MODULE-4

GREEN CHEMISTRY AND ALTERNATIVE ENERGY RESOURCES

GREEN CHEMISTRY:

The concept of green chemistry was coined by Paul Anestas of America. He enunciated 12 principles of Green Chemistry in 1994 towards ideal synthetic methods to save natural resources. Green chemistry is the use of chemistry for pollution prevention by environmentally-conscious design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. It is a approach in chemical science that efficiently uses renewable raw materials, eliminating waste and avoiding the use of toxic, hazardous reagents and solvents in manufacture and application of chemical waste.

Major Environmental Pollutants

1. Carbon Monoxide (CO):

Sources: It is released by burning of charcoal, forest fires and from automobiles**.**

Ill Effects: Carbon monoxide interferes with the blood's ability to carry oxygen to brain, heart and other tissues and in particular dangerous for people having heart disease and for pregnant women which may cause stillbirths. Low level of CO poisoning may lead to headache. At high level may lead to difficulty in breathing or even death.

Control: It can be controlled by using catalytic converter, which converts toxic gases into nontoxic gas.

2. Oxides of Nitrogen:

Sources: Oxides of Nitrogen are produced when fossil fuel is burned especially in power plants, automobile exhaust, forest fires and during lightening. These oxides of nitrogen compounds also contribute to acid rain formation.

Ill Effects: These NOx effects plants and human health. High concentration of NO_2 effect leaves of plants and retard photosynthetic activity. It causes internal bleeding, lung cancer, pneumonia and respiratory problems in humans.

Control: It can be controlled by using catalytic converter, which converts toxic gases into nontoxic gas.

3. Oxides of Sulphur:

Sources: Oxides of Sulphur are produced because of volcanic eruptions, vehicular exhaust and burning of fossil fuels in power plants.

Ill Effects: These generate acid rain and damage plants, trees, buildings and also cause breathing problems, irritation to eyes, nose and throat.

Control: These can be controlled by using low Sulphur content fuel.

Basic Principles of Green Chemistry

The twelve principles address a range of ways to reduce the environmental and health impacts of chemical production, and also indicate research priorities for the development of green chemistry technologies.

1) **Prevention:** It is better to prevent waste than to treat or clean up waste after it has been created.
2) **Atom economy:** Design synthesis so that final product contains maximum proportion of starting materials. It is measure of amount of starting materials that end up useful products.
3) **Design Less hazardous chemical synthesis:** Synthetic methods should avoid using or generating substances toxic to humans and/or the environment.
4) **Designing safer chemicals:** The products should be designed to be fully effective with little or no toxicity.
5) **Use Safer solvents and reaction conditions**: Avoid using solvents, separation agents, or other auxiliary chemicals. wherever possible, use safer ones.
6) **Design for energy efficiency**: The chemical reactions should be conducted at ambient temperature and pressure whenever possible.
7) **Use of renewable feedstocks:** Whenever it is practical to do so, renewable feedstocks or raw materials are preferable to non-renewable ones.
8) **Reduce derivatives:** Avoid using blocking or protecting groups. Since such derivatives use additional reagents and generate waste.
9) **Use Catalyst**: These 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**: Include in a process, real time monitoring and control during synthesis to minimize or eliminate biproducts.

12) **Minimize the potential of accidents:** Design chemicals to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

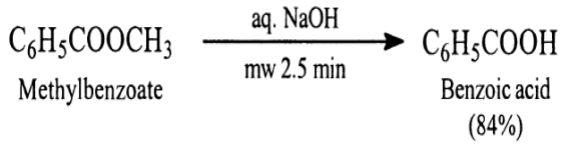
Various Green Chemical Approaches

Greener techniques such as ultra sound assisted method, microwave-assisted method, green solvent reactions, solvent free reactions, biomolecules are the common approaches which reduces the negative impact of the chemical products and processes on human health and environment.

Microwave Synthesis

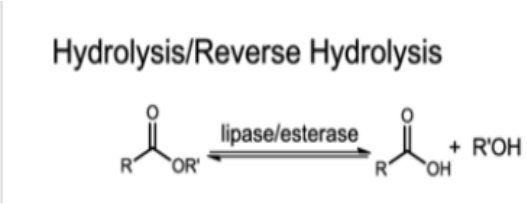
Microwave-assisted organic synthesis is considered to be a promising green chemical approach because it reduces reaction time from days or hours to minutes or even seconds. It helps reduce side reactions and increase yields and purity of compounds. It uses fewer solvents or is almost solvent-free. The microwave irradiation energy acts as internal heat source, which is able to heat the target compounds without heating the entire furnace or oil bath, consequently, saves time and energy. It produces more uniform heating.

A microwave (MW) works by directly coupling with polar solvent in a reacting species. Microwaves radiation are a form of non-ionizing electromagnetic radiation with 300 MHz to 300 GHz frequency with the corresponding wavelength 1 cm to 1 m, which places MW in between Infrared radiations and radio waves. The microwave reactors for chemical synthesis operate at a frequency of 2.45 GHz. For a substance to be irradiated with MW should possess dipole moment i.e. its structure should possess partial positive and negative charges. Whenever there is polarity in the molecule there will be some rotations in the molecule when a microwave radiation is irradiated. Thus, the molecule tries to realign itself with the applied electric field. This rotation lead to friction between multiple molecule which hit other molecules and put them into motion, thus dispersion of energy happens and release of large amount of heat takes place. Solvents having higher dielectric constant are preferred like water, methanol, DMF, ethyl acetate, acetone, acetic acid, etc. E.g., Hydrolysis of methyl benzoate to benzoic acid



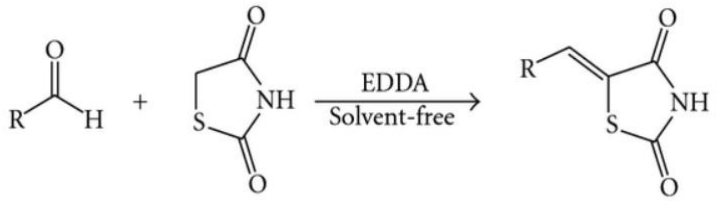
Bio Catalyzed Reactions

Bio catalyzed reactions are the chemical reactions which use biomolecules, especially enzymes or whole cells, as catalysts for the synthesis of new materials. Enzymes are very efficient biocatalysts, present in every living organism to carry out a wide range of chemical reactions, and also finds application as an important tool used in green chemistry. Many organic synthesis are difficult to synthesize, requiring multiple steps, large amounts of solvents and extensive purifications. Using enzymes as catalysts can improve the purity, enhance the speed of reaction highly efficient, mild operating conditions, protection and deprotection of the functional group not needed, mostly single step reaction with highly stereospecific products in nature resulting in a much greener overall manufacturing process.



Solvent Free Reactions

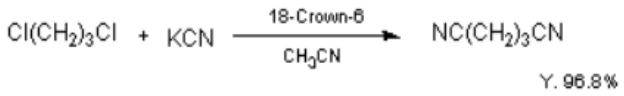
A dry media reaction or solid-state reaction or solventless reaction is a chemical reaction in the absence of a solvent. The reaction follows the fifth principle of green chemistry which avoid using toxic solvents in the chemical reaction. The reactions occur more efficiently and more selectivity compared to reactions carried out in solvents. Such reactions are simple to handle, reduce pollution, comparatively cheaper to operate and are especially important in industry. The solvent-less reactions minimize the production of by-products or waste by avoiding the use of conventional volatile organic solvents. The various solvent-less organic reactions can be carried out by using microwave, ultrasonic, ultraviolet, visible, infrared irradiation, grinding, and milling technology. By using these technologies, the solvent-less reactions become environmentally friendly and economic by minimizing the formation of waste products, reaction time, and energy, respectively.



Phase -Transfer Catalyst

Phase-transfer catalyst or **PTC** is a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs. These are special form of heterogeneous catalyst. Ionic reactants are often soluble in an aqueous phase but insoluble in an organic phase in the absence of the phase-transfer catalyst. The catalyst functions like a detergent for solubilizing the salts into the organic phase. It is used to transfer the desirable active form of an anion from the aqueous phase to organic phase where the reaction occurs. By using a PTC process, one can achieve faster reactions, obtain higher yields, make fewer byproducts, eliminate the need for expensive or dangerous solvents that will dissolve all the reactants in one phase and eliminate minimize waste problems. Phase-transfer catalysts are especially useful in green chemistry by allowing the use of water, the need for organic solvents is reduced. Typical phase-transfer catalysts are quaternary ammonium salts, crown ethers, and phosphonium compounds etc.

Cyanation

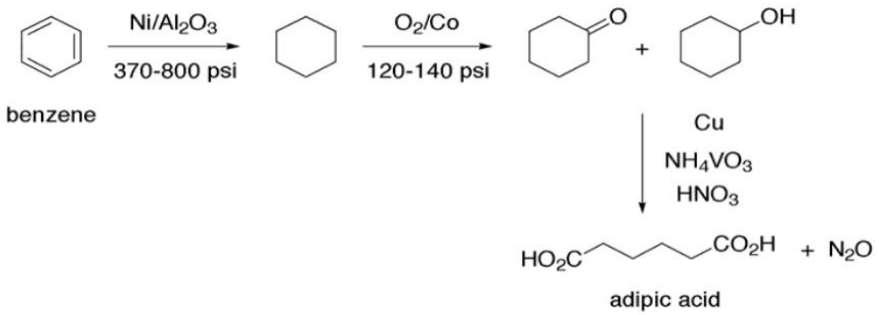


Adipic Acid

Adipic acid is a very important starting material in preparation of resins, nylons, cosmetics, adhesives, lubricants and also used in the pharmaceutical and pesticide industries. It can be prepared from both conventional and green synthesis method.

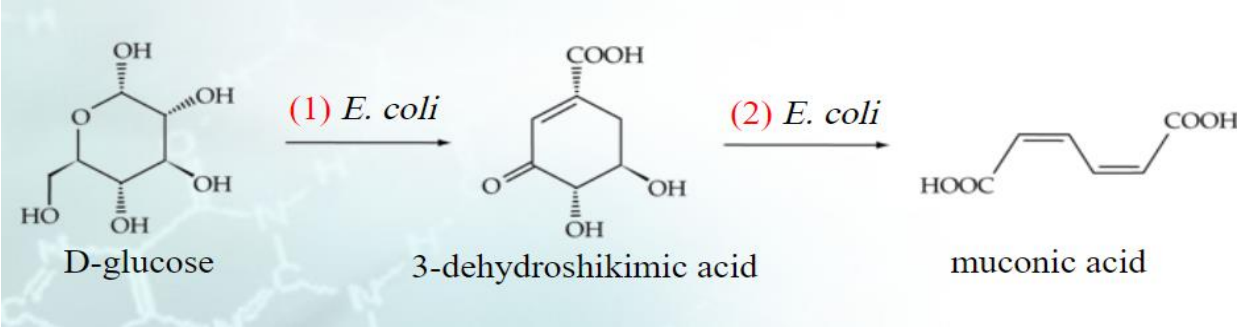
Conventional Method from Benzene

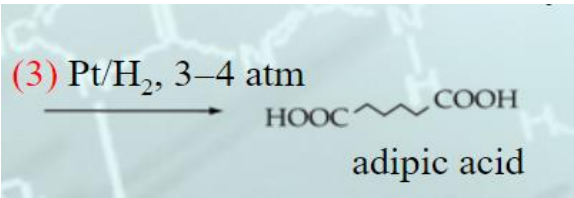
Benzene is hydrogenated over a Ni/Alumina catalyst to form cyclohexane, which is then oxidized in presence of Cobalt catalyst that produces both cyclohexanone and cyclohexanol. These molecules are catalytically oxidized in the presence of nitric acid to form adipic acid.



Green Synthesis from Glucose

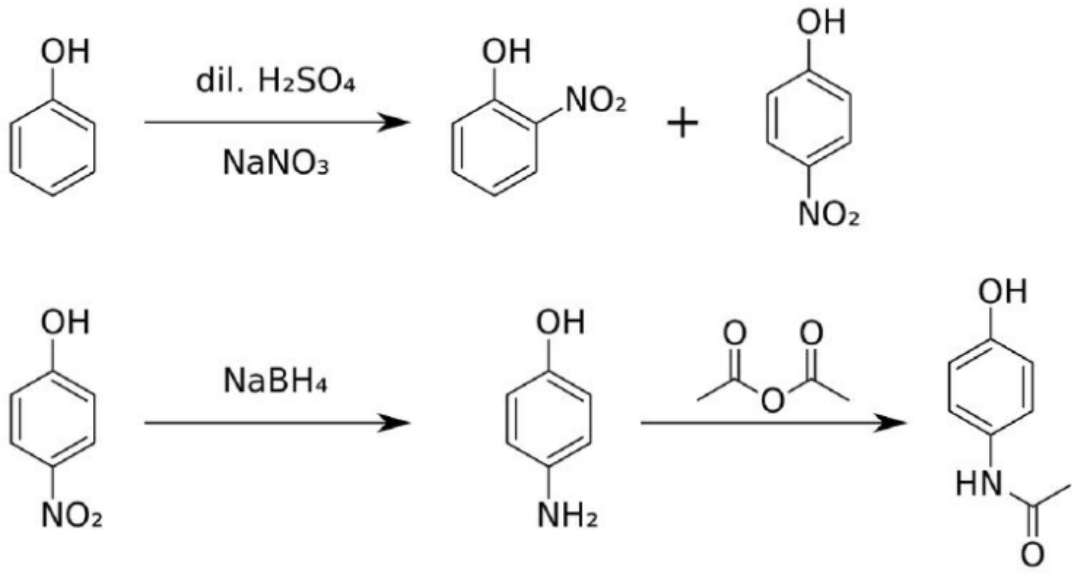
E. coli is the biocatalyst which catalyzes the two-step reaction to produce cis, cis-muconic acid. The corresponding muconic acid undergoes hydrogenation in presence of platinum catalyst to give adipic acid.





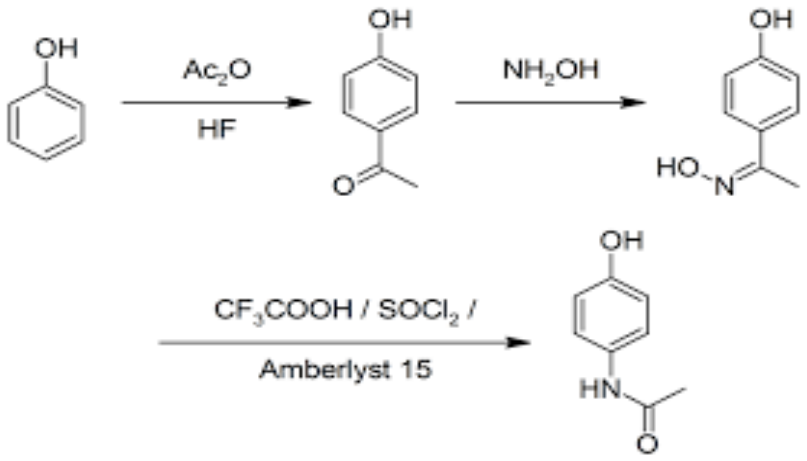
Paracetamol

Paracetamol is a pain reliever and a fever reducer.Conventionaly it can be prepared from phenol. It is prepared by nitrating phenol with sodium nitrate, separating the desired p-nitro phenol from the ortho-byproduct, and reducing the nitro group with sodium borohydride. The resultant p-aminophenol is then acetylated with acetic anhydride to get the desired product.



Green Synthesis of paracetamol

Paracetamol is synthesized by Hoechst-Celanese reaction which involves direct acylation of phenol with acetic anhydride catalyzed by HF. The ketone obtained is converted to a ketoxime with hydroxylamine, followed by the acid-catalyzed Beckmann rearrangement to give Paracetamol.



GREEN FUEL

Green fuels also called green hydrocarbons, biofuels, are fuel produced from biomass sources through a variety of biological and thermochemical processes. Green fuel, also known as biofuel, is a type of fuel distilled from plants and animal materials, believed by some to be more environmentally friendly than the widely-used fossil fuels.Eg., Hydrogen & Biodiesel.

Hydrogen Production by Photocatalytic Water Splitting

Splitting of water to get hydrogen by using a photocatalyst and by using solar energy is called photocatalytic water splitting.

This process can be more efficient if the photocatalyst is directly suspended in water so that the reaction takes place in one step. Figure given below represents a photocatalyst with a cocatalyst (catalyst nanoparticles).

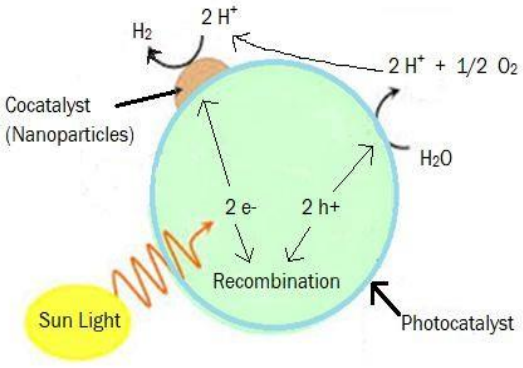


Figure: Representation of photocatalytic water splitting

The light energy excites an electron in the semiconducting photocatalytic material which leaves a hole (h^+) that will react with the neighboring water molecule.

$$H_20\ (l) + [h\gamma] + 2h^+ \rightarrow 2H+\ (aq) + ½\ O_2$$

The H^+ ions combine with electron to produce hydrogen at the surface of the cocatalyst.

$$2H^+ + 2e^- \rightarrow H_2\ (g)$$

The produced hydrogen can be used as the fuel in hydrogen fuel cell.

Hydrogen Production by Photo-Electro Catalytic Water Splitting

Photo electrocatalytic (PEC) water splitting is one of the most promising artificial photosynthesis approaches for solar fuel production. The reaction takes place at the electrode-electrolyte interface. Two electrodes are connected externally through the circuit. One electrode coated along with photocatalyst.

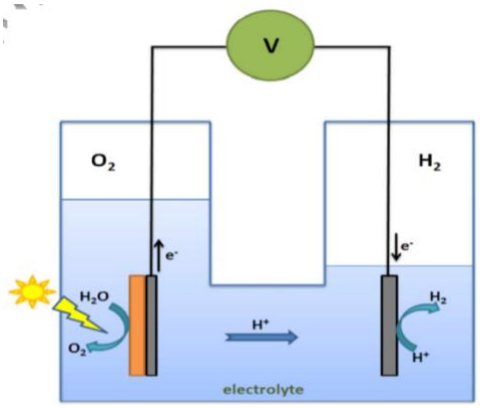


Figure: Schematic Representation of typical photoelectrochemical cell

The light energy excites an electron in the semiconducting material (electrode) which leaves a hole (h^+) that will react with the neighboring water molecule.

$$H_20\ (l) + [h\gamma] + 2h^+ \rightarrow 2H+\ (aq) + ½\ O_2\ (g)$$

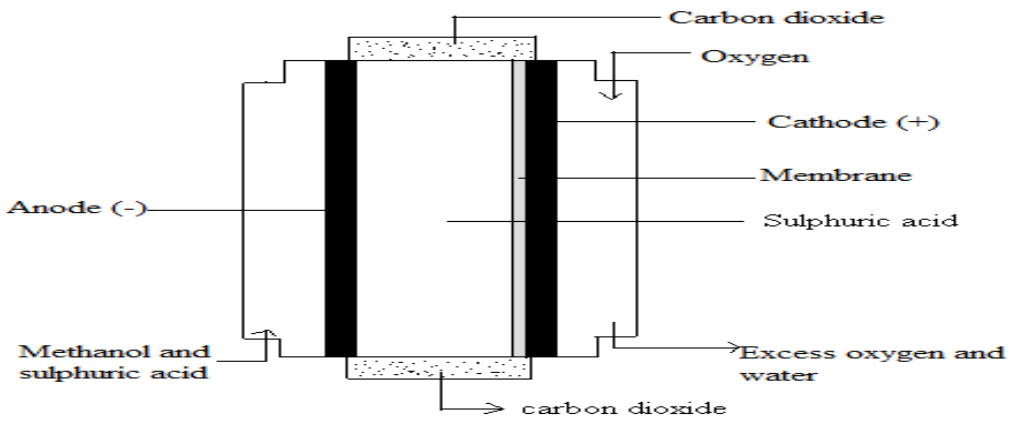
The H^+ ions combine to produce hydrogen.

$$2H^+ + 2\ e^- \rightarrow H_2\ (g)$$

The produced hydrogen can be used as the fuel in hydrogen fuel cell.

Methanol –Oxygen fuel cell

In Methanol-Oxygen fuel cell, methanol is used as fuel and oxygen as oxidant. Methanol containing some sulphuric acid (3.7M) is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber and sulphuric acid (which is the electrolyte) is placed in the central compartment. Both the electrodes are made of platinum. A membrane is placed adjacent to the cathode on the inner side to minimize the diffusion of methanol into the cathode thereby reducing the concentration of methanol near the cathode. In the absence of a membrane methanol diffuses through the electrolyte into the cathode and undergoes oxidation itself. The emf of the cell is 1.2V at 25°C.



The electrode reactions are,

At anode: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6\ e^-$

At cathode: $3/2\ O_2 + 6H^+ + 6\ e^- \longrightarrow 3\ H_2O$

Net cell reaction is: $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + H_2O$

Applications:

- ✓ Large scale power production.
- ✓ Military applications

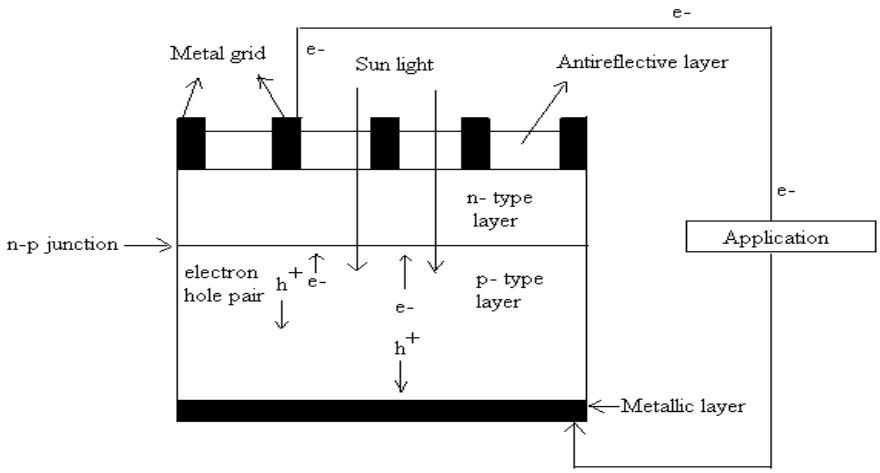
SOLAR ENERGY

Introduction: Energy is very essential to human being. The coal, petroleum, natural gases were basic forms of energy. But today all these forms are being slowly depleting from earth's surface. The world is looking for new form of energy such as solar energy, as gained lot of importance. Solar energy is radiant light and heat from sun that is harnessed using a range of technologies such as solar power to generate electricity. The radiations of sun are capable of producing heat,

causing chemical reactions or generating electricity. It is one of the most renewable and readily available sources of energy. *Photovoltaic cells or solar cells are semiconductor devices they convert sunlight falling on them into direct electricity*. As long as light falls on the solar cell it generates electrical power. When the light falling on the solar cell stops, generation of electricity stops.

Construction & Working of a Photovoltaic cell.

Photovoltaic cells are composed of thin matter of ultra-thin layer of phosphorous doped (n- type) silicon on the top and boron doped (p-type) silicon. Hence p-n junction is brought together to form a metallurgical junction. The diode has two electrical contacts one of which is in the form of a metallic grid and other is a layer of noble metal on the back of the solar cell. The metallic grid allows light to fall on the semiconductor between the grid lines. An antireflective layer (Silicon nitride) is coated in between metal grids to prevent reflection of sunlight. When light radiation falls on the p-n junction diode, electron hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n- type end and holes are drifted to and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between two ends through the external circuit. Thus photoelectric current is produced and available for use.



Applications

- ✓ It may be used in the field of portable power supplies.
- ✓ In the field of satellites.
- ✓ Military Purposes.
- ✓ Solar Water heating's.

QUESTION BANK

1. *Briefly explain any six basic principles of green chemistry.*
2. *Explain any two air pollutants.*
3. *Explain the following i) Phase transfer catalyst ii) Solvent free reaction*
4. *Explain the synthesis of Paracetamol by conventional and green route from phenol.*
5. *Explain the synthesis of Adipic acid by conventional route from Benzene and green route from Glucose.*
6. *With a neat diagram explain the production of Hydrogen by Photocatalytic method*.
7. *Describe the hydrogen production by photo electrocatalytic method.*
8. *Explain the construction and working of photovoltaic cells*.
9. *Describe the construction and working of Methanol –Oxygen fuel cell*
10. *With suitable example explain microwave synthesis and bio catalyzed reactions.*

Prashantha. Somayaji
Asst. Professor
Dept. of Chemistry
Canara Engineering College