Technology Development for Clean Fuels Production and CO_2 Mitigation

Presentation at

CONFRONTING CLIMATE CHANGE: TOWARDS CARBON NEUTRAL CITIES

5TH CMS VATAVARAN,

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NEW DELHI

BY

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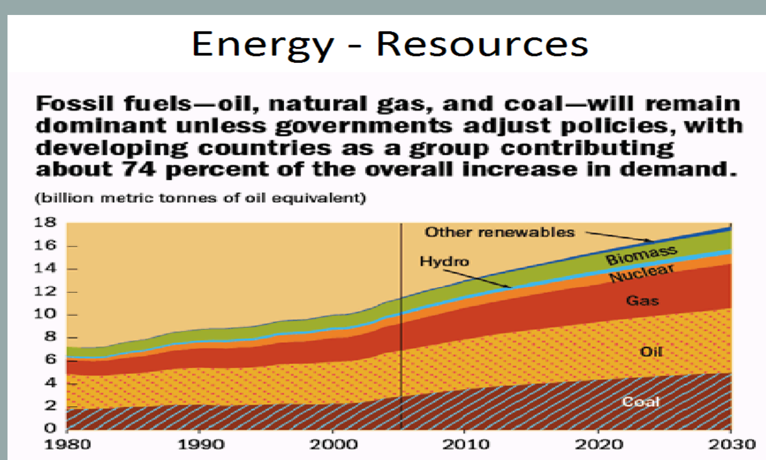
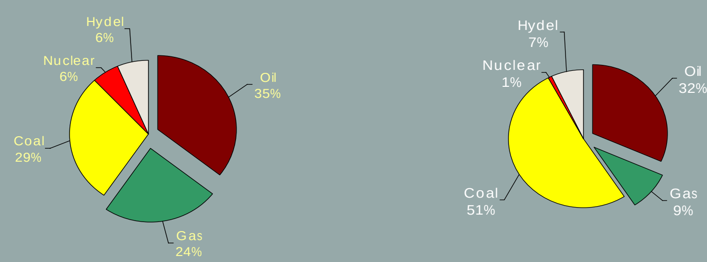
Global Energy Resources



Energy Basket

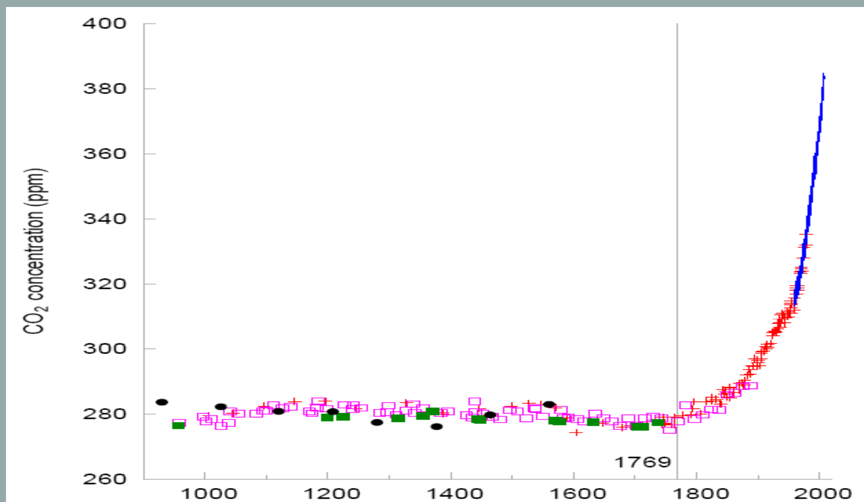
World	India*



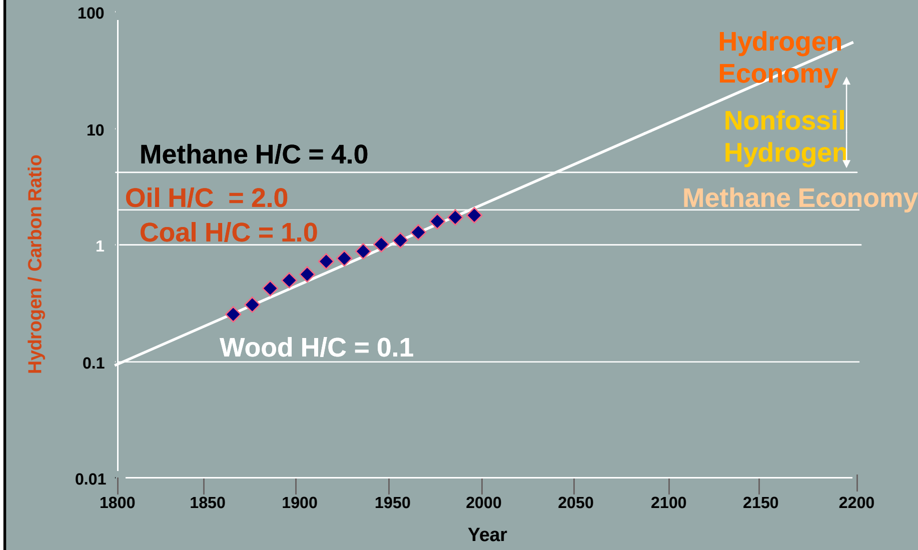
Source: BP Statistical Review 2008

*India's consumption based scenario excluding export

CO2 EMISSIONS IN CARBON BASED ECONOMY



Trend in H/C in Global Energy Consumption



Global Energy Scenario

- **Energy Security And Climate Change Are The Major Challenges Of Today**
- **Concerted Efforts Are Being Made World wide For Clean Affordable And Secure Energy Source And Hydrogen Is One Possibility**
- **But A Hydrogen -Based Economy Is Still Too Distant**
- **Improving Existing Energy Systems,Facilitating Their Cleaner Use While Including Carbon Sequestration –These Are The Priorities**

Transportation Sector

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- **Energy Demand From Transportation Sector Is Growing (1.8% per year), Also Leading To More Greenhouse Gas Emissions.**
- **Technological Advances / Innovations Are Vital To Improve Sustainability In This Sector Both With Respect To Cost Effective ,Environment Friendly Clean Fuels Production Practices And Utilisation.**

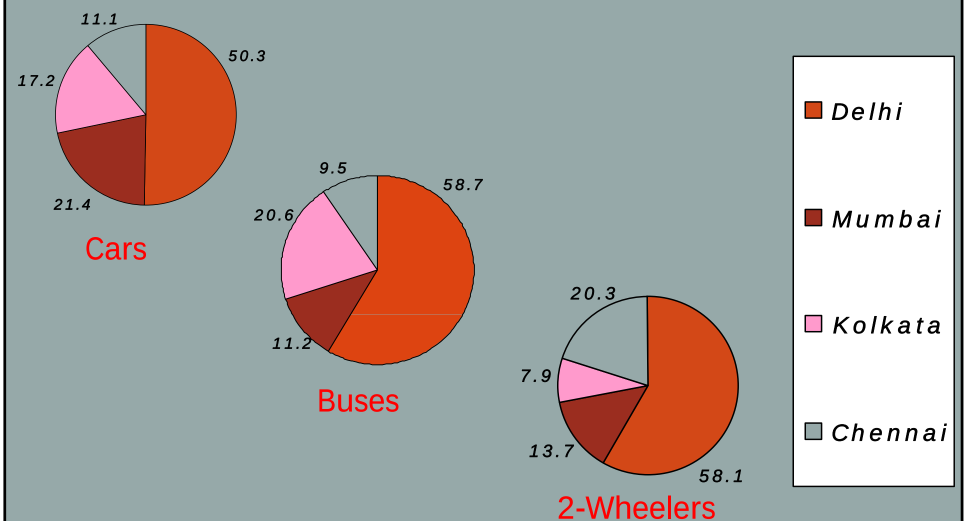
AUTOMOTIVE FUEL CONSUMPTION IN INDIA (IN MILLION TONS)

Product	1991/92	2007/08
Gasoline	3.57	14.61
Diesel	22.68	58.85

VEHICLE POPULATION IN INDIA (IN MILLIONS)

YEAR	2 & 3 WHEELERS	PASSENGER CARS	MUVs	COMMERCIAL VEHICLES
2000	38.75	4.26	0.97	2.42
2005	52.07	5.61	1.23	2.97

VEHICLE DISTRIBUTION IN INDIAN METROS



FUEL CONSUMPTION PATTERNS

- NATIONAL CONSUMPTION :DIESEL : GASOLINE 5 :1
- DELHI CONSUMPTION : DIESEL : GASOLINE 1 : 2
- GASOLINE USED BY 2&3 WHEELERS IS 2/3rd OF THE TOTAL PRODUCTION

EFFECT OF GASOLINE CHARACTERISTICS ON EMISSIONS

Property	CO	HC	NOx	Benzene	Others
Sulfur↓	↓↓↓	↓↓↓	↓↓↓	0	↓↓ (SO_2)
Aromatics↓	0	↓↓	↑	↓↓	0
Benzene↓	0	0	0	↓↓	0
Olefins↓	0	↓↓	↓	0	↓↓ (O_3)
Oxygenates↑	↓↓	↓	↑	0	↓ (CO_2)
RVP↓	0	↑	0	0	0
E100↑	0	↓	0	0	0

↑↑↑ High ↑↑Moderate ↑ Low

EFFECT OF DIESEL CHARACTERISTICS ON EMISSIONS

Property	CO	HC	NOx	PM
Sulphur↓	↓	↓	↓↓↓	↓↓↓
Density↓	↓↓	↓	↓	↓↓
PAH↓	↑	↑	↓	↓
CN ↑(50)	↓	↓↓	-	↓
T95↓	↓	↓	↑	↓↓

↑↑↑High ↑↑ Moderate ↑ Low

Clean Fuels Production

- **Sulphur Is The Prime Pollutant**
  - SO_2 Emissions
  - Acid Rain
  - Poisoning Of Catalytic Converter
  - Increased SOx,Nox
- **Our Road Map To Clean Fuels Production Has A Phased Sulphur Reduction Timetable**
  - April 2003 Bharat Stage II < 500 ppm Sulphur In Gasoline In Four Metros
  - April 2005 Bharat Stage III < 150 ppm Sulphur In Gasoline In Four Metros and 11 major cities Bharat Stage II Throughout Country
  - April 2010 Bharat Stage IV < 50 ppm Sulphur In Gasoline in four Metros and 11 major cities. Bharat Stage III in rest of country

INVESTMENTS MADE IN REFINING SECTOR FOR CLEAN FUELS PRODUCTION

- India 2000 to Bharat Stage II Rs. 17000 crores
- Bharat Stage II to Bharat Stage III Rs. 18000 crores
- Bharat Stage III to Bharat Stage IV Rs. 17500 crores
- Total Rs. 52500 crores

Desulphurisation of Transportation Fuels

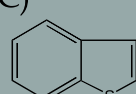
- **Current Practices Are Hydro Desulphurisation Based.**
  - **Energy Intensive. High Capital And Operating Costs**
  - **Associated CO_2 Emissions Are Also High**
- **Investments Involved Are Very High**
- **Need of the Hour is to develop Energy Efficient, Low Cost and Environment Friendly Desulphurisation Technology.**

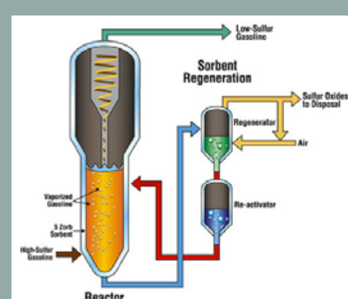
Global Efforts for Development of Low Cost Technologies for Gasoline Desulphurisation

- **Focus Has Been on Alternative Routes for Desulphurisation**
  - **- Adsorbents/ Reactive Adsorbents for Selective Removal of Sulphur Compounds**
  - **Catalysts for Oxidation of Sulphur Compounds to Sulphones**
  - **Catalysts for Alkylation of Sulphur Compounds to Higher Boiling Species**
  - **Membranes for Selective Permeation of Sulphur Compounds**
- **Adsorptive Desulphurisation Holds Maximum Promise**
- **Adsorptive Desulphurisation Has Lower Hydrogen Requirements (and Hence Lower CO_2 Emissions) and Also Achieves Sulphur Reduction With Minimum Octane Loss**
- **Adsorption technology has the options of being used either as stand alone or in combination with current hydrodesulphurisation technologies for overall economics**

S Zorb™ gasoline

- Developed by Phillips Petroleum Co.
- New ownership SINOPEC
- Adsorbent based on Ni/Zn/Al/Si
- T = 700-800°F (371–427°C)
- P = 7-21 kg/cm^2
- Typical reduction from ≈ 1000 to 10 ppm S
- Low octane loss

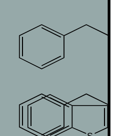




But Complicated Reactor involving Fluidisation

Hydrotreating: + $3H_2$ —Catalyst→ H_2S +

S Zorb: + $2H_2$ + Sorbent → Sorbent-S +



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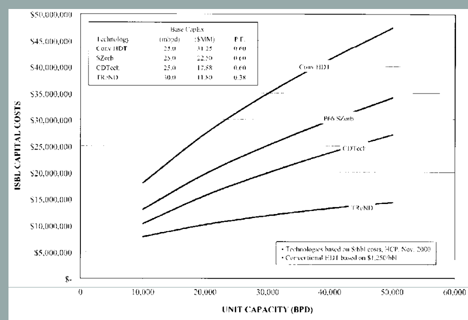
Capital cost estimates and diesel cost impact for various sulfur removal technologies*



* "A novel vapor-phase process for deep desulphurization of naphtha/diesel", DOE-report, B.S. Turk, R.P. Gupta, S.K. Gangval (RTI)

	Hydrotreating	S Zorb	TReND
Capital costs ($/bbl)	1200-1800	800-1200	500-700
H2 consumption (scf/bbl)	1000	400	20-100
Cost impact (¢/gal)	6-10	4-8	2-4

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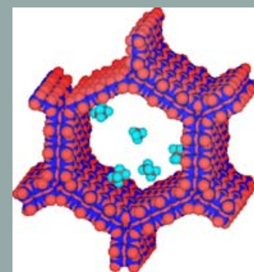
Collaborative Development of Adsorptive Desulphurisation

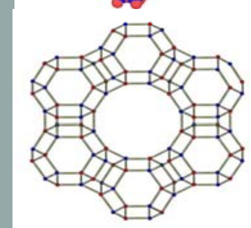
- Adsorptive Desulphurisation Technology Requires Development of Advanced Adsorbent Material and Development of Process Technology Based on This Adsorbent.
- IIP Has Commercialised Several Large Scale Separation Technologies in the Petroleum Refining Sector and Has Expertise in Adsorptive Separation Process Development .However Adsorbent Material Synthesis Is Not IIP's Specialisation
- In SINTEF , IIP Has Found World Class Expertise for Advanced Adsorbent and Catalyst Development.
- This Collaborative Development Programme Under INPIC Was Drawn up Based on Complementarity of Expertises Available With Both Partners

Typical adsorbents

- Zeolites (Y, X, clinoptilolite...)
- Mesoporous systems (MCM-41, SBA-15...)
- Oxides (alumina, silica, alumina-silica...)
- Activated carbon

- Metals inserted by ion exchange or impregnation (Cu, Ni, Fe, Zn, Na, Ag, Ga, Ce etc.)





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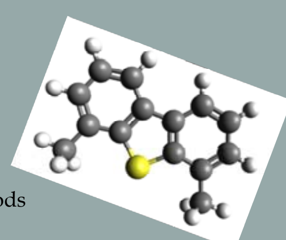
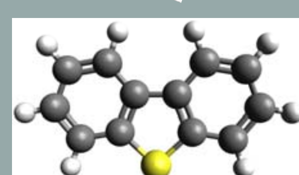
Development of low carbon emitting adsorption technology for Ultra Low Sulfur Diesel (ULSD) production

- Adsorbent development
  - Mesoporous supports
    - Structure
    - Pore size (20 – 60Å)
    - Acidity (Si/Al ratio)
  - Metal species combinations
  - Metal loadings
  - Ion exchange/impregnation methods
- Screening in liquid phase
  - Model feed: Dibenzothiophene (DBT) in n-hexadecane
  - UV spectrophotometry
- Upscaling
- Evaluation
  - Model feed
  - Commercial diesel



4,6-DMDBT



DBT

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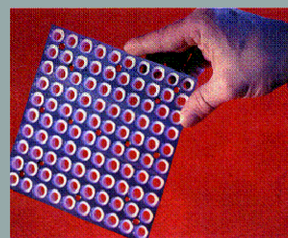
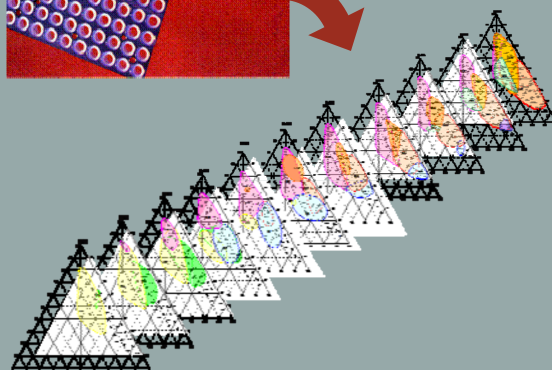
Combi ScreeningSINTEF

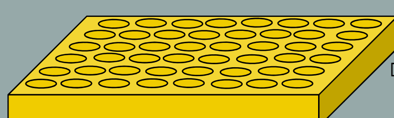
Develop New
HT technology



R&D
Using HT Technology

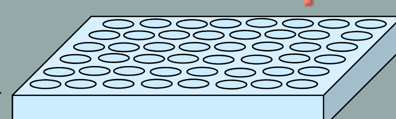


Test procedure – main steps



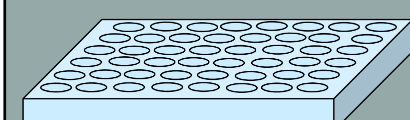
Pretreatment: 450°C in He for 1 h

Ceramic microplate

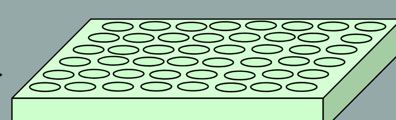


Adsorbent (30mg) + DBT/4,6DMDBT (500mg/l)/n-hexadecane (0.9 ml)
Rotation for 24 h at RT

Teflon (PTFE) microplate



Dilution of liquid samples
18µl + 900µl n-hexadecane



250µl samples for UV analysis

Polystyrene microplate

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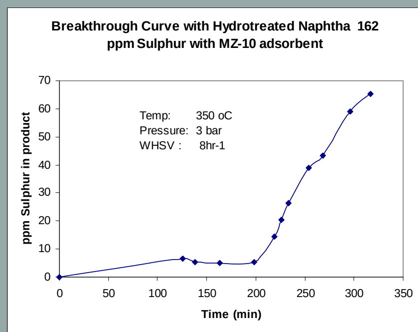
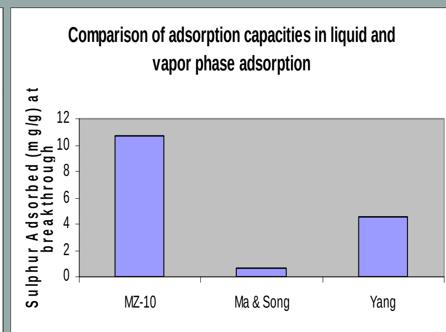
Adsorptive desulfurization of commercial gasoline





MZ-10: SINTEF, IIP (BT cap < 5 ppm product, 350 °C)

Ma & Song: I & EC 2005, 44, 5768 (BT cap < 1 ppm product, 200 °C)

Yang: Ind & EC Res, 2003, vol 42, No 13(BT cap < 1 ppm product, ambient temp)

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Process optimisation and adsorbent evaluation at IIP

- Breakthrough data generated in automated desulfurization unit selected adsorbents from combinatorial screening under fixed operating conditions
- Operating parameters
  - Pressure: 3 bar-9 bar
  - Temperature 250 to 350°C
  - WHSV 4-12 hr^{-1}

- Gasoline can be desulphurised to <30ppm
- Hydrogen requirement is about ten times lower than conventional hydrodesulphurisation process
- Temperature is same as in HDS process
- There is no octane loss

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Approach to process integration

- The effluent from the conventional naphtha hydrodesulfurization unit can be directly routed to the adsorption unit without any major changes.
- The deep desulfurized product from the adsorber can then be processed as per normal flow scheme that is routed to air condenser, separator and fractionator
- Additional facilities envisaged will be for the adsorber regeneration loop and will comprise furnace for regenerator gas heating, heat exchanger and regeneration gas compressor
- Regenerator effluent can be handled in the existing Claus Unit for sulfur recovery

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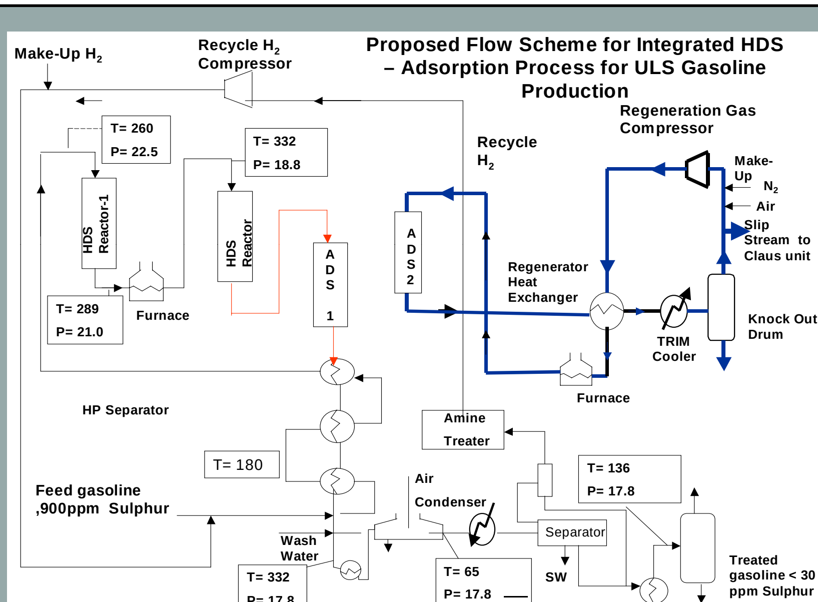

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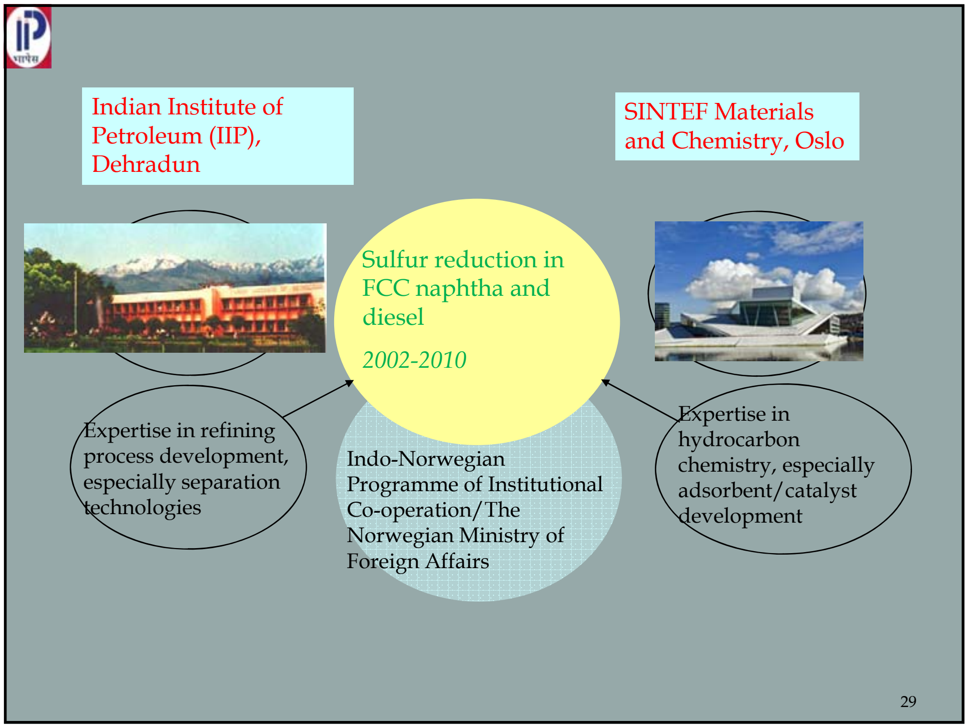
Indian Institute of Petroleum (IIP), Dehradun
SINTEF Materials and Chemistry, Oslo
Sulfur reduction in FCC naphtha and diesel
2002-2010
Expertise in refining process development, especially separation technologies
Indo-Norwegian Programme of Institutional Co-operation/The Norwegian Ministry of Foreign Affairs
Expertise in hydrocarbon chemistry, especially adsorbent/catalyst development
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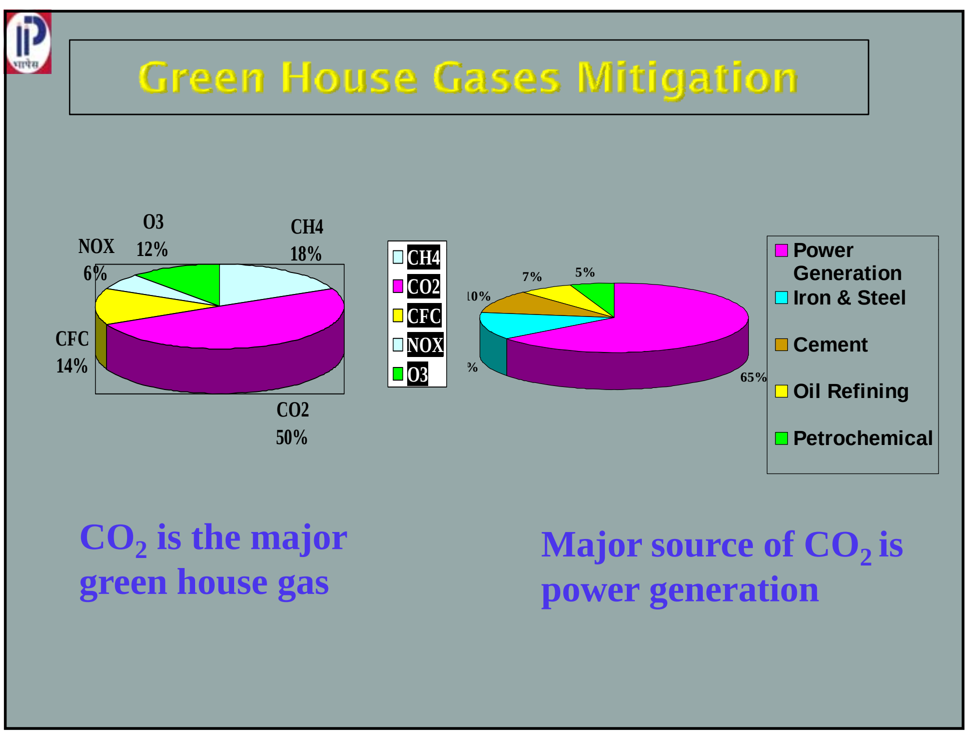

Green House Gases Mitigation
O3 12%
NOX 6%
CH4 18%
CFC 14%
CO2 50%
CH4
CO2
CFC
NOX
O3
10%
7%
5%
65%
Power Generation
Iron & Steel
Cement
Oil Refining
Petrochemical
CO_2 is the major green house gas
Major source of CO_2 is power generation

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

Global Measures For Green House Gas Mitigation

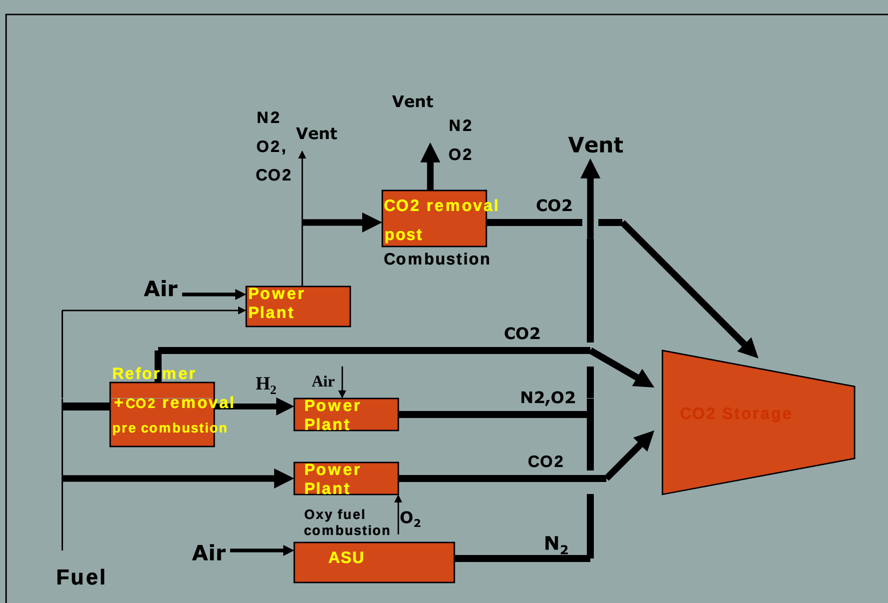
- Worldwide agreement that steps are necessary to contain rising CO_2 levels
- Less agreement on how best to achieve this

CO_2 Sequestration

CO_2 Sequestration Involves

- Capture
- Transport
- Storage of CO_2 in Geological Formations

Carbon Dioxide Management



Typical Composition Of Flue Gases

CO_2	3-5%	(NG fired)
	11-14%	(Coal fired)
O_2	12-15%	(NG fired)
	3-4%	(Coal fired)
Water	4-5%	
NOx	300-500 mg/Nm3	
SOx	700-1200 mg/Nm3	
SPM	130-150 mg/Nm3	
Temperature	150 ^{0}C	
Pressure	Atmospheric	
Typical flow	1.5 MMCM/hr for 210 MW plant	

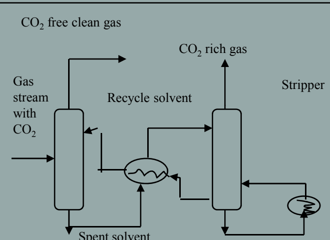
Operational Constraints under which CO_2 recovery process must perform in Post Combustion CO_2 capture

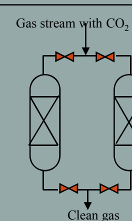
- Low pressure
- High temperature
- Presence of oxygen
- Presence of SOx ,NOx
- Presence of water vapor
- Soot
- Fly ash
- SPM

Cost Associated with Implementation of CO_2 Capture Technologies

- **Substantial Cost Factor is Associated With Implementation of CO_2 Capture Technology in Power Generation**
- **This Cost Varies with Plant Type- Greater for Gas Fired Plant Than Coal Fired Plant**
- **Cost of Electricity Generation Estimated to be 40% Higher if Current Technology for CO_2 Capture Used in Power Plants**
- **Large Scope for Development of More Efficient CO_2 Capture Technologies**

Processes Available For CO_2 Capture





Absorption

- **Chemical and Physical Absorption can be used**
- **Corrosion/Foaming Problem**

Adsorption

- **Alumina, zeolite, Act. Carbon can be used**
- **Regenerate Beds by Pressure Swing/Temperature Swing**

In Principle, Membranes and Cryogenic Separation can also be used

Development of PSA Technology for CO_2 Capture from Flue Gases: Global Status

- Pilot Plant Reported from JAPAN, Tokyo Electric Power Co.(Pressure Temperature Swing)
- US Dept of Energy has sponsored major projects at several Universities,Research Institutes
- CO_2 Removal at High Temperature by PSA being Studied at Air Products USA
- PSA Technology for CO_2 Removal from Flue Gas Under Development by CRC Australia
- Reports of Commercialisation of PSA Technology from Korea

CO_2 Capture By PSA

- PSA is a commercially proven unit operation with large applications in hydrogen production, air separation, drying.
- A number of commercially available adsorbents have been tried for CO_2 removal
- Available adsorbents work best at temperatures below 50^0 C . Zeolites appear better but effect of moisture will have to be considered

COST OF CO2 CAPTURE USING CHEMICAL ABSORPTION, PSA/VSA AND GAS SEPRATION 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
CO2 recovery rate(%)	90	90	90	75 [80]	90	90
CO2 purity(%)	>98	>98	44	48 [90]	43	62
Energy Penalty(%)	36	21	47	28	52	45
Capture cost US$/tonne CO2 avoided	47	34	61	40 [25]	78	64

Development Of Indigenous PSA Technology For CO_2 Recovery From Power Plant Flue Gas

SPONSOR **NTPC LTD**

COLLABORATORS IIP
CSMCRI
NEERI
IIT, MUMBAI

OBJECTIVE:

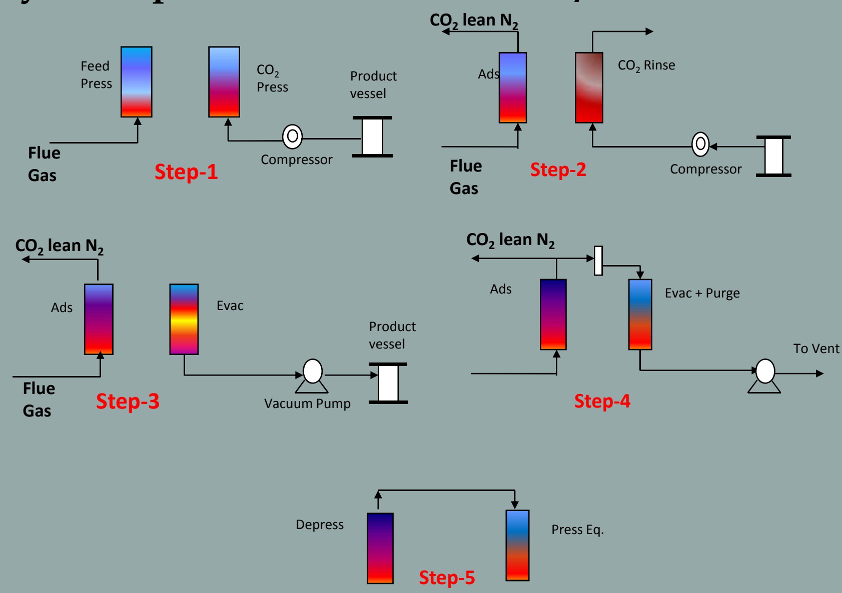
To develop PSA/VSAprocess for capture of CO_2 from flue gas in laboratory scale and use the know-how and experimental information generated to develop and optimise design for a pilot- scale PSA plant to be set up at NTPC

EXPERIMENTATION

•A custom designed three column PSA/VSA unit has been set-up in the laboratory. This unit has been designed to evaluate wide variety of PSA/VSA cycles for CO_2 recovery

•A large variety of metal exchanged zeolite adsorbents has been evaluated in this unit at low pressures and elevated temperature conditions, under which CO_2 recovery from power plant flue gas is required

Cycle Steps for Two Column PSA /VSA Unit



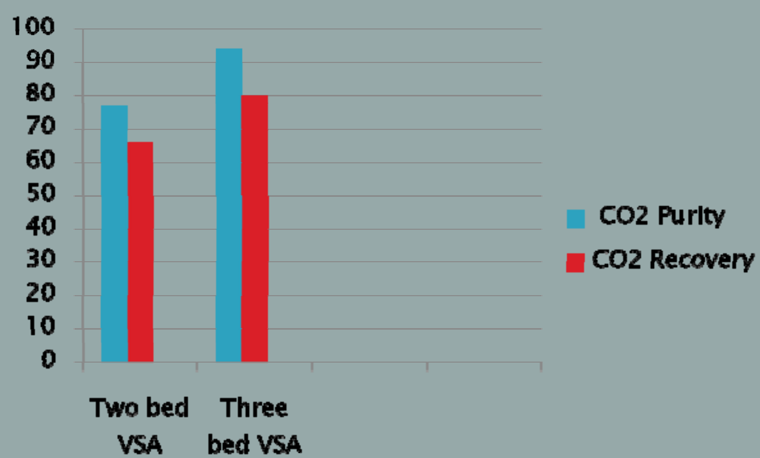
Power requirements in CO2 recovery

- Amine processes 0.55 Kw-hr/Kg CO_2
- PSA processes 0.53 Kw-hr/Kg CO_2
- PTSA 0.56 Kw-hr /Kg CO_2

Power estimation in CO2 recovery by PSA

- Adiabatic work of compression ;Power consumed in feed adsorption
- Power consumed in evacuation
- Power consumed in rinse
- Total power : 0.30 Kw-hr/kg CO_2 at 55^0C

Comparison of Three Column and Two Column Results



ROUND UP

•A novel three column, eight step VSA cycle has been developed for CO_2 recovery from power plant flue gas.
•This cycle uses a strong adsorptive rinse in a co-current depressurization step .
•CO_2 enrichment is from 12 vol% to > 90 vol% at elevated temperatures and low adsorption pressures with recovery of around 80%.

•Adsorbent testing have been carried out in presence of 5 vol% moisture as typically present in flue gas
• With addition of a guard layer of commercial air drier adsorbent , the performance of the VSA system does not deteriorate
•The system is able to consistently separate and recover CO_2 over repeated cycles.