

Agenda for 'greening' of the chemical industry

Delivering the keynote address, on 'Cleaner and Greener is Smarter; Conversion of Liabilities into Assets' at IGCW 2013 Congress, in Mumbai, on 6th December, 2013, Prof. Sharma, highlighted a range of strategic options for the chemical industry to rationalize its R&D, technology and manufacturing operations.

He traced the genesis of cleaner process concepts to the replacement of the Leblanc process (1773) for manufacture of soda ash, by the Solvay process; and the Lead Chamber process for sulphuric acid by the Contact Process. He explained the rationale behind the replacement of processes based on acetylene with those based on ethylene; of nitrobenzene reduction by iron/acid by direct vapour-phase reduction with hydrogen; and reduction of nitro-aromatics (by Na_2S_x) by catalytic liquid-phase reduction with hydrogen.

He put forth a working eight-point agenda for the chemical industry to rationalize its operations and enhance both economic and environmental performance.

Focus on waste valorization

Emphasizing the commercial significance of valorization of wastes Prof. Sharma described some important commercial approaches to waste valorization.

Sulphur recovery

Sulphur recovery from sour natural gas and hydrogen sulphide (H_2S) in the hydrodesulphurization of heavier petroleum fractions is an example where all recovered sulphur has found outlet. Sulphur dioxide can also be recovered from flue gases by selective absorption and subsequently converted to sulphuric acid or to sulphur.

Friedel-Crafts alkylations (F-C)

There are numerable processes in the manufacture of fine organic chemicals where the F-C process is employed. Waste aluminium chloride from this process has been valorised to polyaluminium chloride, a coagulant used in treatment of water.

Substitution bromination of aromatic substances

Phenolic compounds, benzaldehyde etc., on bromination with bromine yields HBr as a by-product. This is valorised by dual strategies. The first one uses BrCl made from 1+1 mole of bromine and chlorine and the second one involves two-phase bromination with the aqueous phase containing H_2O_2 so that HBr is converted *in situ* to bromine which, due to high distribution coefficient, goes into the organic phase.

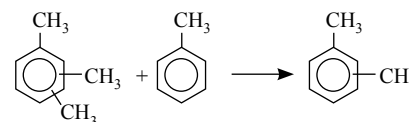
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Value of aromatic substances

Valorisation of toluene and C-9 aromatics

In the manufacture of xylenes by catalytic reforming C-9 aromatics are formed. These are converted by zeolite-catalysed transalkylation to high-value xylenes:



Polychlorinated compounds to high value solvents

Unwanted polychlorinated compounds like tri- and polychlorinated ethane have been valorised through chlorinolysis at high temperature to CCl_4 and C_2Cl_4 . An excellent example in this regard is the manufacture of epichlorohydrin where allyl chloride is reacted with Cl_2 in an aqueous medium when hypochlorous acid reacts with allyl chloride. However, the equilibrium quantity of Cl_2 gives the unwanted trichloropropane. A novel approach was adopted to separately make pure aqueous HOCl by absorbing Cl_2 in hot aq. caustic soda solutions and simultaneously stripping HOCl, in a centrifuge.





Design safer and efficient processes

Prof. Sharma enumerated a variety of commercially successful examples where substitution of conventional processes by newer process alternatives had led to economic and environmentally better processes.

gal absorber reactor, followed by absorption in water.

Valorisation of by-product streams from manufacture of phenol

In the manufacture of phenol, a mixture of alpha-methyl styrene (AMS) and cumene is often formed. This AMS-cumene mixture is converted to the desired unsaturated dimer using cationic ion exchange resin, and in the process 93-95% of the desired dimer is formed. The above crude mixture could also be used to make high purity *p*-cumylphenol as a chain terminator in making polycarbonates and phenolic resins. In this a cationic ion exchange resin was used as a catalyst.

Valorization of by-products from the manufacture of ethyl benzene

In this process *m*-/*p*-diethylbenzene mixture, obtained as a by-product in the manufacture of ethyl benzene, has been used to make value-added divinylbenzenes, essential for making cationic and anionic ion exchange resins.

Recycle of polymeric substances

Polyethylene terephthalate resins can be recycled via alkaline hydrolysis to give polymerisation grade terephthalic acid and monoethylene glycol. Improved strategies are needed for polystyrene, ABS, polyamides and polycarbonate.

Ethylene oxide

Ethylene oxide by chlorohydrin process replaced by direct oxidation of ethylene with oxygen.

Propylene oxide

Propylene oxide via chlorohydrin process replaced by epoxidation with H_2O_2 or hydroperoxides (*tert*-butyl hydroperoxide; ethylbenzene hydroperoxide; cumene hydroperoxide).

Phenol

Phenol via sulphonation and alkali fusion or via chlorination and alkaline hydrolysis replaced by cumene-type processes; catechol and hydroquinone via hydroxylation of phenol with H_2O_2 .

Benzaldehyde

Benzaldehyde from toluene via side chain chlorination and hydrolysis replaced by direct oxidation of toluene in liquid phase.

Anthraquinone

Anthraquinone from phthalic anhydride (PAN) and benzene with stoichiometric amount of $AlCl_3$ replaced by direct oxidation of anthracene or reaction of naphthaquinone and butadiene (New possibilities of zeolites-based reaction between PAN and benzene are being explored).

m-Phenoxybenzaldehyde

m-Phenoxybenzaldehyde, required for very efficient and safe insecticides in the pyrethroids series, can be made via a safer and cleaner process based on *m*-phenoxytoluene, which in turn is obtained by a pollution-free process involving vapour phase dehydration of *m*-cresol and phenol. This replaced the process based on bromination of benzaldehyde followed by Ullmann reaction with *m*-cresol in the presence of copper catalyst.

Phenylethyl alcohol

Phenylethyl alcohol via reaction of benzene with ethylene oxide, in the presence of stoichiometric amount of $AlCl_3$, replaced by hydrogenation of styrene oxide (obtained by newer epoxidation processes).

Diphenyl oxide

Diphenyl oxide and related compounds via Ullmann reaction, using Cu based catalyst, replaced by vapour phase dehydration of phenols.

p-Aminophenol

p-Aminophenol from *p*-nitrochlorobenzene replaced by direct reduction and rearrangement of nitrobenzene or via acetylation of phenol followed by oximation and Beckmann rearrangement (to get paracetamol directly).

Replace hazardous chemicals with safer chemicals

Synthetic strategies also focused on replacing toxic or hazardous chemicals with more benign ones:

- Process based on phosgene / methyl isocyanate (MIC) replacement: Isoproton from *p*-Cumidine and urea + dimethylamine
- Processes based on HCN replacement: Acrylonitrile based on acetylene and HCN replaced by ammoxidation of propylene; Adiponitrile from butadiene and HCN replaced by dimerization of acrylonitrile or

reaction of ammonia with adipic acid

- Replacement of the conventional method of making chloromethyl ether, which contains carcinogenic dichloro derivative, by a route based on HCl and methylal.
- Replacement of reduction based on the use of sodium metal in liquid ammonia by electrochemical processes.
- Selective production of *para* substituted aromatic compounds. For e.g., in the chlorination and nitration of toluene unwanted *ortho* isomer is inevitably obtained in larger quantity. A zeolite based chlorination has now opened up the possibility of significant increase in the content of the *para* isomer.

Invest in electrochemical processes

Prof. Sharma also emphasized why electrochemical route need more investments and the importance of electrochemical reactions in several fine chemical manufacture.

Examples he discussed included:

- Expensive reductions, e.g. Birch reduction, can be carried out at lower cost and under safe conditions.
- Oxidation of *para*-methylanisole to *para*-anisaldehyde.
- Conversion of nitrobenzene to *para*-aminophenol.
- Reduction of pyridine to piperidine.
- Electrohydrodimerization of acrylonitrile to adiponitrile: Use of quaternary ammonium salts.

Shift from high-pressure to low-pressure operations

Prof. Sharma highlighted some of the important commodity products where low-pressure reactions have economically replaced high-pressure processes.

- Very high pressure (>1000 atm) for LDPE replaced by low pressure (<40 atm) processes.

- High pressure (~200 atm) Oxo process replaced by low pressure (40-50 atm) process.

- Very high pressure (~1000 atm) carbonylation process for acetic acid replaced by low pressure (~40 atm) process.

- High pressure (~100 atm) hydrogenations replaced by low pressure (<10 atm) processes.

Enhance process safety using superior metals

A strategy to improve process safety has been to use designer metals for specific uses in plant operations. Some of these are titanium (Ti) and Ti-lined vessels; Tantalum for aggressive chemicals; Teflon and PVDF lined valves/ fittings and vessels; and structural high performance adhesives for joints.

Develop 'More from less' strategies

Emphasizing his favourite theme of getting 'more from less', he described some commercial successes.

Acetone to diacetone alcohol

In this process a homogeneous catalyst – sodium ethoxide – was used and Na removal was done with phosphoric acid, to crystallise Na₂HPO₄. This often caused separation problems and clogging, resulting in a lot of downtime, a loss in yield and substantial reduction in capacity utilization. In a modified process, Na was removed using a cationic ion exchange resin and a neat process was optimized. Debottlenecking of the separation train, along with the above critical change, allowed the plant capacity to go up by a factor of 4-5.

Recovery of sparingly soluble organic substances from aqueous waste streams

In some fine chemicals processes the desired relatively non-volatile substance, in the presence of sparingly

soluble solvent in water, is recovered via steam distillation. The aqueous layer can be treated in the above steam-stripping mode. However, in such cases, from overall efficiency point of view, it would be useful to consider the Short Path Distillation method to recover the solvent and the desired substance.

Recovery of ores from aqueous effluents

The valorisation of lean copper and nickel ores via hydrometallurgical processes is an outstanding example where reactive solvent extraction is used to recover Cu/Ni sulphates. This was a sequel to winning real lean ores containing uranium. The lean aqueous effluents from electroplating industry can be valorised to recover heavy metals via fluidized bed electrodes, solvent extraction, precipitation, etc.

Nanofiltration in recovery and removal of chemicals

In recent years Nanofiltration (NF) for removal of pesticides, APIs, recovery of amino acids from aqueous solutions, and for solvent exchange in pharmaceutical manufacturing have found wider use.

Develop bio-waste valorisation technology for value-addition

Touching on the importance of valorisation of wastes from agriculture, fruit/vegetable residues etc., Prof. Sharma maintained that this approach will probably provide several options to high value chemicals provided technology barriers are overcome.

He observed that bagasse from cane sugar industry is a potential candidate for valorisation to give high alpha-cellulose material. The potential of steam explosion to give 95% alpha-cellulose, and separately hemi-cellulose and lignin needs to be exploited as hemi-cellulose can be acid hydrolysed to fermentable sugars and lignin has many uses as lignosulphonates.