STUDY ON INDUSTRIAL APPLICATIONS OF GREEN CHEMISTRY PRINCIPLES

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Abstract:
The concept to eliminate or reduce the generation and/or use of toxic and hazardous reagents by the design of chemical products and processes is known as green chemistry. In 1998, 12 Principles of green chemistry were published to provide guidelines for the further development of industries. Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Since the last decade, this concept is given special focus like conferences with the specialized theme of green chemistry, journals publishing special issues, books, etc. So many industrial processes are explored to demonstrate the application of the appropriate green chemistry principle. Each principle is connected with an appropriate industrial case to make a better understanding application. Different industrial examples are searched and compiled which represent a real-time industrial application of each principle of green chemistry. The reader will have a ready example of each principle to understand its industrial applications.

Keywords: green chemistry principles, industrial applications, green chemistry applications

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1. HISTORY OF GREEN CHEMISTRY

As a part of the movement to deal with pollution, ideas were developed under the Pollution Prevention Act of 1990, U.S. govt adopted 12 ideas as principles in national policy to reduce pollution not by only waste disposal and treatment but by modifications in design. A regulatory agency U.S. Environmental Protection Agency (EPA) had developed an approach to implement all principles of U.S. national policy eventually known as "green chemistry". EPA Office of Pollution Prevention and Toxics launched a research grant program for encouraging researchers to replace hazardous and toxic compounds with green options to reduce their impact on the environment and human health. Worldwide meetings and conferences were carried out in the late 90s to spread awareness towards green chemistry. At last, in 1998, total 12 principles were published to guide people for further development. In the last decade many governments gave special attention to implementing all in their countries.

PRINCIPLES OF GREEN CHEMISTRY

1. "Prevention: Preventing waste is better than treating or cleaning up waste after it is created".
2. "Atom economy: Synthetic methods should try to maximize the incorporation of all materials used in the process into the final product".
3. "Less hazardous chemical syntheses: Synthetic methods should avoid using or generating substances toxic to humans and/or the environment".
4. "Designing safer chemicals: Chemical products should be designed to achieve their desired function while being as non-toxic as possible".
5. "Safer solvents and auxiliaries: Auxiliary substances should be avoided wherever possible, and as non-hazardous as possible when they must be used".
6. "Design for energy efficiency: Energy requirements should be minimized, and processes should be conducted at ambient temperature and pressure whenever possible".
7. "Use of renewable feed stocks: Whenever it is practical to do so, renewable feed stocks or raw materials are preferable to non-renewable ones".
8. "Reduce derivatives: Unnecessary generation of derivatives—such as the use of protecting groups—should be minimized or avoided if possible; such steps require additional reagents and may generate additional waste".
9. "Catalysis: Catalytic reagents that can be used in small quantities to repeat a reaction are superior to stoichiometric reagents (ones that are consumed in a reaction)".
10. "Design for degradation: Chemical products should be designed so that they do not pollute the environment; when their function is complete, they should break down into non-harmful products".
11. "Real-time analysis for pollution prevention: Analytical methodologies need to be further developed to permit real-time, in-process monitoring and control *before* hazardous substances form".
12. "Inherently safer chemistry for accident prevention: Whenever possible, the substances in a process, and the forms of those substances, should be chosen to minimize risks such as explosions, fires, and accidental releases".

2. INDUSTRIAL APPLICATIONS OF PRINCIPLE #1: WASTE PREVENTION

2.1 Introduction

Any industry along with products also produces waste. At the industrial level, this waste can't be ignored. Manufacturers always try to reduce waste products or byproducts by choice of reactions, process design, and recycling. This prevention can be monitored quantitatively by calculating the yield of the reaction, which compares obtained product quantity to the expected quantity. Yield becomes an important criterion in the selection of reaction.

2.2 Comparison of Phenol Synthesis Methods

A comparison of some important production methods of Phenol to understand the selectivity of methods on the basis of waste generation is done here. The first process is the Hock process, which forms Cumene Hydroperoxide by oxidation of Cumene, which sequentially produces a mixture containing phenol and acetone when treated with Sulphuric Acid. 0.62 kg acetone is produced per kg phenol produced, which when not used turns into waste. This Second Process is DSM and Solutia Method, in which Toluene is oxidized to Phenol. Benzoic Acid & Benzaldehyde are obtained as Co-products. Markets of these coproducts were small, so a lot of waste was produced in form of these byproducts. A recent method is developed by ExxonMobil which makes a coproduct, Cyclohexanone but it can be reused in this process unlike coproducts of other methods. This process involves three steps; the First step is hydro alkylation in which Cyclohexylbenzene (CHB) is obtained by a reaction of Benzene and Hydrogen. Cyclohexane is a coproduct generated is dehydrogenated back to Benzene. The yield of this step comes out to be

97%. The second step involves the oxidation of CHB to Phenyl cyclohexyl hydroperoxide. The third step involves cleaving of hydroperoxide with H_2SO_4 to give Phenol and Cyclohexanone. Coproduct obtained in this reaction i.e. Cyclohexanone is an important intermediate in the synthesis of Nylon 6,6 and Nylon 6. This method emphasizes on reuse or recycling of coproducts obtained to reduce waste generation [1].

2.3 E-Factor

In 1992, the Concept of the E-Factor was coined by Roger Sheldon. It is now majorly used in calculating the amount of waste generated per kilogram of product produced. It is a means to get the environmental acceptability of a process.

To understand this concept of E-Factor, an example of the synthesis of Ethylene Oxide is taken. Earlier, Chlorohydrin intermediate was used for preparation. The E-Factor for the whole process was found to be 5, which means 5 kg of waste was produced for every kg of Ethylene Oxide produced. Due to this, waste disposal was a major problem. Also, this waste does not take water contaminated by chlorine byproducts into consideration. Then the process was modified, which used molecular Oxygen, removing the need for Chlorine. The E-Factor of this process came out to be 0.3. When E-Factors of both processes were compared, the later process was found to generate 16 times less waste than the first one, & also eliminated the waste water formation [2].

In this manner, E-Factor became useful in designing new and safe synthesis methods and thus reducing waste generation.

2.4 Industrial Steps for Waste Prevention

Some steps can be implemented in industries to reduce manufacturing waste. Use of excess raw materials in the process can be reduced. Waste can be reduced by redesigning product packaging i.e. by implementing reusable or recycling packaging materials like air packs or corn-based packing peanuts. Waste developed can be recovered by using techniques like Electrolysis, Filtration, Reverse Osmosis, Centrifugation, etc. A closed loop manufacturing system can be adopted in which all byproducts are reused in the same reaction to get more product. Generally, the Industrial Waste stream majorly contains wastewater. So, the use of water in operations can be reduced. In these ways, Industrial Waste can be prevented [3].

3. INDUSTRIAL APPLICATIONS OF PRINCIPLE #2: ATOM ECONOMY

3.1 Introduction

The Second Principle of Green Chemistry comes down to preventing waste on a molecular level. Atom Economy shows the efficiency of a reaction. It shows how much percentage of reactants converted into products i.e. greater the atom economy.

$$\%\ \text{Atom Economy} = \frac{\text{Molar Mass of Product}}{\text{Molar Mass of All Reactant}} \times 100\%$$

3.2 Atom Economy of Ibuprofen Synthesis Methods

Ibuprofen is one of the most used drugs in pharmaceutical industries. So, Ibuprofen synthesis should give maximum atom economy to reduce cost and waste. Here comparison of two Synthesis methods of Ibuprofen; Boots' Process & Hoechst's Process is done.

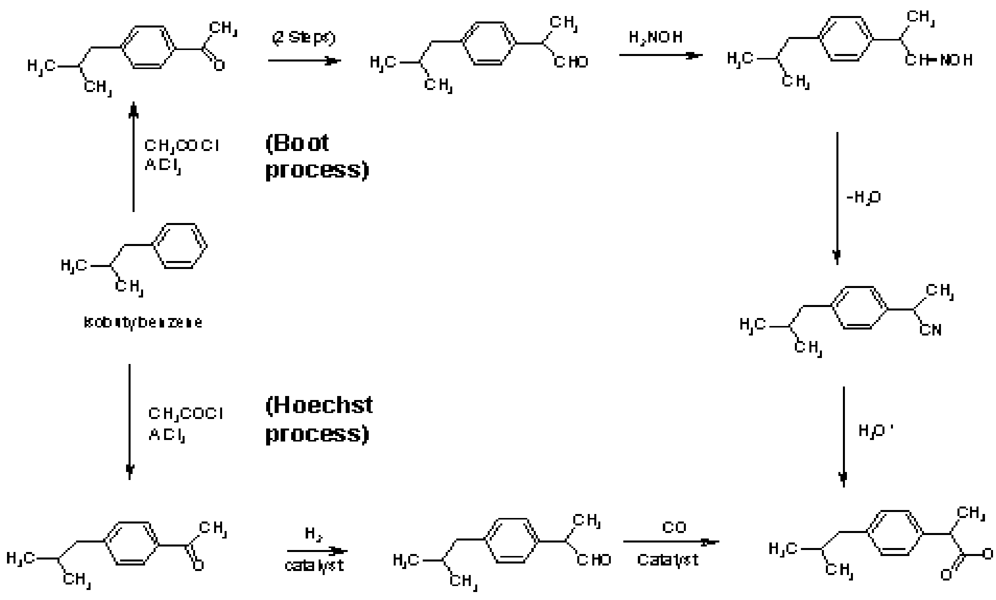

Figure 2.1 Synthesis of Ibuprofen [5]

Table 3.1 Analysis of Product Stream & Effluent Stream in Boots' Synthesis [4]

Reagent		Used in Ibuprofen		Unused in Ibuprofen	
Formula	Mol. Wt.	Formula	Mol. Wt.	Formula	Mol. Wt.
$C_{10}H_{14}$	134	$C_{10}H_{13}$	133	H	1
$C_4H_5O_3$	102	C_2H_3	27	$C_2H_3O_3$	75
$C_4H_7ClO_2$	122.5	CH	13	$C_3H_6ClO_2$	109.5
C_2H_5ONa	68		0	C_2H_5ONa	68
H_3O	19		0	H_3O	19
NH_3O	33		0	NH_3O	33
H_4O_2	36	HO_2	33	H_3	3
Total		Ibuprofen		Waste products	
$C_{20}H_{42}NO_{10}ClNa$	514.5	$C_{13}H_{18}O_2$	206	$C_7H_{24}NO_8ClNa$	308.5

Table 3.2 Analysis of Product Stream & Effluent Stream of Hoechst process [4]

Reagents		Used in Ibuprofen		Unused in Ibuprofen	
Formula	Mol. Wt.	Formula	Mol. Wt.	Formula	Mol. Wt.
$C_{10}H_{14}$	134	$C_{10}H_{13}$	133	H	1
$C_4H_6O_3$	102	C_2H_3O	43	C_2H_3O	59
H_2	2	H_2	2		0
CO	28	CO	0		0
Total		Ibuprofen		Waste Products	
$C_{15}H_{22}O_4$	266	$C_{13}H_{18}O_2$	206	$C_2H_4O_2$	60

By using this data, the atom economy of both processes is calculated. For Boots' Process, % A.E. comes out to be 40%. It means that more than half the materials used in process are wasted. Now at the other side, Hoechst Process involves three step reaction and its % A.E. comes out to be 77%. Boots process & Hoechst Process starts with same initial reactant, but use of different catalyst results in reduction in steps & increment in atom economy [4].

4. INDUSTRIAL APPLICATIONS OF PRINCIPLE #3: REDUCE DERIVATIVES

4.1 Introduction

The process of derivation which is not necessary (consumption of some groups and modification of chemical or some physical processes) must be reduced or kept away if possible, as they require some more compounds which can be hazardous to the Eco-system. They even increase the amount of waste generated. This is one of the main principles in Green Chemistry to avoid the usage of some processes which may be physical or chemical in nature which includes blocking and unblocking groups and using the processes which are biological in nature. One of the best ways of doing this is to use an Enzyme that can often react with one site of the molecule and leaves another site of the molecule.As a result, the groups which are not protecting are not required [26].

4.2 Developments

The Industrial production of semi-synthetic antibiotics like penicillin and amoxicillin is one of the best examples of the use of enzymes to avoid the protecting groups. For the first industrial manufacturing Penicillin G(R=H) is first protected as its silyl ester[R=S(Me)3] then reactswith phosphorous pentachloride at -40○ C to form the chlorimidate 1 subsequent hydrolysis gives the desired 6-APA from which semi-synthetic penicillin are manufactured. This process is substituted by a modern enzymatic process using pen-acylase. This synthesis occurs in water at just above room temperature. This way of production has many benefits from a green chemistry point of view as it does not use a silyl protecting group. Thus, with reaction with the catalyzed immobilized enzyme penicillin amide, several chemical steps were replaced by enzymatic reaction and the requirement of very low temperature was also not there. The organic solvents and some unsuitable conditions were also removed by this [23].

4.3 Present scenarios

More than ten thousand tons of APA-6 are produced per annum and much of it with the greener enzymatic process.Hence this is a significant illustration of green chemistry making a difference [27].

5. INDUSTRIAL APPLICATIONS OF PRINCIPLE #4: USE OF RENEWABLE FEEDSTOCKS

5.1Introduction

A raw material or a feedstock should be made renewable rather than disposing of whenever possible economically and technically. Reusing and recycling of the compounds should be practiced more often. Due to the increasing usage of sources that are not renewable and increasing population, the demand for the renewable resources is increasing more and a great emphasis is laid upon this sector of green chemistry. The concern for the renewable feedstocks is growing because of various changes in atmosphere like acid rain, Global warming, increasing water levels in oceans, and increasing temperature on the Earth. This because more usage of non-renewable resources and they cause pollution in nature. The Renewable sources are Environment friendly [6].

5.2 Present and Future scenarios

From the last 10 years, many changes have been made in the advancements of fuels, chemicals and raw materials from renewable feedstocks. These for example include biodiesel from plant oils and algae, bioethanol and butanol from sugars and lignocelluloses, plastics, etc. Many advances are aiming for reducing dependence on chemical Industry in oil. Various products like surfactants, polyols, ethane, polymers, etc. Are reused or in different cases made from reusable sources.

The U.S. Government by 2030 plans a well-established economical bio-based products industry to create new opportunities in rural America and protect and enhance the environment, strengthen the energy requirements and a next step for the well and safe caretaking for Environment [14].

5.3 Advancements

Tetrahydrofuran (THF) is useful ether solvent, but it is produced from petrochemicals and thus it's not reusable. The substitute for THF is 2-Methyl THF. Its structures and properties are almost same to those of THF but it is obtained from renewable feedstocks. The transition from mineral oil-based lubes to biodegradable lubricants from renewable resources is on-going.The consumption of plastics is reducing in commercial sector to promote the use of renewable sources. There are many advances and developments in biomass conversion technologies and bio-refineries for the advancements for Economy [6].

5.4 CO_2 as feedstock in Sugarcane industries

The chemical industries consume various non-renewable feedstocks and inefficient use of mass and energy that will result into emissions of harmful products into atmosphere and harms the environment. For this case rather than discarding carbon dioxide into the atmosphere, one can use the same as chemical feedstock for manufacturing of fuels and chemicals. The use of CO_2 in this case reduces the dependency on petroleum products. This environmental – oriented step results in the consumption of CO_2in sugarcane fermentation and bioethanol itself. However, utilization of CO_2 does not always reduce the greenhouse effects. Several experiments have been made on the optimization of bio refinery. The Sugarcane industry shows one of the activities like manufacturing sugar and ethanol. Despite them being the products, the use of CO_2 was neglected initially. 1 ton of processed sugarcane produces 50.6L of ethanol and 39.7 kg of CO_2 from fermentation. To increase the sustainability, chemical utilization of CO_2 was done. The main aim of Eco-pole is to increase the sustainability of sugarcane industry by using CO_2 as feedstocks. The Eco-pole shows good performance regarding the raw material and the products. Eco-pole is dependent on technical, environmental grounds and based on Mass and energy balance [21].

The availability of high amount of CO_2 was assumed in this. The carbonates, methanol and various other derivatives were assumed to be the feedstocks. The main problem was the transportation of such feedstocks in the industry. They were aggregated as products of Eco-pole. The larger the bioethanol plant, higher will be the CO_2 supply and larger chemical plants in the eco-plants would be possible. Moreover the CO_2 has to be compressed up to 5 bar for simulation process [21].

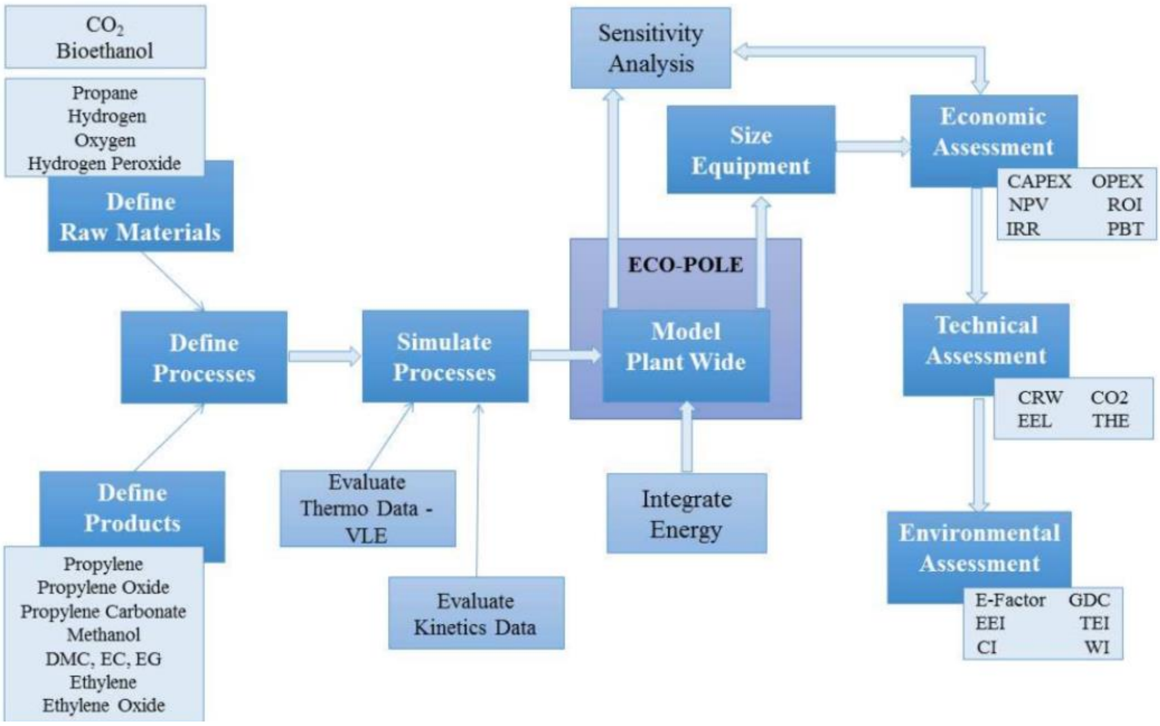

Fig 5.1 Design development steps [22]

6. INDUSTRIAL APPLICATIONS OF PRINCIPLE #5: SAFER SOLVENTS AND AUXILIARIES

6.1 Introduction

This principle promotes use of Safer Solvents, which includes any substance which do not directly take part in reaction, but are necessary for occurring of process. Solvents dissolves all reagents and maintain temperature of the reactions. In Industries, Safer & Non-toxic solvents should be chosen so that they do not harm environment along with performing their functions [6].

6.2 2-Methyltetrahydrofuran (2-MeTHF)

2-MeTHF is considered as perfect green alternative to Dichloromethane and Tetrahydrofuran which are used in many reactions as solvents, but are harmful for environment. While 2-MeTHF is derived from renewable sources like Corncobs and bagasse. It is both economy and environment friendly [8].

6.2.1 Features and Benefits

It forms lower peroxide than THF. It forms azeotrope rich with water, so it is easily dryable unlike THF or DCM. It has very less miscibility in water which results is reduction in waste stream due to easy separation. It has higher boiling point (353K) than THF, which promotes reaction at high temperature and reduces reaction time. It has low heat of vaporization because of which it saves energy during distillation and recovery [7].

6.2.2 Alternative to THF for organometallic reactions

1. Grignard Reaction
2. Reformatsky reaction
3. Hydride reduction

6.2.3 Alternative to DCM for biphasic reaction

1. Alkylation
2. Amidation
3. Nucleophilic Substitution Reaction

6.3 Cyclopentyl Methyl Ether (CPME)

CPME is an environment friendly green alternative to THF, 1,4 Dioxane, tert-Butyl methyl ether (MTBE) and many other solvents of ether. CPME not only minimize the waste stream of solvent, but also prevents chances of laboratory accidents due to its unique composition which resists peroxide formation [8].

6.3.1 Features & Benefits

It is hydrophobic ether solvent, so used in many organometallic reactions and also provides better yield and selectivity than THF. It has high boiling point, low heat of vaporization and low miscibility in water [7].

6.3.2 Applications of CPME

1. Asymmetric Michael Alkylation
2. Alkylation of Chiral Amide
3. Glycosidation
4. Asymmetric hydrogenation of $NaBH_4$

5. Amide synthesis by the reaction of acid chloride with amine
6. Bromination of alcohol with PBr3
7. Reaction of Carbon anion with aldehyde
8. Alkylation of amine
9. Sulfonylchloride synthesis by the reaction of sulfonic acid with PCl5.
10. Reduction of ethyl benzoate using Lithium Aluminium Hydride
11. Reaction of Ketone using $NaBH_4$
12. Bromination of alcohol with PBr3

7. INDUSTRIAL APPLICATIONS OF PRINCIPLE #6: DESIGN FOR ENERGY EFFICIENCY

7.1 Introduction

Energy is a main issue in 21st Century. The economy of a country depends upon its usage of energy and manufacturing products. Energy is required in many reactions for the manufacturing of products and in manufacturing process. The requirement of energy must be calculated so to decrease the emissions affecting the environment. Hence an ambient condition must be maintained and not at elevated temperatures and pressures.1973 oil crisis had initiated the campaign of renewable energy and design for energy efficient processes. As a result many advances are in progress for further development of Energy efficient sources. The successful approaches have been made to this with the use of microwave irradiation, sonication reaction or biological processes [6].

7.2 Improving energy efficiency in the chemical industry

Waste generated from the industries may often have energy content and it may be possible to convert this waste into useful contents. Old vehicle tires cannot be used and neither be sent to landfill and hence many are shredded and used as fuel in cement industry. Waste solvents from manufacture of paints, varnishes, inks, etc. are made to use as liquid fuel in various industries. Similarly, the advancements of molecular sieves means that processes like purification of ethanol can be carried out at ambient temperature instead of distillation column. To remove solvent a rotary evaporator (Rotovap) can be used which involves use of heat source, vacuum pump, rotating motor and chiller. The heat, vacuum and rotation vaporize the solvent and chiller cools the vapors back to liquid. For the case of bioplastics, the use of renewable sources in production positively affects energy consumption and CO2 emissions and other pollutants. Coca-Cola, a world-wide-scale company for the time being, manufactures bottles made of 30% polyethylene (PE) blends, while American company Nature Works uses bottles made from lactic acid polymers (PLA) made from lactic acid, obtained by fermentation of dextrose obtained from starch, most commonly corn [14].

7.3 Advancements in Efficiency of energy

With the increasing use of energy price and protection of environment, various industries look forward for the energy implementation to improve in economic and environmental way. The industries mainly depend on the fossil fuels and gases for the manufacturing work but these traditional methods must be replaced by the new methods for better sustainability and welfare. To tackle this difficulty, a novel energy efficiency estimation method combining just-in-time (JIT) learning and subspace model identification (SMI) with noise elimination called e-JITSMI method. This method can choose the sampling data, estimate noise effect and compute the model. Thus data selection, noise elimination and modeling the data are main steps of method which are dependent on various formulas [18].

\In 2009, Energy Efficiency Design Index (EEDI) of ship was developed for reduction of greenhouse gases from the ship and uses the solar energy for the ship which can reduce fuel consumption and greenhouse gas emissions of ship. The CO2 charged from the ships was 2.4% of total greenhouse gas. The CO2 can be expressed as in grams of CO2 per ship’s capacity mile and the equation is:-

$$FEEDI= (EME+EAE+EEF-RE)/fi*V_{capacity}*V_{ref}*f_w$$

Here, EME is the CO2 emission from the main engine, EAE is the emission from auxiliary Engines, ; EEF is the CO2 emission from shaft generators and motors; ERE is the CO2 emission reduction by energy saving technologies for main powers; fi is the correction factor for ship specific design elements; $V_{capacity}$ is the deadweight Tonnage (DWT) rating for bulk ships and tankers; V_{ref} is the ship speed at maximum design load condition; f_w is the coefficient indicating the decrease in ship speed due to weather and environmental conditions. This value should be 10% more efficient by 2015, 30% by 2025 [19].

Considering many factors and energy conversion efficiencies of photovoltaic devices, availability parameters for the new ships, and the effects of different latitudes, declination angles, hour angles and bevel angles can be analyzed. With solar energy employing as auxiliary power of ship at 39.1. Of north latitude, its energy conservation and emissions reduction value were concluded [19].

8. INDUSTRIAL APPLICATIONS OF PRINCIPLE #7: LESS HAZARDOUS CHEMICAL SYNTHESIS

8.1 Introduction

The production of substance that damage Environment and Human beings should be avoided. Some man-made methods should be adopted so to reduce this or it has very low toxicity to the humans and surroundings. Many chemical reactions are toxic in nature. Even though there might not be any harmful substances in product, the main aim of green chemistry is to decrease the level of contamination. The main aim is to decrease the synthesis of such harmful chemicals or to use such methods of production wherein there is no such contamination. Using biological enzymes is one such example. This idea of green chemistry sounds very intuitive, but various factors like economy, technology, policy, environment, etc. will affect how the process will work and up to what extent [6].

But there are various cases in which chemists use all the harmful components to manufacture the compounds that are favorable thermodynamically and kinetically. The use of such chemicals will be continuous until the new technology substitutes the old and the benefits are promised [23].

8.2 Advancements

Chlorine is used in many industries for preparation of polymers, cells, etc. Mercury cell process was very much used in production of chlorine. But the resultant gas from this method was very harmful and contaminated the Environment and affected the human health. But this process is replaced by the use of membrane cell for chloro alkali process. The increased use of this cellulose-based technology has resulted in reduction of dependence for Mercury cells. It has no emissions of mercury like the previous methods [6].

There are many recent advances for this principle like Development in maleic acid synthesis from bio-based chemicals, Simple and green technique for sequestration and concentration of silver nanoparticles by polysaccharides immobilized on glass beads in aqueous media [28].

8.3 Use of 5MP in industries

N-methyl-2-pyrrolidone (NMP) is a widely used chemical solvent in various industries. However, many experiments have concluded that it is a toxic reagent. Hence there must be substitutes for the compound. This review shows the processes involved in the production of 5-methyl-2-pyrrolidones.N-methyl-2-pyrrolidone (NMP) is used as solvent, agro and pharmaceuticals intermediates, resins, waxes and others. Its cost is very high and because of its toxicity, need for its substitutes are required. The production of N-substituted-5-methyl-2-pyrrolidones was proposed as substitutes for it. There are no restrictions or hazard are included in it. They are already employed as solvents, waxes, etc. They are prepared by 2 stages, liquid-phase process which involves the reaction of fossil-derived lactones with aqueous alkyl amines, followed by hydrogenation over carbon-supported metal catalysts. Typical yields around 70% for dimethyl derivative, using either Pd or Rh catalysts [20].

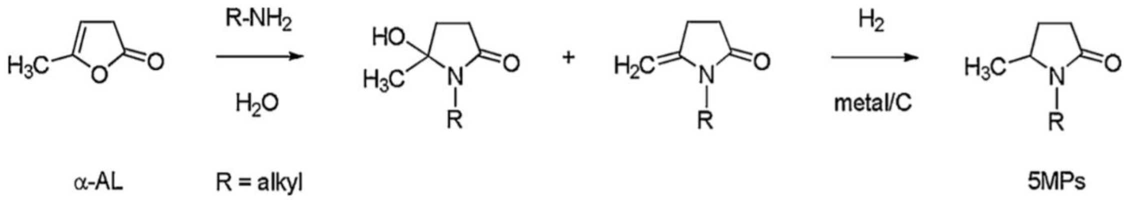

Fig 8.1 Process for the industrial manufacture of 5 MPs [20].

9. INDUSTRIAL APPLICATIONS OF PRINCIPLE #8: DESIGNING SAFER CHEMICALS

9.1 Introduction

The designing of chemicals must be such that the toxicity of the chemicals should be decreased. This is one of the main aim of green chemistry to reduce or control the toxic agents in the Eco-system. Reducing toxicity is the main aim of chemists and scientists. The challenge comes in identifying what makes a compound Hazardous. When it comes to compounds that have never been designed before, toxicity becomes a even larger issue. This field of toxicity will allow us to test the molecule’s toxicity and a constant effort has to be made in to decrease the toxicity of material [6].

Thus, minimizing toxicity and maintaining the function the chemical is a very challenging work. This requires a great knowledge of toxicity and environmental science. The field of toxicity is progressing rapidly, incorporating an applying the developments made in molecular biology to show the mechanisms of toxicity [23].

9.2 Advancements

Pesticides are very harmful to the Eco-system and human beings. The toxicity of such pesticides should be reduced. Pyrethoid Pesticides have the dual benefits of breaking down in sunlight in 2-3 days and have much lower acute toxicity to humans than phosphorus, or chlorine-based pesticides. Certain polymers like polyphenylsulfone are manufactured which are less flammable than the more well-known polymers. It is used widely in interior panels of aircraft and has been also introduced in trains as well. Detergents were made on basis of sodium salts of alkyl benzene sulfonic acids, and the alkyl group was branched. These compounds were not decomposed naturally and cause problems like sewage difficult to manage. Now these compounds are replaced with the sodium salts of linear alkyl benzene sulfonic acids, which are degraded easily [14].

Another example is the use of toxic organic tin-based organic compounds (Sn), previously coated on the outside to prevent the capture of seaweed and plankton. This compound is degradable and non-toxic [26].

9.3 Design of safer chemical in LI batteries

Lithium ion batteries and their packs are used in various vehicles and storage applications. When such batteries thermally impacted under abusive conditions might explode and cause damage to environment also. Hence to prevent this transfer of either of electrons and ions should be switched off before the temperature gets to the highest. Hence a novel PTC material, poly (3-Octylpyrrole): poly (styrenesulfonate) is used as conductive framework for cathode of Lithium ion batteries. The main reason was that large PSS anions-doped P3OPy has a high conductivity, which makes it easy mixed with carbon black to form highly conductive composites. The doped PSS anions may be again doped from the host skeleton of P3POy due to accelerated motion of polymer chains at high temperature leads to a transition of P3OPy/C from a p-doped conductive state [17].

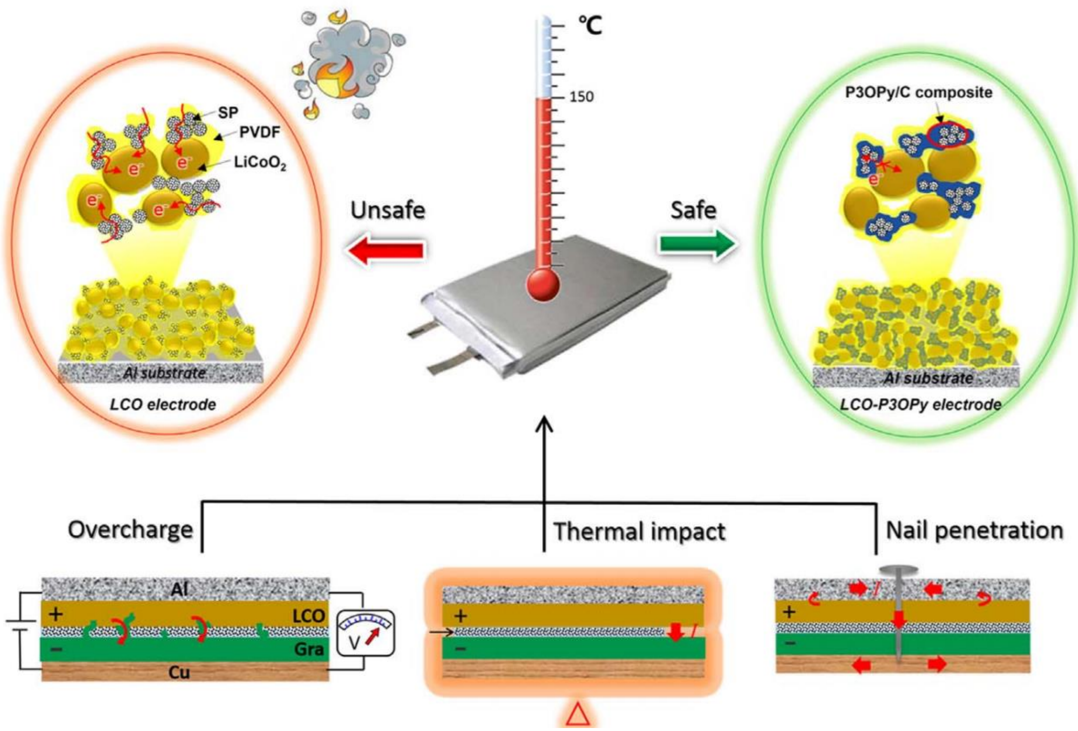

Fig 9.1working mechanism of lithium ion batteries with and without a PTC cathode under abusive conditions [17]

10. INDUSTRIAL APPLICATIONS OF PRINCIPLE #9: CATALYSIS

10.1 Introduction

A catalyst is a substance that is used in the chemical reaction to accelerate the speed of reaction. It lowers the activation energy of the reaction and increases the speed. It remains unchanged at the completion of reaction. Many Chemical reactions are slow in nature, may even emit harmful and toxic compounds in Environment. The Use of a Catalyst will reduce these conditions and hence it enhances the reaction. Nowadays, with the improving technology, use of Catalysts in industries is increasing every day to reduce the time and increase the production. In order to decrease the damage caused by chemicals and manufacture of compounds and working towards an approach of green chemistry, the use of catalyst is at prime to improve the conditions for the reaction. Apart from the industrial areas, catalysts play a very crucial role in reducing harmful pollutants from environment like NOx and control it's emissions into the Eco-system. Various methodologies are accepted to decrease the emissions of volatile matter and Ash into the environment and a step is taken for the minimization of waste emitted from the industries [24].

10.2 Developments

For the Acylation reaction of Phenols and Alcohols, Amberlyst-15 acts as a catalyst. It is an active catalyst for the acylation of phenols and alcohols by means of acetic anhydride as an acylating agent at the room temperature. This will result in a very positive way in terms of Environment. This method is very Environment friendly [25].

This reaction was performed by Prof. ManojPande and Prof. Shriniwas D. Samant from the Institute of Chemical Technological in Mumbai. They set up a very easy method for the acetylation of Alcohols and Phenols using an acylating agent in the presence of Amberlyst-15.The product (Acetates) were obtained in good content.Amberlyst-15 is inexpensive material and possess unique properties as environmental nontoxicity, reusability, non-corrosiveness and chemical and physical stability-allowing for its versatile synthetic applications. The reaction was carried out of p-bromophenol with acetic anhydride and the product was 4-bromophenylacetate obtained in 20 minutes and was reused for four cycles with same energy and efficiency [25].

Earlier Acylation reaction was done with acid chlorides in presence of pyridine. This method does not require the use of additives and economically is very useful [25].

10.3 Advancements of lignin-derived catalysts

This review explains the role of lignin-derived catalysts for Green Synthesis over the last two decades as a substitute for the fuel based Industries. The structure of lignin is discussed. Various pretreatment activities of lignin is done like physical activation, chemical activation, Thermal treatment, gas activation, Template activation, etc. These catalysts thus promote the transformations of organic compounds, oils into the desired valuable product and fuel. Presently, the dependency on Petroleum Industry chain is more. But this resource tends to exhaust in nearby future. Thus various alternatives are invented or produced to tackle this. Lignocellulosic biomass is the most accessible and the most logical carbon-based feedstocks for fuels. Lignin is the second most abundant raw material on the Planet, occupying 15-40% of dry lignocellulosic biomass. It is also the largest natural sources of aromatics. One of the newly developing applications in lignin is carbon-based material such as activated carbon, catalyst and catalyst support. Before this, it was obtained from wood, coal or agricultural waste. Coal is non-renewable and cost is higher as compared to lignin. It has high surface area and pore volume and is widely used as catalysts support. Lignocellulosic biomass has major three components like Cellulose, hemicelluloses and Lignin [22].

10.3.1 Thermal Treatment

Raw Lignin generally undergoes acid pretreatment to remove any inorganic ash. Thermal Treatment involves pyrolysis, gasification, hydrothermal carbonization, and flash carbonization. Water and other volatile compounds are removed by this process. During this treatment it was heated initially at low temperature under N2 atmosphere. These lignin derived chars should be given further modifications to give catalysts porosity and abundant active sites by physical and chemical activations [22].

10.3.2 Physical Activation and chemical activation

After the initial two processes, lignin requires physical treatment. It includes gas activation and Template activation and it introduces high porosity into the lignin derived char. In Gas activation raw lignin is heated at 350ºC-1000ºC for short time. After some processes, a lignin derived activated carbon is formed with proper time. In Template activation raw lignin is initially impregnated with hard or soft template; then after proper treatment it gives template Activated Carbon. This introduces well-ordered pore-size and distribution in AC's [22].

It is the most crucial tool to transfer raw lignin into the desired form and is also preferred more over the physical activation processes as the process is generally carried out in one step and it produces high yield of target materials with well distributed porosity. This process generally involves base activation, acid activation, salt activation and ion exchange.

In Base Activation Alkali Metal Hydroxides line NaOH and KOH introduces well developed porosity into carbon framework during modification of carbon based materials. For Acid activation acidic groups as sulfonic groups and phosphoric groups are grafted on the surface of lignin-derived materials. These lignin-derived solid acids activation show high catalytic activities in various reactions like esterification, dehydration, etc. Salt activation is a powerful method to prepare support or catalyst. It is a useful method to produce lignin-derived catalyst supports or catalysts. Two main types of metal salts including carbonates and chlorides are used activators. Ion exchange is an important tool to immobilize various metal or non-metal species on the α-position.

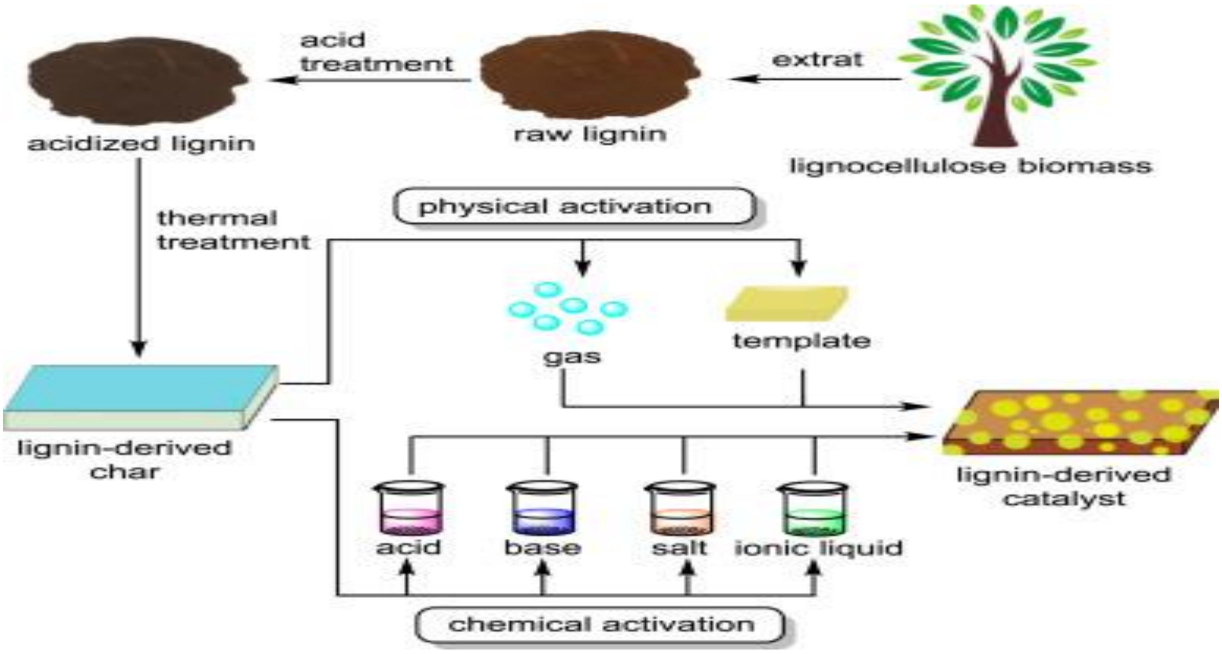

Fig 10.1 Lignin transformation into catalyst [22].

11. INDUSTRIAL APPLICATIONS OF PRINCIPLE#10: DESIGN FOR DEGRADATION

11.1 Introduction

According to this principle, Design of any chemical product should be done in such a way that they get degraded into innocuous products and don't persist in the environment. Some chemicals are toxic in nature and when they are not degraded, they become harmful to nature.

11.2 Biodegradability of Surfactants

Soaps or Detergents should be designed in such a manner that they break down easily in environment. Earlier Branched Alkyl benzene Sulfonate was used as detergent. But now it is not used widely, because of its non-biodegradability. As it contain branches, no good sites are present where microbes can perform β-oxidation. So, if these type of detergents or soaps are ended up in river or lake water directly, they will not get degraded and will spread their toxicity in water sources. On the other hand, Sodium dodecylbenzene Sulfonate is a major detergent because it contains polar group (sulfonate) and nonpolar alkyl group. LAS is mainly used as detergent in laundries. It quickly degrades under presence of Oxygen [9].

Similarly, Surfactants like Nonylphenol Ethoxylates (NPEs) which was used in detergents, cleaners, etc. is now generally prohibited in use, because it is not biodegradable in nature and is highly toxic. Environmental Protection Agency (EPA) has provided alternatives of NPE to industries. Some of them are C9-11 Alcohols, Ethoxylated (6EO), C12-15 Alcohols, ethoxylated (9EO), Ecosurf EH-9, D-Glucopyranose, Benzenesulfonic acids (C10-13-alkyl derivatives), Sodium lauryl Sulphates, Sorbitan monostearate, etc. Industrial use of this biodegradable surfactants can surely resist degradation of planet [10].

Other than Surfactants, Biodegradable plastics are also in development which can cause a big industrial revolution.

12. INDUSTRIAL APPLICATIONS OF PRINCIPLE #11: REAL TIME ANALYSIS FOR POLLUTION PREVENTION

12.1 Introduction

According to this principle, Analytical methods should be developed for real time & in process mentoring of reactions, so that formation of any hazardous substances can be controlled. If such techniques are implemented in industries, adjustment can be done to minimize hazards. This methods act same as the mirror of a vehicle do. As mirrors provide real time view of surroundings which helps in prevention of any accidents. Similarly, Real time reaction monitoring prevent production of pollutants or any toxic substances [6].

Process Analytical Chemistry is used to monitor ongoing transformation and to act upon it immediately to prevent unwanted outcomes. This technique includes both live monitoring and environmental shortcomings related to traditional analysis. In situ method for monitoring has many advantages. When action is taken immediately, it prevents accidents, save energy & formation of byproducts that would create pollution [12].

Analytical methods are mainly used with two important steps of process industry: One is pretreatment of sample i.e. Extraction or Separation; & other one is signal acquisition step. Since first step deals with high volumes of solvent, it becomes a center for generation of waste and thus of analytical chemists concerns. So this step is monitored analytically to stop production of hazardous substance on time [12].

Figure 1.1 Ultrameter II (Myron L.) [13]

Several Analytical techniques like IR, UV, Raman, NMR, etc. are used for monitoring of reactions. These techniques provide real time information of concentration, temperature, pressure, reaction rate, etc.

12.2 Use of Ultrameter II for real time analysis

This instrument was developed by Mike Alberson who was an expert of storm water pollution prevention. While analyzing water samples, he used to send samples to lab for their quality check. But because of significant change in critical properties of water by the time they reach the lab, reports were very inaccurate. Also, by the time reports had been returned to him, it was too late to modify processes and to develop cost and nature efficient process because of manufacturer's deadlines. Also, during the lab analysis, further storm events contributed to ongoing pollution.

Alberson thought of an onsite testing equipment. Then he used Ultrameter II 6P for testing of pH and TDS quickly of water sample with accuracy level of laboratory. He was then able to develop onsite remediation of pollution with a lesser time [11].

In another case, he used Ultrameter II to prevent environmental contamination because of high pH run off resulting from soil treatment using lime. By performing testing onsite using Ultrameter II, he determined pH of runoff to be 12.5. Then, he used retention pond containing carbon dioxide (CO_2) percolation control techniques. He used CO_2 injection to form Carboxylic acid which lowered the pH from 12.5 to 6.8. This technique was continuously used for testing until the acceptable limit of pH reached. In this way, real time analysis of off-streams reduced environmental pollution [11].

So, here it is discussed that how on-time and onsite analytical methods for testing are proven very useful to industries and how these methods causes reduction in production of hazardous contaminants.

13. INDUSTRIAL APPLICATIONS OF PRINCIPLE#12: INHERENTLY SAFER CHEMISTRY FOR ACCIDENT PREVENTION

13.1 Introduction

The last principle of Green Chemistry focuses on prevention of any industrial accident. Inherent chemistry should be applied in industries. Here the word Inherent means to eliminate the hazard by using process route or materials which are non-hazardous. Routine or accidental emissions during any process can harm human health. Accidents can be prevented by proper handling and periodical maintenance of hazardous Substances. Other way is to alter the reagents used.

A way to inherent safer process is classified into four steps: Minimize, Substitute, Moderate & Simplify. Hazardous substances should be used, if necessary only. They can be replaced with any safer alternative. Every parameter that are responsible for hazard should be assessed wisely. A design should be done in a manner to reduce complexity and errors [15].

13.2 Production of Glyphosate

Glycophosate (sold as Roundup) is an herbicide widely used by farmers all over the world. In its manufacture process, Sodium salt of 2,2'-

iminodiethanoic acid is used as intermediate, which is prepared from Ammonia, Methanal & Hydrogen Cyanide. Although HCN is very useful reagent, it is highly toxic. Recently, a new method is developed to produce Sodium salt intermediate. Ammonia & Epoxymethane give reaction and form 2,2'-iminodiethanol, which is then converted to Sodium salt of 2,2'-iminodiethanoic acid. As HCN is not used in this process, it is relatively less hazardous and its consequences are also not so dangerous [14].

13.3 Examples dealing with inherent safety tradeoffs:

1. Chlorofluorocarbon (CFC) are proved as safer refrigerants in cases of explosion/fire and acute harmful & toxic hazards in comparison with alternative refrigerants like Sulphur dioxide, Ammonia, Propane, etc. CFC can be used for temporary applications as its longer use causes depletion in Ozone layer which ultimately causes Environmental Damage.
2. Supercritical processing methods are gaining lot of interest nowadays because of their efficiency and also non-hazardous nature towards environment. Supercritical materials like Water and Carbon dioxide are used as reaction and extraction solvents in many process industries.

13.4 General causes of an industrial accident

According to an analysis, almost all (89%) accidents take place due to failure in major unit operations and piping system. Most critical in all of them is failure in piping system (27%) succeeded by storage tank (18%), then reactor (16%) and finally heat exchanger (11%). Digits in braces indicates hazard causing chances of that particular equipment. Major reasons for an accident are extreme process conditions (21%), mechanical and equipment failure because of poor construction materials (18%), lack of analysis of incompatibility and reactivity of certain chemicals (16%), poor designing (15%), improper protection of equipment (11%), etc. These are the basic but strong contributors of an industrial accident which are generally overlooked by process designers [16].

By using methods like Fault Tree Analysis (FTA) or Event Tree Analysis (ETA), a probability chart can be prepared which can be useful in identifying failure probability of any equipment, and thus analysis and improvement can be done on that particular.

CONCLUSION

The green chemistry principles were introduced to reduce pollution has been implemented in so many industrial processes. Still research work is going on to replace toxic and hazardous chemicals and processes. Many research groups are working on it and new work is going on. Some processes/ green substances are mentioned here to understand the applications. All principles would be implemented to replace the hazardous processes as well as chemicals substances with safe and green processes and chemicals. Real applications covered in this paper may help new researchers to understand implementation and real applications of green chemistry principles.

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