CATALYSIS AND CHEMICAL INDUSTRY : CHALLENGES AND OPPORTUNITIES

Catalysis for Sustainable Development

CSIR – NEERI, Nagpur

February 4, 2014

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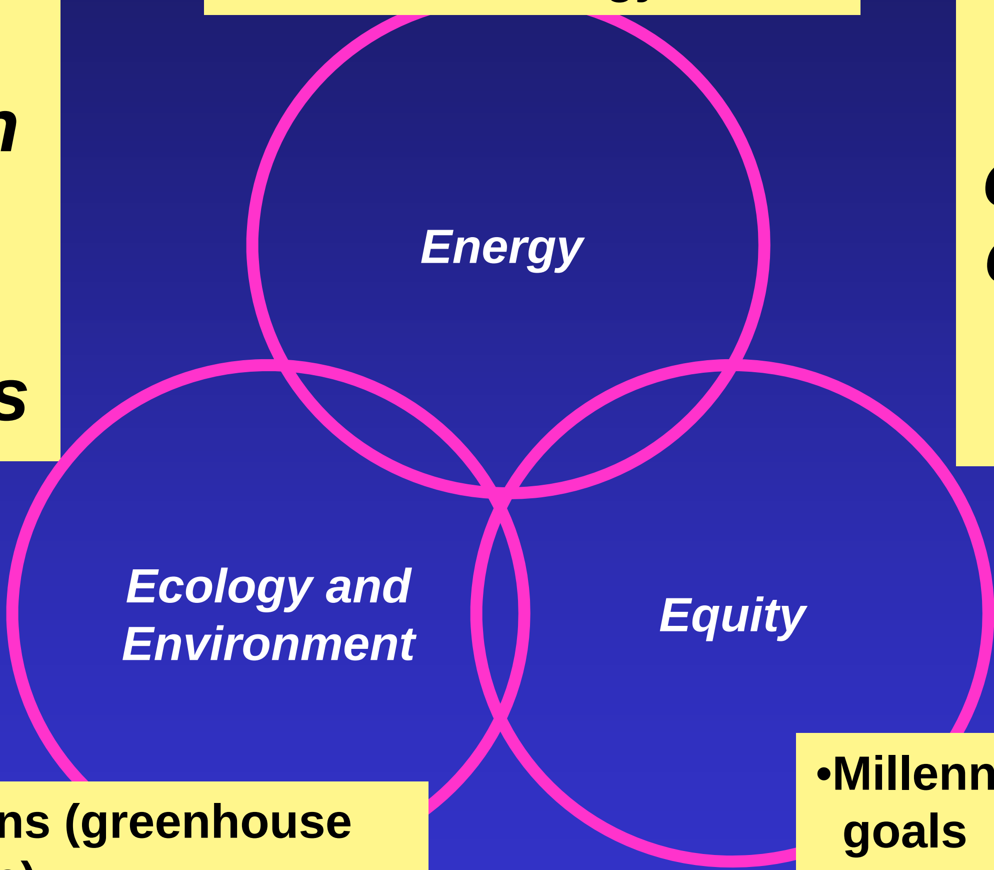
Our civilization is at historic crossroads

- Clean energy
- Energy efficiency
- Renewable energy



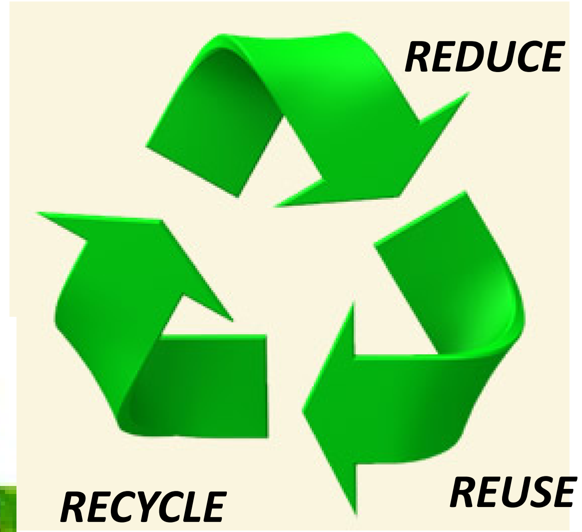
Key : Sustainable Consumption Conservation of Natural Resources

- Reduced emissions (greenhouse gas/carbon dioxide)
- Materials from renewable resources
- De-carbonization

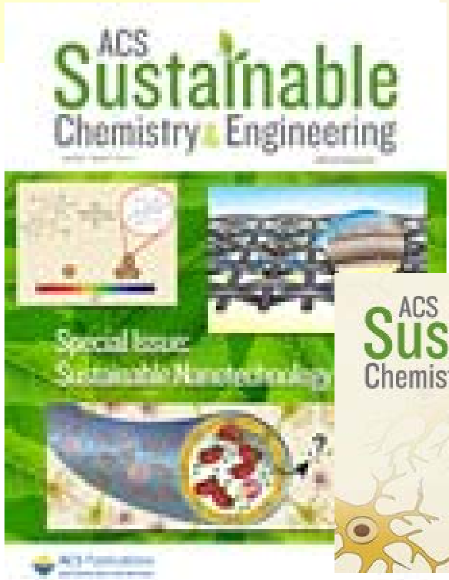
- Millennium development goals
- Access and entitlement
- Equitable distribution
- Climbing the economic ladder

CHEMICALS AND MATERIALS

- **Exclusive dependence on fossil fuel based resources**
- **Generation of wastes that need disposal**



Sustainability is the key concern of science, technology, industry and society today



Can the chemicals and materials needs of humankind be based on the concept of sustainability of both resources and environment?

THE STRUCTURE OF THE CHEMICAL INDUSTRY

Crude Oil

93%

7%

fuel (energy)

Transportation & heating

Feed-stocks

Commodity Chemicals

Polymers

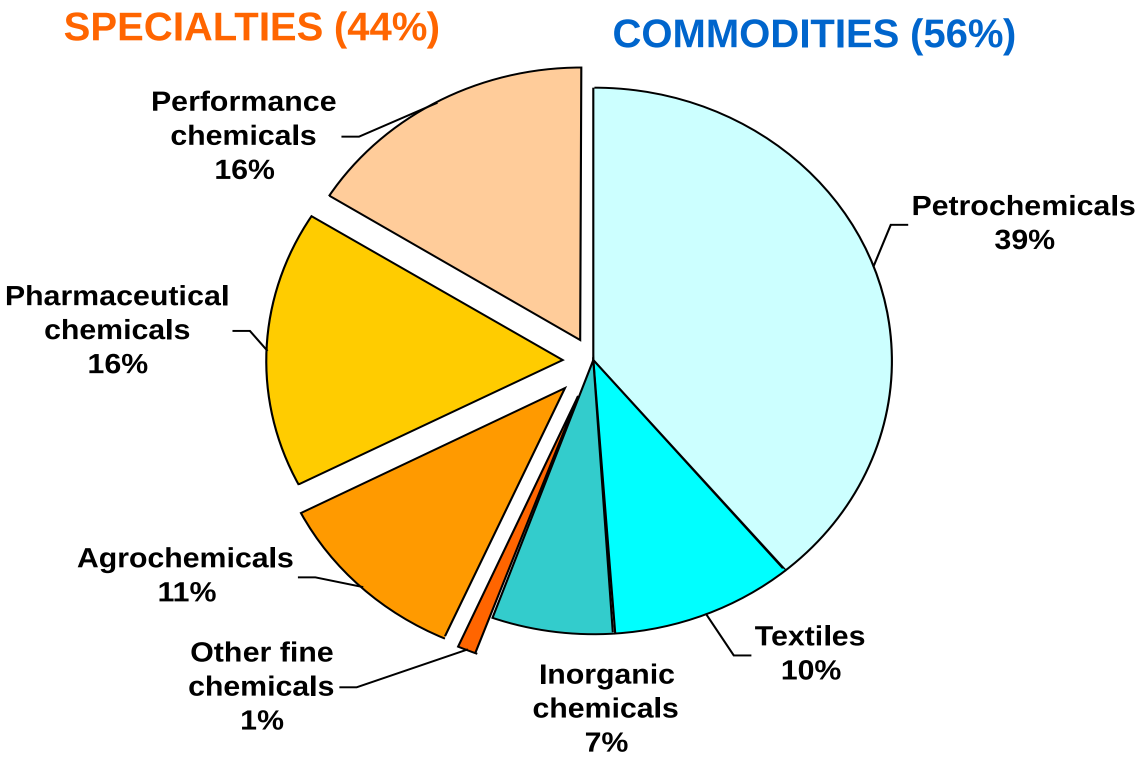
Synthesis

Specialty & Fine Chemicals

Pharmaceuticals

Liquid to C2/C3 to natural gas to shale

WORLD CHEMICAL MARKETS

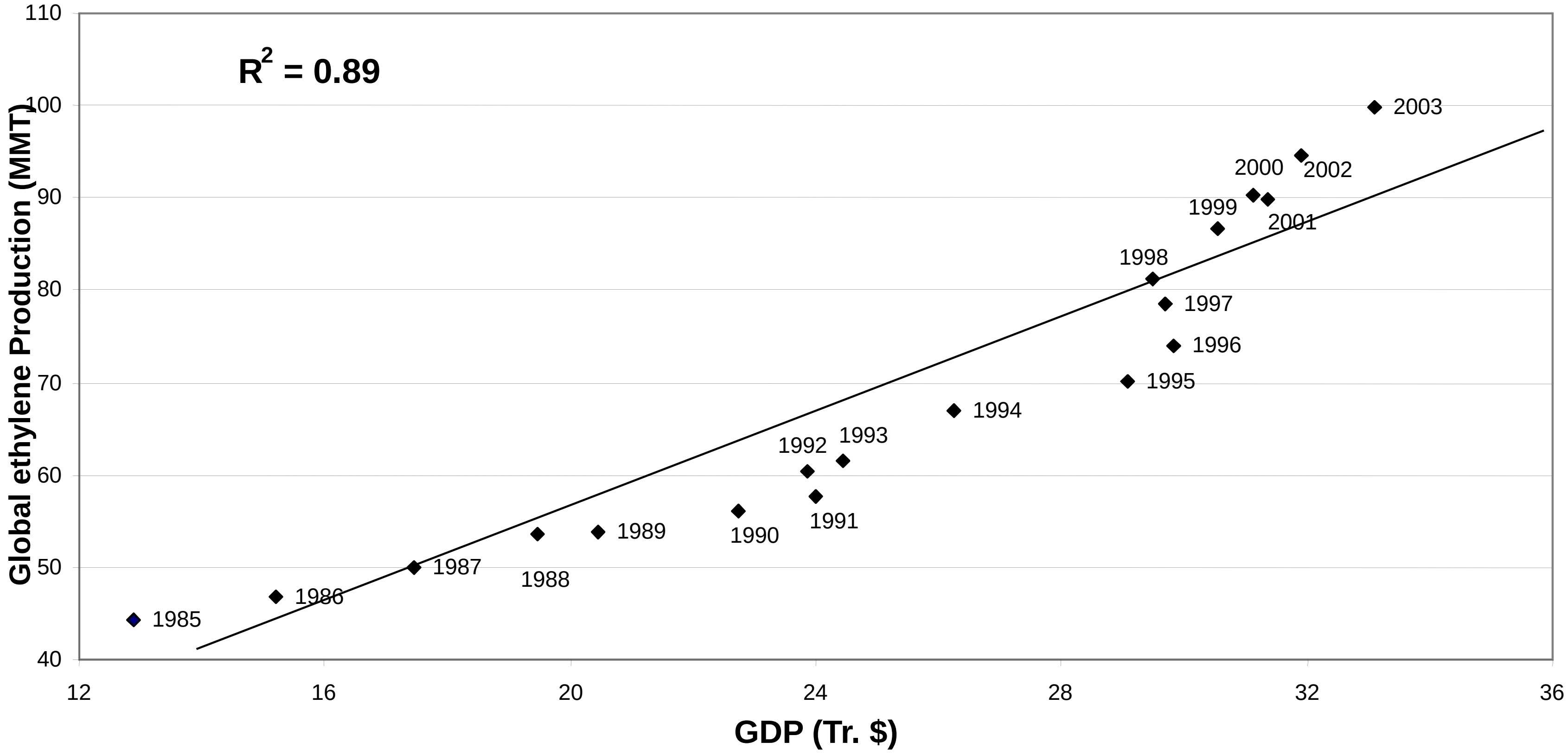


Total Size - 3 tr. USD (2010)
~ 5.3% of global GDP
Growing @ 1.5 times GDP

Petrochemicals dominate with share ~40%

Source: Chem Systems/ BAG

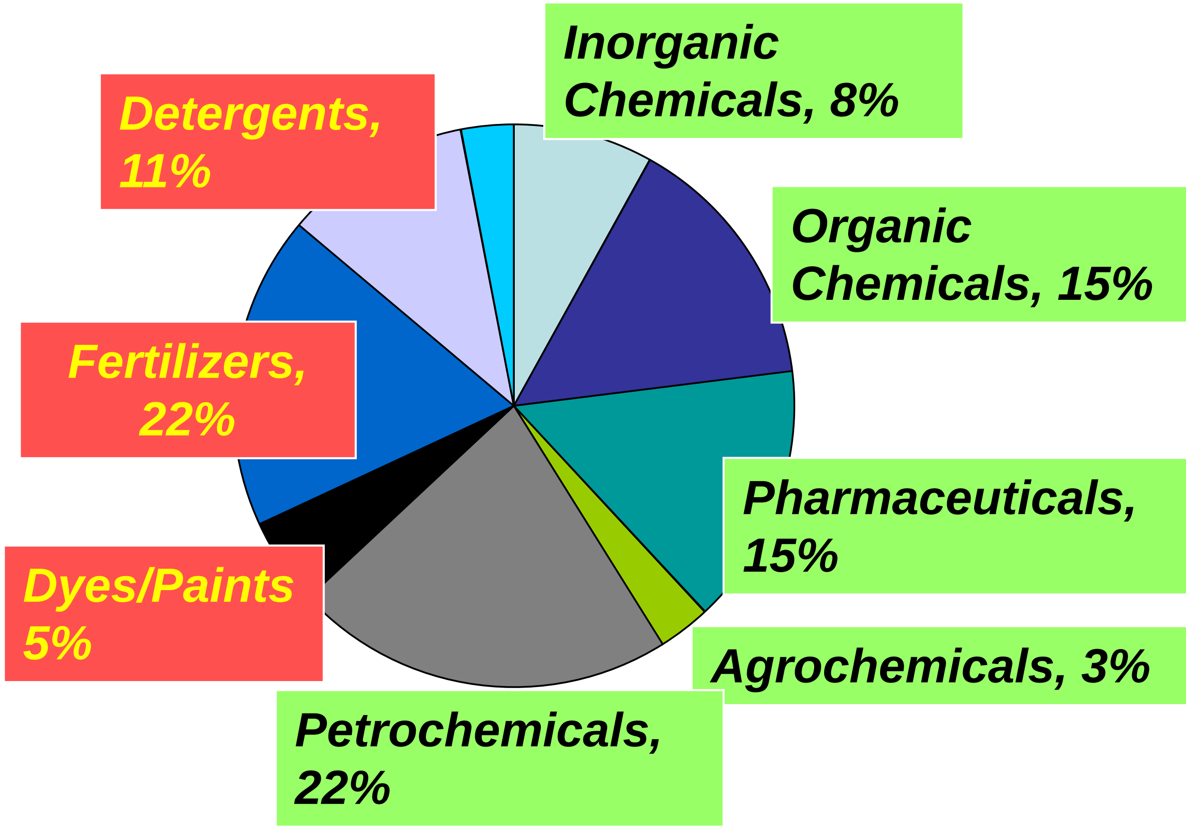
ETHYLENE CONSUMPTION & GDP



A Strong Correlation over 2 decades

INDIAN CHEMICAL INDUSTRY

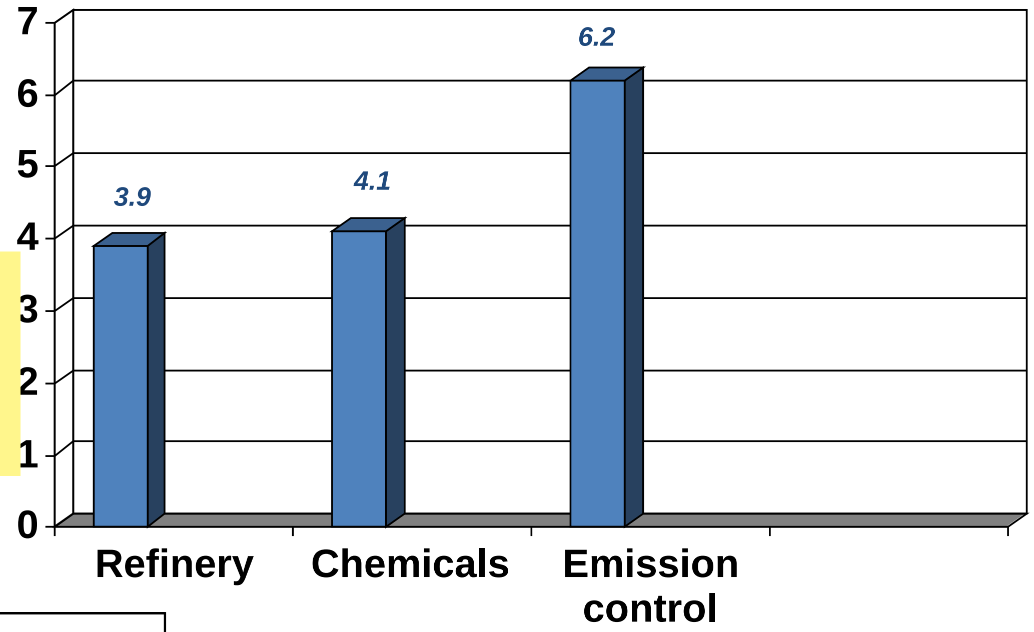
- Chemical industry in India contributes to 3 % of its GDP and 14 % of its exports
- Revenues : US $ 55 billion in 2007-08 and CAGR of 11 % (2002-07)
- Projected to grow to US$ 75 billion by 2011
- Indian Chemical industry 12 th largest in the world and 3 rd largest in Asia

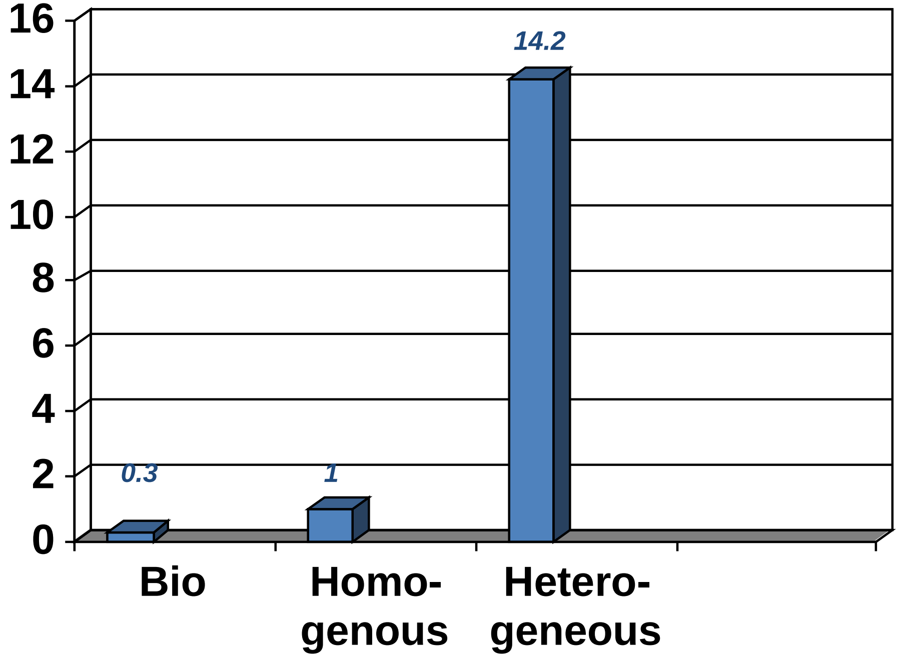


Commodity chemical industry is technologically mature; all innovations are incremental in nature

CATALYSIS : DRIVER FOR INNOVATION IN CHEMICAL INDUSTRY

World market : $15.5 bn
Growth : 5 to 6%





Heterogenous catalysts : $14.2 bn

Chemical Weekly, September 15, 2009, p. 201

HISTORY OF CATALYSIS : SCIENCE AND TECHNOLOGY

SCIENCE

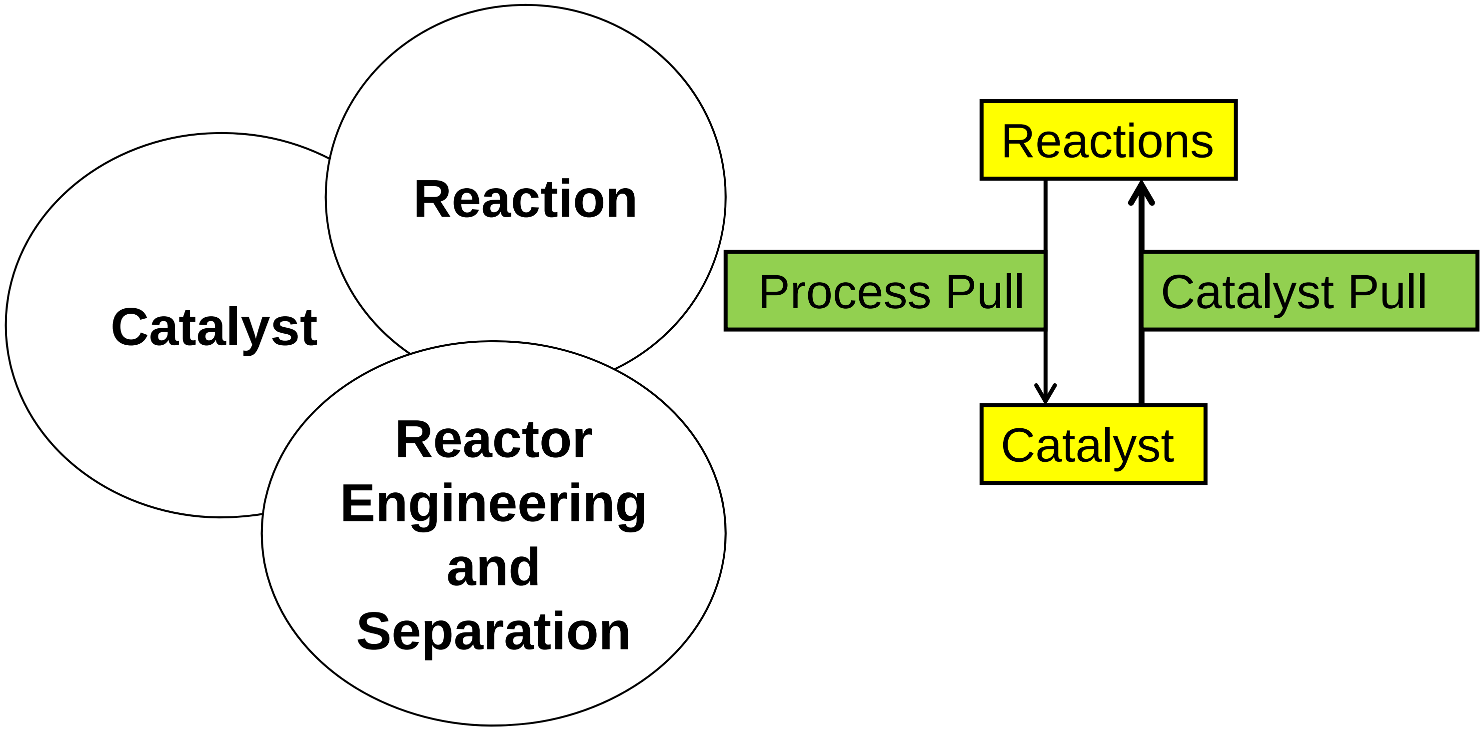
1830	Definition of catalysis : Berzelius	1960	Hydrogen spill over and reconstruction of metal surface: Somorjai
1880-90	Quantitative measurement of catalytic reaction rates: Ostwald	1970	Structure sensitive and insensitive reactions : Boudart
1920	Thermodynamic limits of catalysis : Nernst/Haber	1970	Strong metal-support interaction
1930	Mechanism of catalytic reaction : Horuiti / Polanyi	1975	Pore size and selectivity : Haag
1940	Concept of active sites and their heterogeneity : Taylor	1980	Confinement of reagents in pores: Fraissard
1960	Shape selectivity : Weisz	1990	Molecular catalysis and surface science

HISTORY OF CATALYSIS : SCIENCE AND TECHNOLOGY

TECHNOLOGY

1888	Contact process for H_2SO_4	1961	Steam reforming
1913	Ammonia synthesis : Haber, Bosch, Mittasch	1969	Bimetallic reforming
1923	Synthesis gas to methanol: M. Pier	1970	Ammoxidation of propylene: Sohio
1936	Catalytic cracking : Houdry	1974	Acetic acid via carbonylation of methanol : BP
1937	Direct air oxidation of ethylene to EO : Scientific Design	1975	Butane to maleic anhydride
1940	Alkylation of benzene with propylene to cumene	1988	Selective oxidations (TS-1): Enichem
1942	Fluid catalytic cracking (FCC)		
1950	Liquid phase p-xylene oxidation to DMT/TA/ o-xylene to phthalic anhydride		

FACETS OF CATALYTIC TRANSFORMATIONS



Technology emerges only when there is a process pull

POSSIBLE AND PRACTICAL

- **Possible : Realm of invention**
- **Practical : Realm of innovation**

Just because something can be done, does not mean that it will or should be done

W. F. Banholzer and M.E. Jones, AIChE J, 2013

CATALYSIS TECHNOLOGY : END SEGMENTS

- **Refinery : Fuels and chemicals**
- **Fertilizers**
- ***Petrochemicals – Commodity chemicals***
- ***Fine and specialty chemicals***
- ***Chemicals / fuels derived from biomass***
- **Polymers**
- **Renewable energy**
- **Emission control and environmental**
- **Fuels and Chemicals fromCarbon dioxide**

REFINERY CATALYSTS : CHALLENGES

- **THE TOP OF THE BARREL**
  - **Methane activation**
  - **Syn Gas conversion**

- **THE BOTTOM OF THE BARREL**
  - **Residue conversion**
  - **Bitumen Processes**
  - **Gasification**

METHANE CONVERSIONS

- **Catalytic combustion**
- **Cracking**
- **Coupling – Ethylene (Siluria Tech, CA)**
- **Oxy-halogenation – Vinyl chloride**
- **Aromatization**

SYNGAS CONVERSIONS

- **Ethanol (Celanese)**
- **Ethylene glycol (non oxalate, Eastman-Johnson Mathey Davy)**
- **Acetic acid (BP)**

METHANOL / ETHANOL CONVERSIONS

Methanol

- Ethylene (UOP/Hydro)
- Propylene (Lurgi)
- Styrene (Reaction with toluene) (Exelus)
- p-Xylene (Reaction with toluene) (SABIC-Lummis)

Ethanol (Petrochemical)

- Acetone
- Ethylene (BP)
- Propylene
- Isobutylene
- Butanol
- Acetic acid

C_2 / C_3 CONVERSIONS

Ethane

- Acetic acid
- Ethylene oxide
- Acetonitrile
- Vinyl acetate
- Vinyl chloride

Propane

- Dehydrogenation to propylene (PDH)
- Acrylic acid
- Acrylonitrile

COMMODITY CHEMICALS: OPPORTUNITY FOR INDIAN R&D

- **Large capacity manufacturing exploiting economies of scale**
- **High capital costs and low manufacturing costs**
- **Engineering and design intensive; marry catalyst performance with reactor design**
- **High reliability and process safety**
- **Cost of feed-stocks often exceeds 90 % of the cost of products**
- **Proven technology licensors with long experience**

Little appetite for risk taking; Indian catalyst R&D unlikely to make an impact

CATALYTIC PROCESSES FOR FINE CHEMICALS

- **Hydrogenation**
- **Alkylation and Acetylation**
- **Oxidation**
- **Amination**
- **De-oxygenation and hydro-treatment**
- **Metathesis**
- **Fast pyrolysis**

PROCESS CHARACTERISTICS COMPARISION

Fine chemicals	Commodity Chemicals
• Batch	Continuous
• Liquid phase, lower temperatures	Gas / vapor phase, high temperatures
• Slurry, CSTR	Fixed, trickle, moving, fluidized beds, continuous catalyst regeneration
• High turn over frequencies	High turn over numbers

CATALYTIC HYDROGENATION

- **Methyl p-toluate to 4-methylcyclohexane methanol**
- **Terephthalic acid to 1,4-cyclohexanedimethanol**
- **Bisphenol-A to hydrogenated bisphenol-A**
- **Methyl benzoate to benzaldehyde**
- **2,2 ‘,4,4- cyclobutanedione to 2,2’ ,4,4 - cyclobutanediol**
- **Di-2-ethylhexyl phthalate to 2- ethylhexyl cyclohexyl-1,2- dicarboxylate**
- **Nitrobenzene to cyclohexylamine**
- **Cardanol to 3 - pentadecyl phenol and 3-pentadecyl cyclohexanol**

SELECTIVE OXIDATIONS

- **Propylene to PO (liquid phase, H_2O_2; BASF-DOW , SKC, Korea)**
- **Propylene to allyl acetate (Showa Denko – Diacel)**
- **Propylene to acrylic acid (Nippon SKK, Showa Denko)**
- **Ketone to oximes (liquid phase)**
- **ε-Caprolactone from cyclohexanone**
- **EG to glyoxal and glycolic acid**
- **Cyclohexene or cyclohexane to adipic acid**
- **n--hexane to adipic acid**
- **Ethylene to acetic acid (Showa Denko)**
- **Isobutylene to methacrylic acid (Nippon SKK)**

AMINATION

- **Benzene to aniline**
- **EO to diethanolamine**
- **Ethylene to mono-ethylamine**
- **Methanol to methylamine**
- **1,4-Butane diol to 1,4-diaminobutane**
- **Cyclohexanol to cyclohexyl amine**

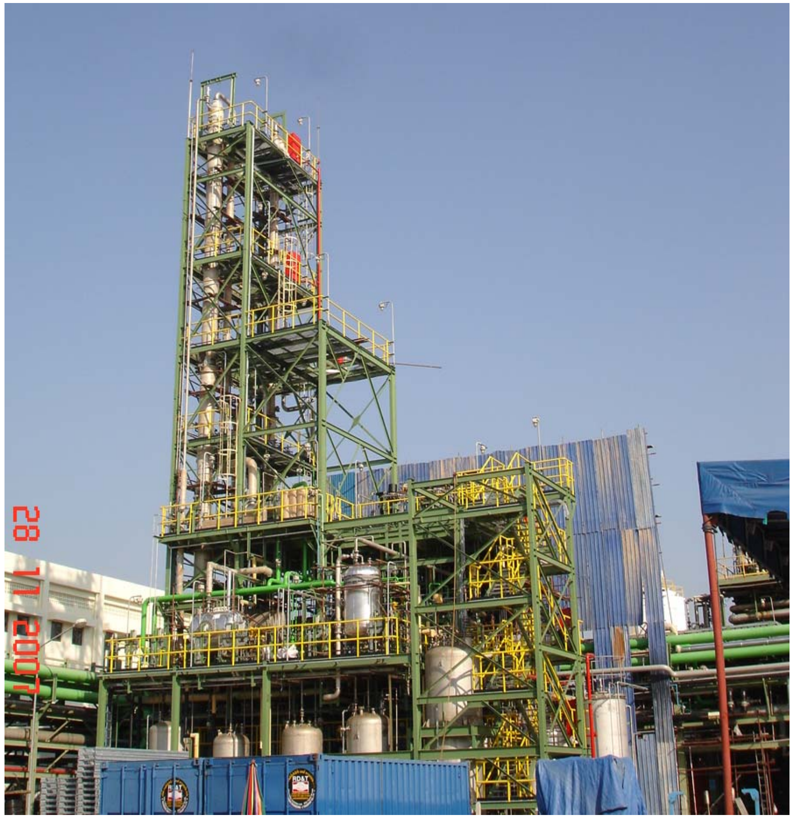
CATALYSTS FOR FINE CHEMICALS : THE NCL EXPERIENCE (2002-10)

- **Epichlorohydrin from allyl chloride and hydrogen peroxide (TS-1)**
- **4-methoxy acetophenone from anisole (Mesoporous Zeolite)**
- **Chlorotoluene from toluene (Zeolite KL)**
- **4,4' – Diaminodiphenyl methane from aniline and formaldehyde (HY)**

In all cases pilot plants were built in industry locations; extensive trials were jointly undertaken to establish process economics; results disappointing , largely due to poor catalyst lifetimes, difficult regeneration protocols; all processes abandoned as unviable

EPICHLOROHYDRIN FROM ALLYL CHLORIDE

- **An improved and patented TS-1 catalyst**
- **Cold extraction as a basis for downstream separation of aqueous and organic layer to minimise hydrolysis of ECH at high temperature**
- **Overall conversion of > 99 % and yield of > 95 % achieved**
- **Basic and detailed engineering package for a 3000 tpa plant performed by NCL for a plant installed at Rayong, Thailand**
- **Two tons of catalyst (first charge) produced at NCL**
- **Six weeks continuous operation in 2009**



View of 3000 tpa Epichlorohydrin plant at Rayong, Thailand

NON HETEROGENEOUS ROUTES TO CATALYTIC ROUTES TO FINE CHEMICALS (2002-10)

- **1,1',1''-tris -4-Hydroxyphenyl ethane (THPE)**
- **Acrylamido methylpropane sulfonic acid (AMPS)**
- **Vinyl benzoate and vinyl- 2-ethylhexanoate**

All processes developed and successfully scaled up and are in operation; capacities have been expanded progressively

CATALYTIC TRANSFORMATION : WISH LIST

- **Glycidyl methacrylate**
- **Diglycidylether of BP-A**
- **2,6-Naphthalene dicarboxylic acid**
- **Tetralone from p-xylene and γ-butyrolactone**
- **2/4-vinylpyridines**
- **M-Toluic acid / Isophthalic acid**
- **Glyoxal and Glycolic acid from EG**
- **Octene-1 from butadiene**

BIOMASS TO CHEMICALS

- **Cellulose**
- **Lignin**
- **Bio-oil**

BIOMASS TO CHEMICALS : CELLULOSE /XYLOSE

- **Cellulose to sorbitol/glycerol**
- **Xylose to levulinic acid**
- **Cellulose to hexitols**
- **Cellulose to ethylene glycol**
- **Cellulose to glucose**

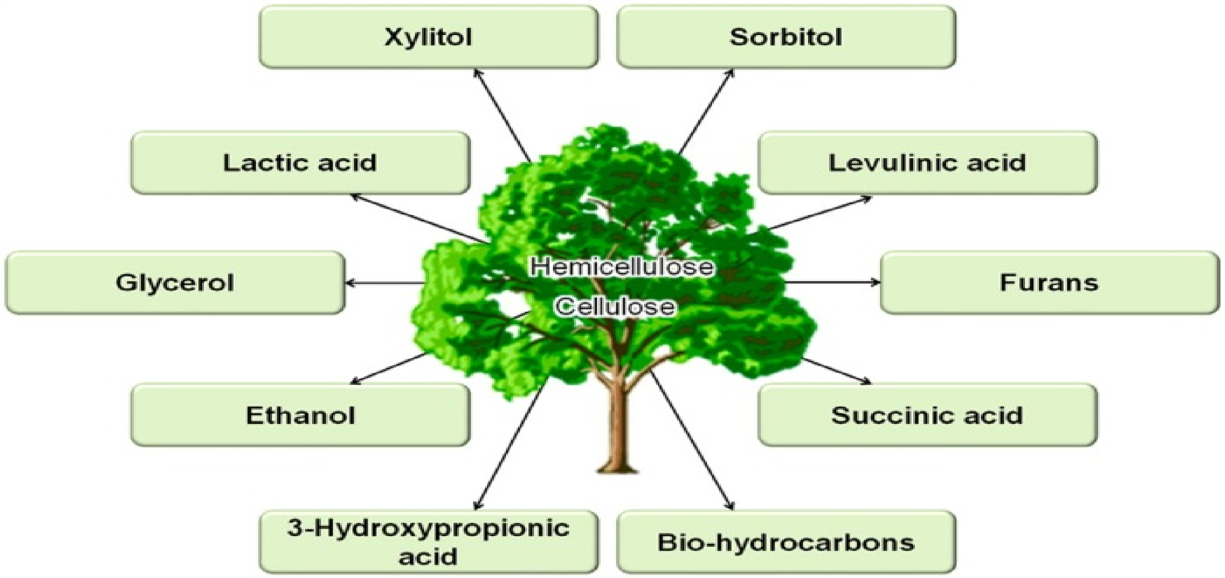
BIOMASS TO CHEMICALS : LIGNIN

- **Lignosulfonate to vanillin (Solvay)**
- **Aqueous phase reforming to Guaicol**
- **Catalytic fast pyrolysis to bio-oil followed by hydro-treatment/cracking**
- **Base catalyzed de-polymerization followed by hydro-deoxygenation to bio-oil**
- **Oxidative de-functionalization of lignin**
- **Hydro-treatment of lignin to aromatics / phenols**
- **Liquid phase reforming / hydro-deoxygenation to aromatics**

BIOMASS TO CHEMICALS : GLUCOSE/SUGARS

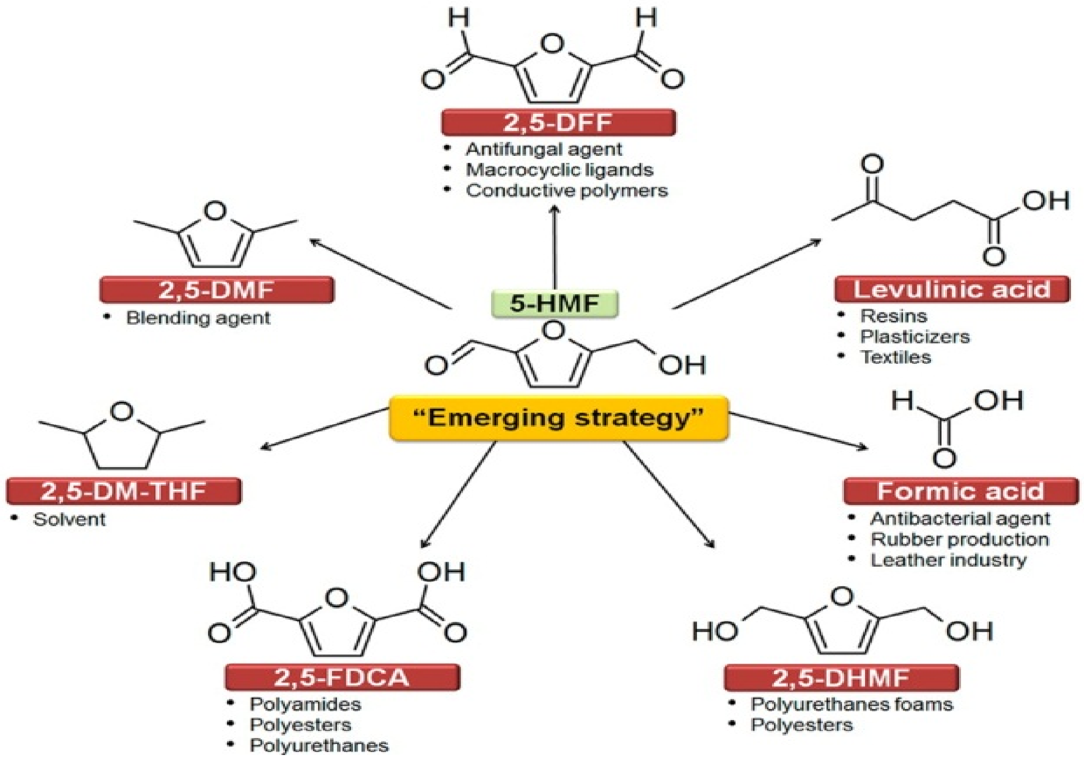
- **Glucose to levulinic acid / ethyl levulinate**
- **Glucose to lactic acid**
- **Hydrogenation of d-Mannose to d-Mannitol**
- **Glucose to formic acid**
- **Gluclose to glucaric acid/hydrogenation to adipic acid**
- **Liquid phase dehydration of sorbitol to isosorbide**

(a)



Xylitol
Sorbitol
Lactic acid
Levulinic acid
Glycerol
Hemicellulose
Cellulose
Furans
Ethanol
Succinic acid
3-Hydroxypropionic acid
Bio-hydrocarbons

(b)



2,5-DFF
• Antifungal agent
• Macrocyclic ligands
• Conductive polymers
2,5-DMF
• Blending agent
5-HMF
Levulinic acid
• Resins
• Plasticizers
• Textiles
"Emerging strategy"
2,5-DM-THF
• Solvent
Formic acid
• Antibacterial agent
• Rubber production
• Leather industry
2,5-FDCA
• Polyamides
• Polyesters
• Polyurethanes
2,5-DHMF
• Polyurethanes foams
• Polyesters

BIO-REFINERY : A PLATFORM FOR SUSTAINABLE CHEMISTRY

Refinery based on fossil resources

Source → Transformation → Products → Downstream process

Oilfields → Refining & Cracking → Chemical Transformation → Formulation

Oil or Gas → Naphtha → Chemicals & polymers → End Product

Bio-refinery based on renewable resources

Source → Transformation → Products → Upstream process

Agricultural fields → Starch & Sugar production → Biotech Trans-formation → Chemical Trans-formation → Formulation

Glucose → Chemicals & polymers → End Product

- Green: Leading role of biotechnology
- Orange: Shared role between biotechnology and chemistry
- Red: Leading role of chemistry

Catalyst Challenges

- ***Creating chemicals from fossil fuel based feed-stocks is about selectively introducing functionality***

- ***Creating chemicals from bio based feeds-tocks is about selectively removing functionality (examples, dehydration, decarboxylation, decarbonylation, deoxygenation)***

FORCES OF CHANGE IN THE CHEMICAL INDUSTRY

- **High cost of new product introductions; difficulties in identifying new growth platforms**
- **Increasing regulatory (environment, health and safety) frameworks**
- **Faster technology diffusion / commoditization of products leading to quicker price / margin erosion**
- **Supply chain is taxed by breadth of markets, products and geography**
- **Increased global segmentation in terms of technology providers , low cost producers and large domestic markets**

CHEMICAL INDUSTRY : 2020 TECHNOLOGY VISION

- **Reduce energy intensity of processes by 30%**
- **Reduce emissions including CO_2 and effluents by 30%; move towards zero discharge goals**
- **Increase use of renewable resources as building block for chemicals ; combine judiciously chemical and biological processes to achieve sustainability goals**
- **Small/ modular chemical plant designs for enhanced safety and reduced quantities of inventory storage**
- **Increase the conversion of stoichiometric processes to catalytic processes; batch to continuous processes**
- **Understand better the impact of chemicals and materials on environment, safety and human health**

EFFICIENCY GOALS FOR PERFORMANCE CHEMICAL INDUSTRY : 2020

- **Reduce feed stocks losses to waste / byproducts by 90%**
- **Reduce energy intensity by 30%**
- **Reduce emissions including CO_2 and effluents by 30%**
- **Increase use of CI building blocks and use of renewables by 13%**
- **Reduce time to market through use of new R&D tools by 30%**
- **Increase the number of new products and applications annually by 15%**
- **Reduction production costs by 25%**

New Process Chemistry Roadmap : Vision 2020
(The American Chemical Society)

THE INDIAN FINE CHEMICAL INDUSTRY

- Fragmented and low capacity
- Low capital/technology intensity
- Relative unfamiliarity with catalytic processes involving reactor types other than batch stirred tank reactors
- Limited in house technology strength
- Inadequate attention towards quality and consistency
- Lack of deep pockets to sustain business cycles
- Poor product marketing skills, especially in global markets
- Easy targets for acquisitions by global companies

INDIAN CHEMICAL INDUSTRY: CONCERNS

- **Branded as low cost supplier/outsourcing/contract manufacturing entity for fine and specialty chemicals**
- **Innovation deficit; few new product offerings based on proprietary knowledge / IP**
- **Low R&D intensity with the exception of drugs and pharmaceutical sector**
- **Limited by conventional engineering practices**
- **Poor application development skills, especially for specialties**
- **Talent deficit; chemistry and chemical engineering education no longer considered fashionable; serious issues of talent retention/flight**

FINE CHEMICALS : STRATEGY FOR CATALYSIS R&D

- **Identify multiple product capabilities from the same set of facilities/ catalysts**
- **Examine chemicals which are single vendor item in the global market, have high export potentials or of strategic nature**
- **Look for chemicals that can be manufactured in existing facilities with incremental capex**
- **Look for opportunities where improved purities of currently produced chemicals can open up new market opportunities**
- **Focus on formulated products (speciality chemicals)**
- **Identify chemicals where India has unique raw material advantages**
- **Define family of chemicals whose selling price is Rs 300 a kg or above and where RMC (inclusive of catalysts) do not exceed 50%**

CATALYSIS SCIENCE, ENGINEERING AND TECHNOLOGY : CHALLENGES

- **Shift from turn over numbers and frequencies to selectivity enhancement**
- **Structured solids with larger pore sizes**
- **Nature of catalyst deactivation; Quick way to determine catalyst life times; product adsorption on surfaces**
- **Use of earth abundant metals in catalysis**
- **Reduced CO_2 production per kg product and enhanced energy efficiency**
- **Reducing footprint of chemical plant**
  - **Vapor phase reactions at high space velocities**
  - **Batch to continuous processes**
  - **Micro-reactors**
- **Reduction in capital cost; decouple capital cost from production volume, especially for fine chemicals**

Bringing new catalytic processes into commercial production is becoming increasingly difficult


1950 - 2010
ncl
Celebrating Sixty
Years of Science
CSIR - INDIA

THANK YOU