbent quantity: 5 gms
- **Microprocessor based**
- Max. Temp: 500 oC
- **Design Pressure: 30 bar**
- Feed Flow : 500 ml/min
- **Single column adsorber**
- Flexibility to evaluate different PSA.VSA cycles
- **Rapid action solenoid valves for RPSA separations**

Effect of Pressure on CO_2 breakthrough with MOF UIO-66



Feed Comp: 15 mol% CO_2 in N_2

Temp: 303 K

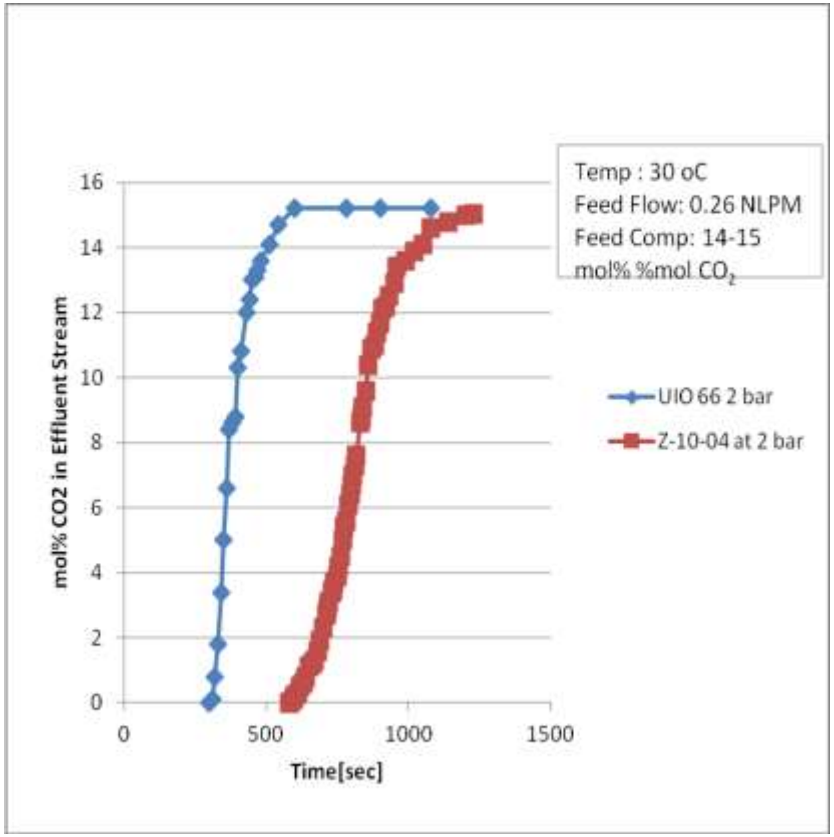
Feed Flow Rate: 0. 26 NLPM

Adsorber Col dia: 1.1 cm

Adsorbent loading: 5 gms

Higher the pressure, higher the breakthrough time

Comparison of CO_2 breakthrough of MOF and Zeolite



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

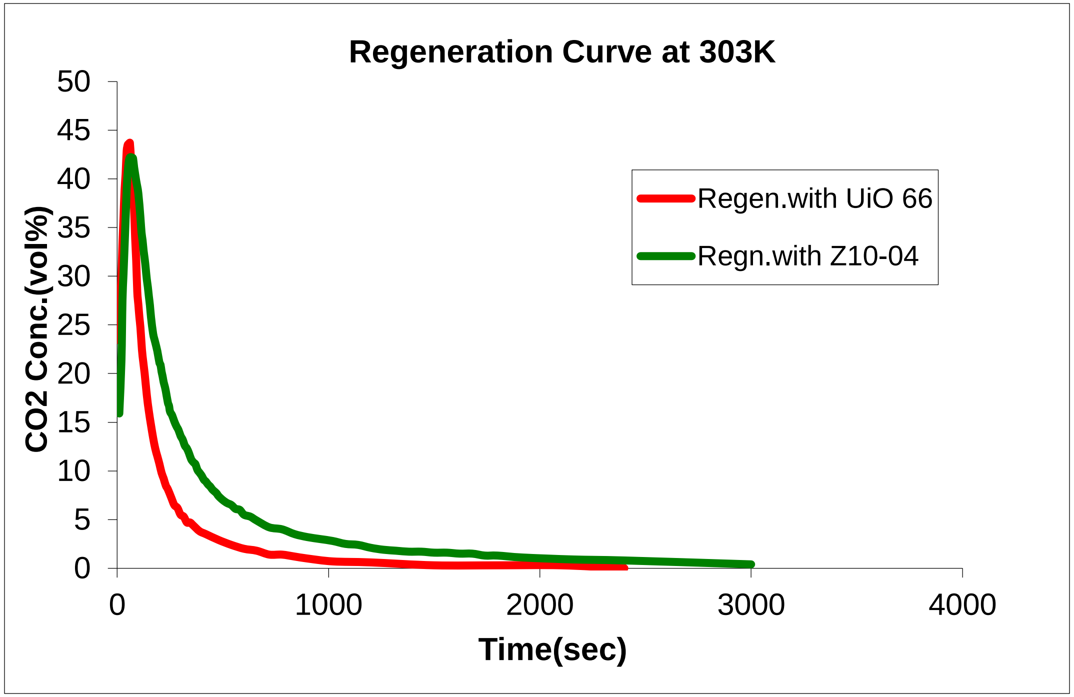
Could impact adsorbent regenerability

Regeneration Studies

Regeneration Studies

- Loaded adsorbent in microadsorber was countercurrently purged with nitrogen along with application of vacuum
- Effluent was monitored for CO_2 concentration
- Nitrogen flow rate was maintained at 0.1 NLPM
- Temperature : 303 K
- Conditions were same for both zeolite Z10-04 as well as MOF (UIO-66)

Comparison of Regeneration Curves



Better Regenerability of MOF is Demonstrated

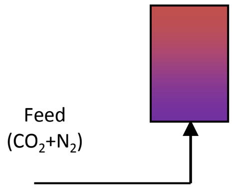
VSA Cycle Studies

Single Column VSA Cycle Studies

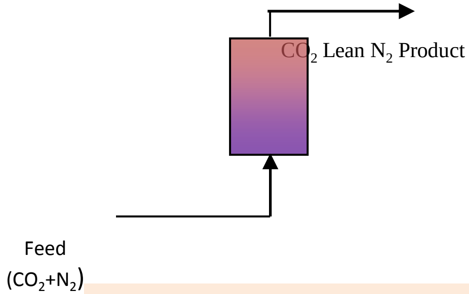
- Six step VSA Cycle was used in the single column microadsorber
  - Feed pressurisation
  - Adsorption
  - Blowdown
  - Cocurrent CO_2 rinse
  - Countercurrent Nitrogen purge
  - Countercurrent Evacuation with Nitrogen purge
- Pure nitrogen was used as countercurrent purge
- Pure CO_2 was used as cocurrent rinse

•Feed 15% CO_2 in nitrogen
•Feed flow :0.26 NLPM
•Pressure , high: 2.0 bar
•Pressure ,low: 0.1 bar
•Temperature : 303 K

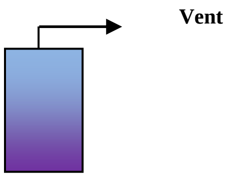
Single Column PSA Cycle Steps



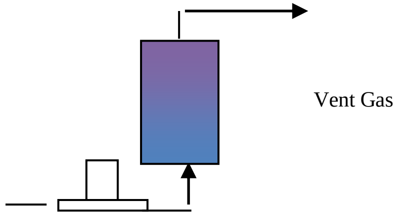
STEP I: Feed Pressurization



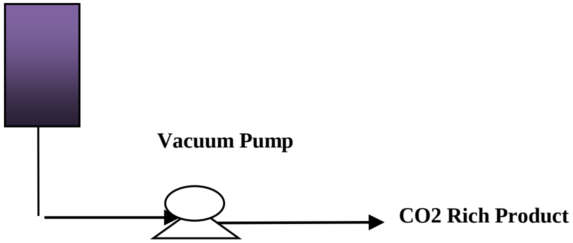
STEP II: Adsorption



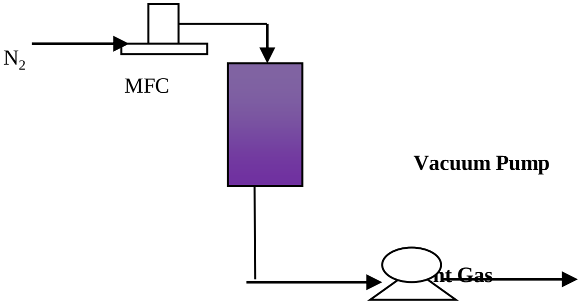
STEP III: Blow-down



STEP IV: CO_2 Rinse

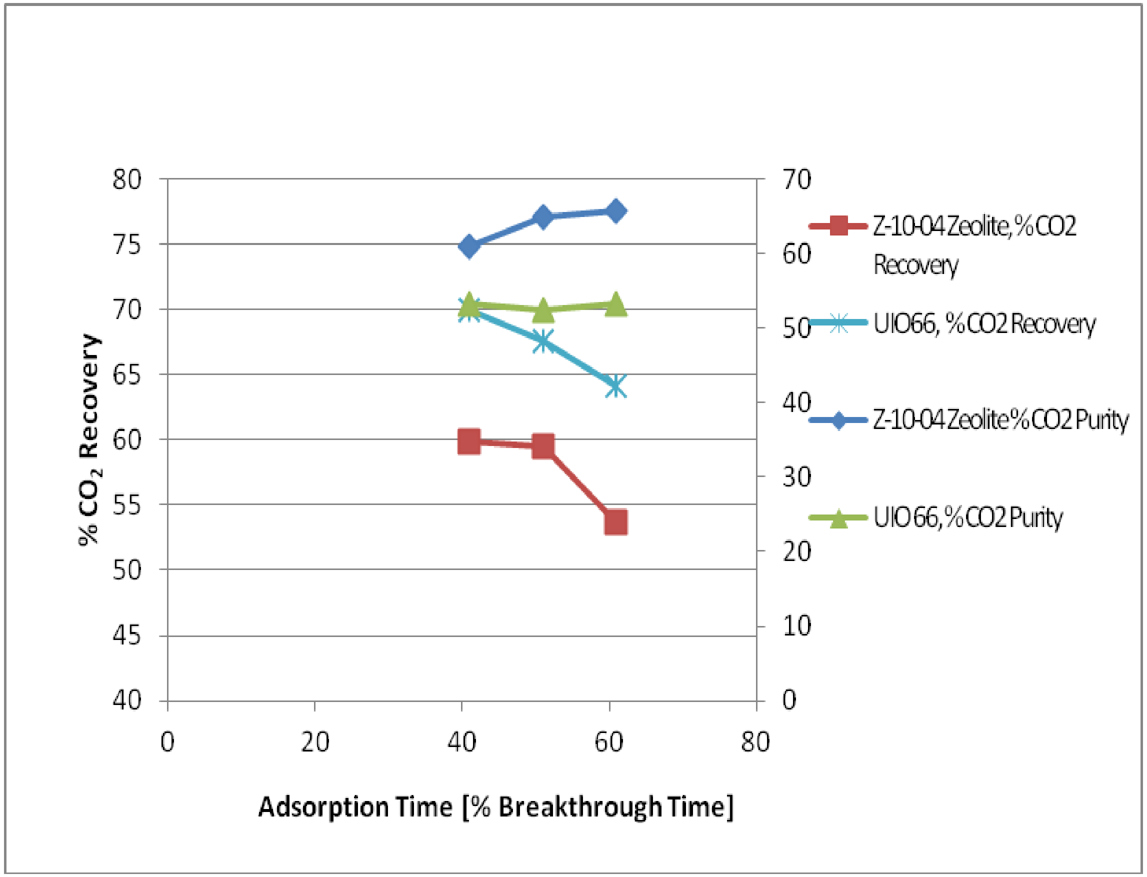


STEP V: Evacuation



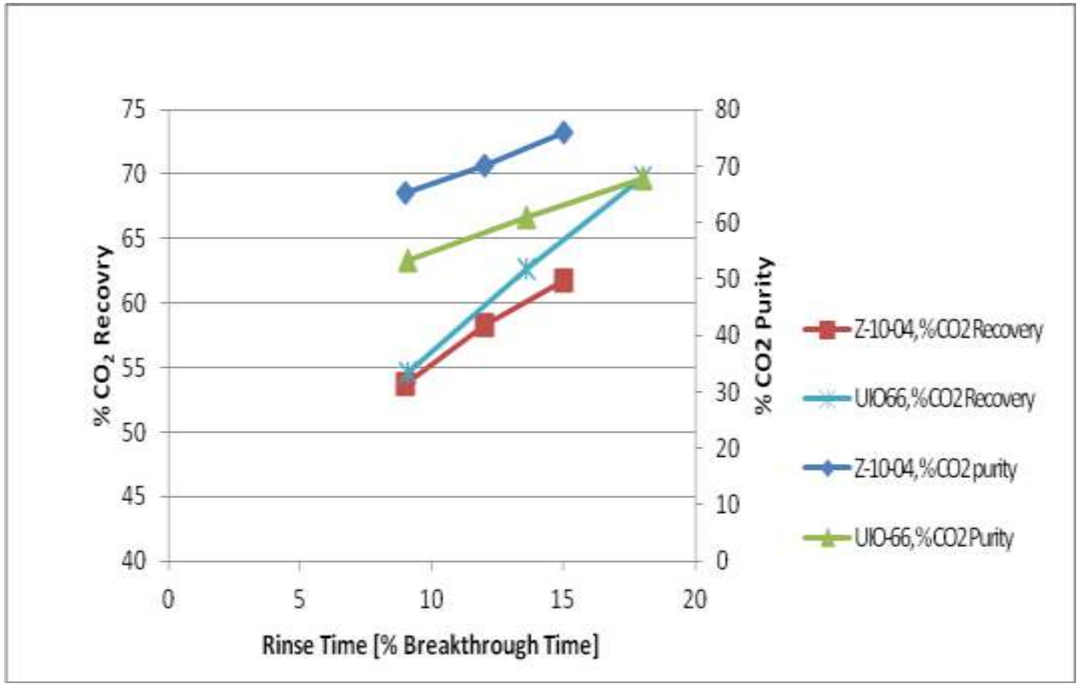
STEP VI: Evacuation+Purge

Effect of Adsorption Time on Performance



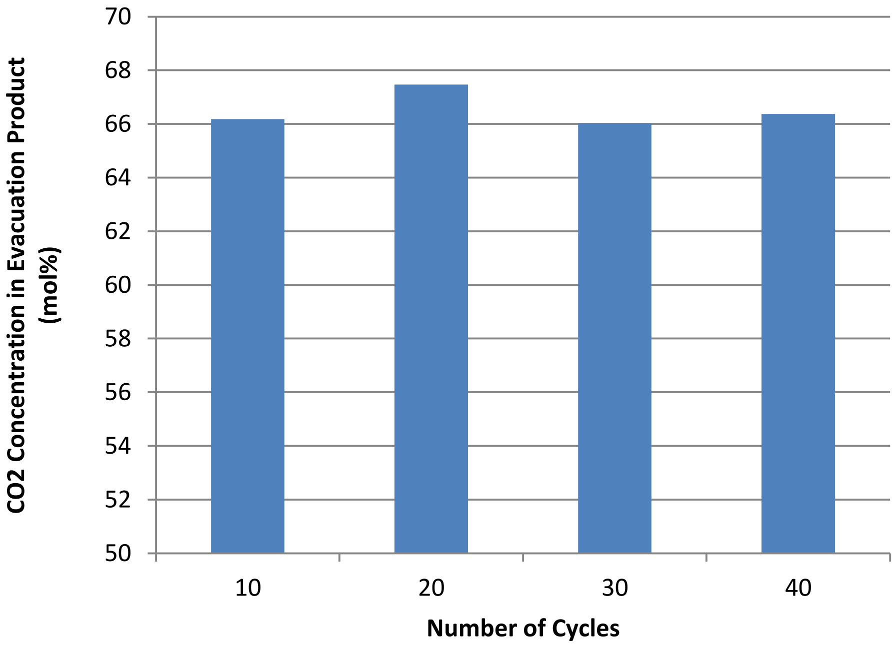
At minimum cycle time CO_2 purities are higher with zeolite but recoveries are lower

Effect of Rinse Cycle Time on Performance



CO$_2$ recoveries are lower with zeolite but purities are higher

Cyclic Stability of MOF for CO_2 recovery

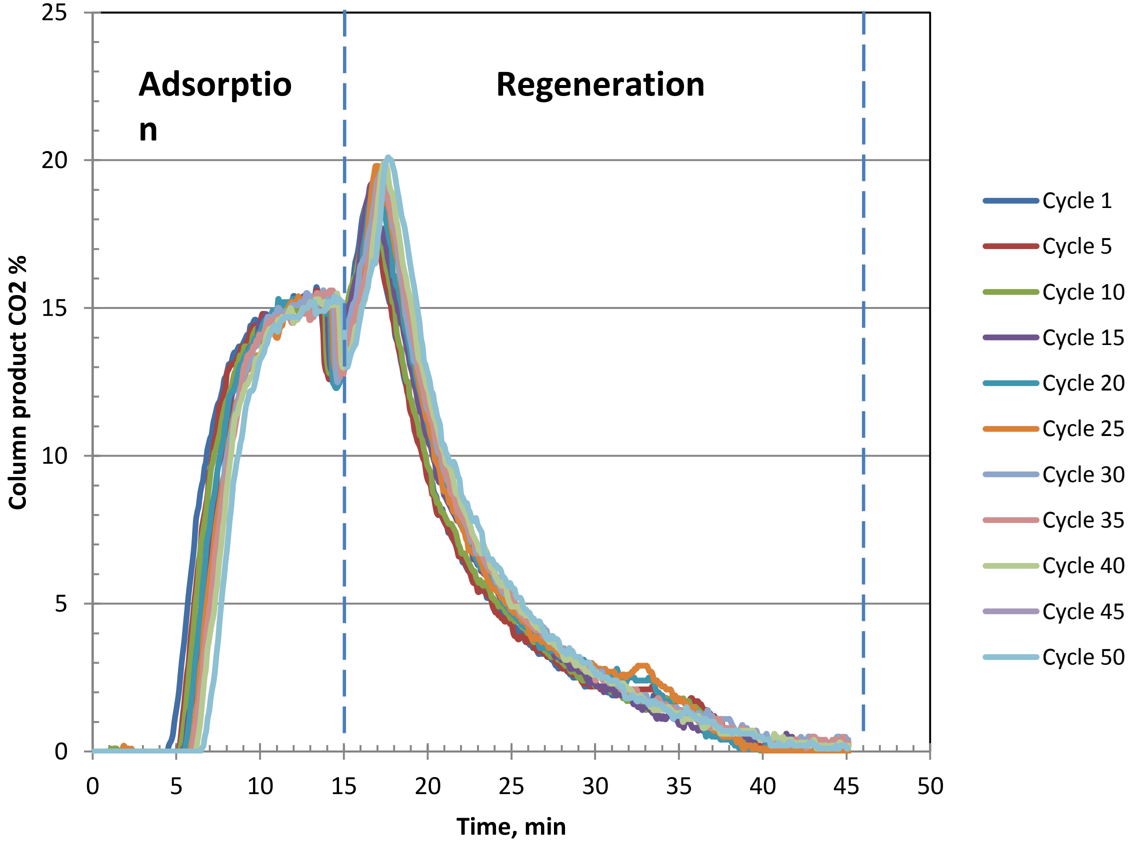


- CO_2 concentrations in product remain constant up to 40 PSA cycles studied

- No deterioration in the adsorbent performance observed

- UIO -66 shows good cyclicity over a large number of PSA cycles

Effect of Moisture on CO_2 breakthrough with MOF



- BT experiments over 50 cycles carried out in presence of moisture

- BT time does not affected in the presence of moisture

- Results demonstrate the regenerability of adsorbent in the presence of moisture

Conclusions

- 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

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- Kinetic diameter is the smallest effective dimension of a given molecule

- O2 and N2 are diatomic molecules not shperes in shape but rateh cylindrical in shape like tiny jelly bean

- Length dimension of the cylindrical shape is a larger dimnesion than the smaller waistline diameter of the cylindrical shape.

Adsorption Isotherms

Equation	**model**
$q=KC$	Henry
$q/q_s=bC/(1+bC$	Langmuir
$q=bC^{1/n}$	Freundlich
$\frac{C^e}{(C_s-C_e)q_e}=\frac{1}{BQ^0}+\left(\frac{B-1}{BQ_0}\right)\left(\frac{C_e}{C_s}\right)$	BET
$q/q_s=bC^{1/n}/(1+bC^{1/n})$	Langmuir-Freundlich
$q_a/q_s=b_a{*}p_a/(1+b_a{*}p_a+b_b{*}p_b+.....)$	Langmuir multicomponent

Dilute stream: Henry

Generally Freundlich and Langmuir satisfactory.

For multicomponent IAST preferable but implicit solution so difficult to implement