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UNIT-III
Green Chemistry

(From the Academic year 2022-23 onwards)

The term **Green Chemistry** is defined as the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.

It is based on a number of principles that both processes and end products are clean and safe. Green chemistry aims to conserve both energy and raw materials. In practice, this means that 'green' processes are often cheaper than conventional methods.

The use of green chemistry is growing because it is environmentally friendly. One of the basic ideas of green chemistry is to *prevent* production of hazardous and polluting materials rather than producing them and then cleaning up.

Green chemistry:

- is safe
- conserves raw materials and energy and
- more cost-effective than conventional methods.

Green Chemistry in practice:

- Approaches to making chemical processes 'greener' include
- redesigning production methods to use different starting materials
- using different reaction conditions, catalysts, solvents *etc*., and
- using production methods with fewer steps.

The principles of green chemistry

Basic principles of Green chemistry listed below are based on the work carried out by scientist Paul T. Anastas.

1. **Prevention of waste products** - it is better to prevent waste production rather than to treat or clean up waste after it has been produced.
2. **Atom Economy** - synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less hazardous chemical synthesis** - Synthetic method should be designed to use and generate substances that possess little or no toxicity to people or the environment.

4. **Designing of safer chemicals-** Chemical products should be designed to effect the desired function while minimizing their toxicity.
5. **Selection of safer solvents-** the solvents selected for a particular reaction should not cause any environmental pollution or health hazard.
6. **Use of renewable starting materials** – Raw materials or feedstock should be renewable.
7. **Design for energy efficiency -**Energy requirement for any synthesis should be minimum.
8. **Reduce derivatives-** Unnecessary derivatives should be minimized or avoided, because such steps require additional reagents and can generate waste.
9. **Catalysis -** Catalysts should be used wherever possible as they facilitate better utilization of starting materials and minimum waste product formation.
10. **Design for degradation-** Chemical products should be designed so that they break down at the end of their useful life to form harmless products.
11. **Strengthening of analytical techniques -** To control hazardous compounds.
12. **Real time analysis for pollution prevention -** Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

ATOM ECONOMY

Atom economy is one of the fundamental and most important principles of Green Chemistry. The percentage yield of a product in a chemical synthesis is catalyzed by

$$\%\ \text{Yield} = \frac{\text{Actual quantity of products obtained}}{\text{Theoretical quantity of products achievable}} \times 100$$

If one mole of a starting material produces one mole of the product, the yield is 100% and such a synthesis may also generate significant amount of unwanted materials (by products) whose percentage is not visible in the above calculation. Such a synthesis is not considered as green synthesis. The reaction or synthesis is considered to be green, if there is a maximum incorporation of the starting materials and reagents in the final product. Thus, the percentage atom utilization (substrate converted) should be taken into account, which is determined by the expression,

$$\% \text{ Selectivity} = \frac{\text{Yield of desired product}}{\text{Amount of substrate converted}} \times 100$$

Atom economy is essentially a measure of how many atoms of reactants end up in the final product and how many end up in by-products or waste. The percentage atom economy can be calculated as 100 times the relative molecular mass of all atoms used to make the desired product divided by the relative molecular mass of all reactants

$$\% \text{ Atom economy} = \frac{\text{RMM of desired product}}{\text{RMM of all reactants}} \times 100$$

The real benefit of atom economy is that it can be calculated at the synthesis planning stage from a balanced reaction equation. Consider the following theoretical reaction:

$$X + Y = P + U$$

Reaction between X and Y to give product P may proceed in 100% selectivity. But the reaction also produces unwanted materials U; its atom economy will be less than 100%.

Numerical Problems:

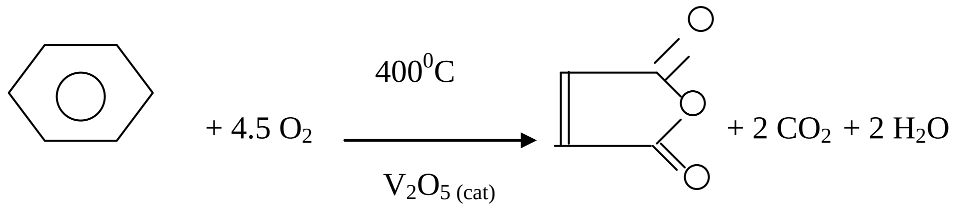
1. $H_3C{-}CH{=}CH_2 + H_2 \xrightarrow{Ni} H_3C{-}CH_2{-}CH_3$

Propene 42   2   Propane 44

$$\% \text{ Atom economy} = 100 \times \frac{44}{42 + 2} = 100$$

2. Maleic anhydride can be synthesized by two different routes.

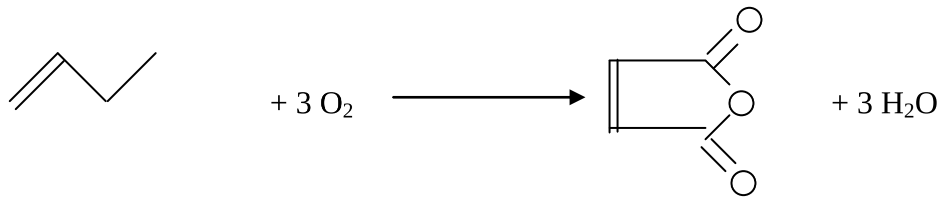
Route 1: Oxidation of benzene



78 $\quad$ 4.5 x 32 = 144 $\quad$ 98

$$\% \text{ Atom economy} = 100 \times \frac{98}{78+144} = 44.1$$

Route 2: Butene oxidation.



56 $\quad$ **96** $\quad$ **98**

$$\% \text{ Atom economy} = 100 \times \frac{98}{56+96} = 64.5$$

3. Phenol can be synthesized by two different routes.

Route 1: $C_6H_6 + H_2SO_4 + NaOH \longrightarrow C_6H_5OH + NaHSO_3$

78 $\quad$ 98 $\quad$ 40 $\quad$ 94

$$\% \text{ Atom economy} = 100 \times \frac{94}{78+98+40} = 43.5$$

Route 2: $C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH + HCl + N_2$

140.5 $\quad$ 18 $\quad$ 94

$$\% \text{ Atom economy} = 100 \times \frac{94}{140.5+18} = 59.3$$

4. Ethanol can be synthesized by three different routes.

Route 1: $C_2H_5Cl + KOH \longrightarrow C_2H_5OH + KCl$

64.5 56 46

% Atom economy = 100 x $\frac{46}{56 + 64.5}$ = **38.17**

Route 2: $C_2H_5NO_2 + HNO_2 \longrightarrow C_2H_5OH + H_2O + N_2$

75 47 46

% Atom economy = 100 x $\frac{46}{75 + 47}$ = 37.7

Route 3: $C_2H_5COOCH_3 + NaOH \longrightarrow C_2H_5OH + CH_3COONa$

88 40 46

% Atom economy = 100 x $\frac{46}{88 + 40}$ = 35.9

5. Hydrogen can be manufactured by reacting methane with steam:

$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$

Calculate the atom economy for the reaction. (A_r of H = 1, A_r of C = 12, A_r of O = 16)

M_r of $CH_4 = 12 + (4 \times 1) = 16$

M_r of $H_2O = (2 \times 1) + 16 = 18$

total M_r of reactants = 16 + 18 = 34

A_r of $H_2 = (2 \times 1) = 2$

total M_r of desired product = 3 × 2 = 6 (there are three H_2 in the balanced equation)

% Atom economy = 100 x $\frac{6}{34}$ = 17.6

Renewable energy sources- Biomass as a renewable energy source:

Renewable sources of plants origin which are used to harness the energy are referred to as biomass. As per an estimate, the total amount of biomass available is about 2000 billion tones. The energy derived from the biomass by burning either directly to provide heat or in power station to produce electricity. Although biomass is a complex mixture of starch, cellulose *etc*, in simple terms of burning process, it can be represented as

$[CH_2O] + O_2 \longrightarrow CO_2 + H_2O.$

The other biomass conversion processes developed are:

1. Thermolysis (450 -800 ^oC) and pyrolysis (1500 ^oC) – Heating wood in the absence of air.
2. Gasification (650 -1200 ^oC) – Air and steam are used to give a product richer in oxygen.
3. Hydrothermolysis- production of an oil-like material called bio-crude with low oxygen content.

$$\text{Biomass} + H_2O \xrightarrow{200\text{-}330\,^oC} \text{Bio-crude}$$

4. Fermentation process – Ethanol
5. Anaerobic digestion

$$\text{Biomass} + \text{Anaerobic bacteria} \xrightarrow{\text{Absence of air}} CH_4$$

Bioethanol

The principal fuel used as a substitute for petrol in road transport vehicles is bioethanol. Bioethanol fuel is mainly produced by the sugar fermentation process. The main sources of sugar required to produce ethanol come from energy crops. The energy crops include corn, maize, wheat crops and sugarcane, *etc*.

Bioethanol Production

Sugar Fermentation Process: Molasses is the mother liquor left behind after the crystallization of cane sugar. It contains about 50% sugar. It is diluted with water to 10% sugar solution. A small amount of dilute sulphuric acid is added. Yeast containing the enzymes, invertase and zymase is added and some ammonium sulphate and ammonium phosphate are also added which serve as food for the enzymes. The temperature is maintained at 303 K. Enzyme, invertase, which acts as a catalyst converts the sucrose sugars into fructose and glucose sugars as shown below.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase catalyst}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The fructose and glucose sugars are then get converted into ethanol in the presence of another enzyme, zymase. The chemical reaction is shown below:

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2\,C_2H_5OH} + 2CO_2$$

The fermentation process takes around three days. The ethanol, so produced contains a significant quantity of water and hence it must be removed. This is achieved by subjecting ethanol containing water to fractional distillation. When ethanol-water mixture is boiled, ethanol first distills over as its boiling point (78.3 ^{o}C) is lower than that of water (100 ^{o}C).

Advantages of Bioethanol

Bioethanol has a number of advantages over conventional fuels.

i) It is a renewable resource i.e. crops like cereals, sugar beet, sugarcane and maize.

ii) It is biodegradable.

iii) It is less toxic.

iv) When it is blended with gasoline the fuel mixture gets oxygenated and as a result, the fuel mixture burns more completely and reduces polluting emissions.

v) It produce less pollutants to the atmosphere and thus ecofriendly.

vi) Ethanol is a high octane fuel and has replaced lead as an octane enhancer in petrol.

vii) It boosts rural economy by growing the necessary crops.

viii) It ensures greater fuel security and avoids heavy reliance on petrol oil producing nations and thus saves foreign exchange.

Biodiesel: Biodiesel is produced from plants origin (non-edible oils derived from seeds of karanji (pongamia), castor, neem, jatropha, *etc*.) and is a liquid fuel largely compatible with petroleum based diesel fuel.

Biodiesel Production

Biodiesel is made by a chemical process called ***transesterification.*** Transesterification (one form of ester is converted into other form) is a process of producing an alkyl ester by reacting triglycerides present in vegetable/non edible oils with an alcohol in presence of a base catalyst.

i) First the triglyceride present in vegetable oils is treated with a drying agent $MgSO_4$, to remove water content.

ii) The process is accomplished by mixing the methanol with NaOH or KOH to make CH_3ONa or CH_3OK which is mixed with a preheated vegetable oil (~55 ^oC).

iii) The process leaves behind two products namely, methyl esters (chemical name for biodiesel) in the upper layer and glycerol (byproduct) in the lower layer.

iv) Glycerol is removed and used in the manufacture of soap. The upper layer consisting of biodiesel is washed with water and dried.

$CH_2OC{=}OR_1$ $\quad\quad\quad\quad$ CH_2OH

| $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ |

$CHOC{=}OR_2 + 3\,CH_3OH \rightarrow CHOH + CH_3COO\text{-}R_1 + CH_3COO\text{-}R_2 + CH_3COOR_3$

| $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ |

$CH_2OC{=}OR_3$ $\quad\quad\quad\quad$ CH_2OH $\quad\quad\quad$ R_1, R_2, R_3 = <u>Alkyl</u> <u>group</u>

Triglyceride + methanol → Glycerol + **Esters (Biodiesel)**

Advantages of Biodiesel

Biodiesel has the following advantages over petrodiesel.

- It is a renewable resource i.e. crops like karanji (pongamia). Castor, neem, jatropha, sunflower, groundnut, *etc*.
- It is safe and biodegradable.
- It reduces air pollutants such as particulates, CO, hydrocarbons, oxides of sulphur and thus ecofriendly.
- It is less toxic.
- It has viscosity similar to petrodisel.
- It has better lubricity.

Power alcohol:

Power alcohol is gasoline blends containing ethanol which can be used as a fuel in internal combustion engines. Awareness of the limited availability of the non-renewable fossil fuels gave stimulus to the production of ethyl alcohol from renewable plant resources.

Now ethanol is used as a fuel in the United States as ***gasohol*** - a blend containing 10-85 % ethanol and 90-15% gasoline (petrol) by volume. Absolute alcohol is required for blending with petroleum in order to avoid phase separation. With suitable modification of the engine, 95% alcohol-water mixture can be used. The main objective of the power alcohol is to reduce oil imports and provide an alternative to non-renewable energy source, gasoline.

The importance of power alcohol as fuel:

1. The power output is good.
2. The use of ethanol in gasoline blends increases the oxygen content (it contains 35% oxygen by weight i.e., twice the oxygen content of MTBE) of the fuels and promotes more complete combustion of the hydrocarbons in gasoline. This reduces carbon monoxide and volatile organic compound (VOC) emissions. Hence ethanol is called an oxygenate.

3. Due to better antiknock property, it can be used in engines with higher compression ratio.
4. Petrol–alcohol blend has the same lubrication as the neat petrol has.
5. Since ethanol is produced from agricultural products (corn and molasses), it has the potential to be a sustainable fuel.
6. Ethanol is biodegradable.

FUEL CELLS

Fuel cell is defined *as*, a galvanic cell in which chemical energy is converted into electrical energy as long as reactants and oxidants are supplied continuously.

A fuel cell differs from a battery in the following aspects

i) In a fuel cell, the reactants do not form an integral part; they are fed from outside the cell.

ii) Fuel cells do not store chemical energy.

iii) Reactants are constantly supplied and the products are constantly removed from the cell.

The fuel cells have the following advantages:

i) Their power efficiency is high.

ii) They are eco-friendly since the products of the overall reactions are not toxic

iii) They can produce direct currents for long periods at a low cost.

Applications:

Fuel cells are about three times more efficient than any other method of providing larger electricity. Hence they are used as auxiliary power generators in space vehicles. Fuel cells are used in car engines, domestic lighting and heating.

Types of Fuel cells:

There are three types of fuel cells:

i) Low temperature fuel cells

ii) Medium temperature fuel cells

iii) High temperature fuel cells

LOW TEMPERATURE FUEL CELLS:

Two typical examples of low temperature fuel cells are

a) Alkaline fuel cell and b) methanol-oxygen fuel cell.

An alkaline fuel cell uses oxygen, hydrogen and a concentrated solution of an alkali.

The methanol oxygen fuel cell uses oxygen, methanol and sulphuric acid.

Methanol-Oxygen fuel cell

Methanol is an efficient electro active organic fuel at low temperatures.

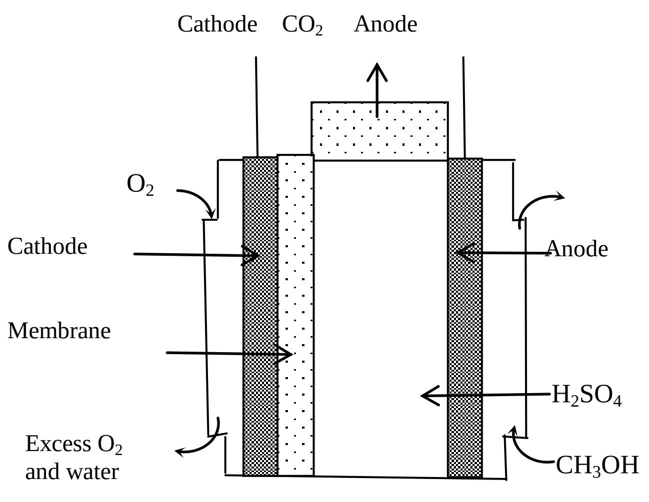
The advantages of methanol are

i) It has low carbon content.

ii) It possesses a readily oxidizable OH group.

iii) It has high solubility in aqueous electrolytes.

Methanol containing sulphuric acid (3.7M) is circulated through the *anode* chamber. Pure oxygen is passed through the *cathode* chamber and sulphuric acid (electrolyte) is placed in the central compartment. Both the electrodes are made of platinum. A membrane is inserted close to the cathode to minimize 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.



Methanol-oxygen fuel cell

The half-cell reactions are

At anode: $CH_3OH\,(l) + H_2O(l) \longrightarrow CO_2(g) + 6H^+(aq) + 6e^-$

At cathode: $1\tfrac{1}{2}\,O_2(g) + 6H^+(aq) + 6e^- \longrightarrow 3H_2O(l)$

The overall reaction is

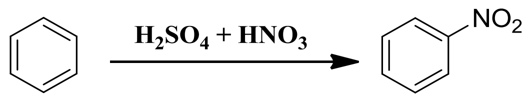
$$CH_3OH\,(l) + 1\tfrac{1}{2}\,O_2\,(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

The advantage of acid electrolyte is that the CO_2, a product of the reaction, can be easily removed. The cell potential is 1.21 V at 25 ^oC.

Applications: The methanol-oxygen fuel cell is used in military applications and in large scale power production.

Questions

1) Briefly discuss the principles of green chemistry.
2) How is bio-ethanol synthesized? What are the advantages of bio-ethanol as fuel?
3) What is a fuel cell? Write the half-cell reactions taking place at anode and cathode of MeOH-O_2 fuel cell.
4) How is Biodiesel prepared? Mention its advantages.
5) Define % of atom economy. Calculate the % atom economy for the formation of nitrobenzene from the following equation.



(Given At. Wt of C = 12, H = 1, O= 16, N = 14, S =32)

6) Calculate the % atom economy for the following reaction:
   $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$
   [Atomic weight of C=12, H=1, O=16].
7) Describe the construction and working of MeOH-O_2 fuel cell.
8) What is power alcohol? Mention its advantages.
9) Define the terms (i) Atom economy and (ii) Fuel cell.
10) Distinguish between fuel cell and a battery. Give examples.