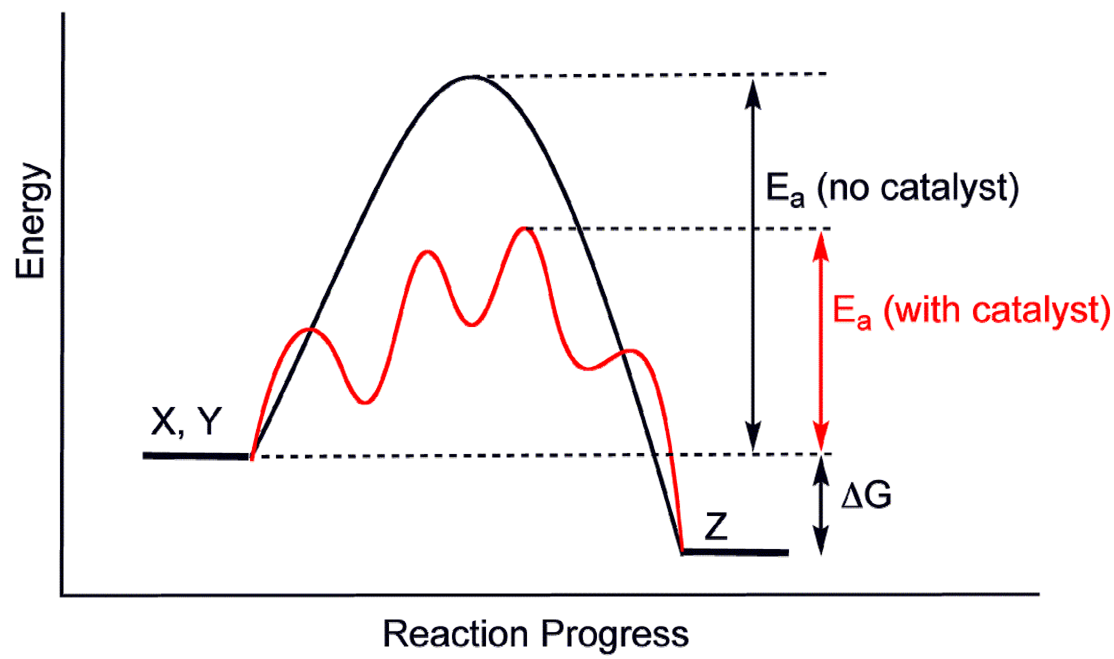
Principle 5:

Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.



Green Chemistry - Catalysis

Catalysis is described as *homogeneous* when the catalyst is soluble in the reaction medium and *heterogeneous* when the catalyst exists in a phase distinctly different from the reaction medium.

- **Catalysts increases the rates of reactions, by lowering their activation energy, thus providing a new pathway.**

- **Catalysts can select one out of several possible pathways thus improving the utilization of raw materials, energy and avoiding the formation of undesired by-products.**

- **Only small quantities of catalysts are needed for a reaction.**

- **Catalysts can be recycled for repeated use.**

- **In this way catalysis gives an important contribution to the development of sustainable technologies and environmentally friendly processes.**

Green Chemistry - Catalysis

Turnover number (TON)

Turnover number (or) *catalyst productivity* is defined as the number of moles products produced with one mole of catalyst

$$\text{TON} = \frac{\text{Percentage of Yield}}{\text{Equivalent of Catalyst}}$$

Turnover frequency (TOF)

Turnover frequency (or) *catalyst activity* is defined as the number of moles of product produced per mole of the catalyst per unit time.

$$\text{TOF} = \frac{\text{Percentage of Yield}}{\text{Equivalent of Catalyst X Time}}$$

ADVANTAGES OF CATALYSIS

The Jones Reagent (Stoichiometric)

$$3\ PhCH(OH)CH_3 + 2\ CrO_3 + 3\ H_2SO_4 \longrightarrow 3\ PhCOCH_3 + Cr_2(SO_4)_3 + 6\ H_2O$$

Atom Economy = (360/860) × 100 = 42%

Byproduct = $Cr_2(SO_4)_3$ *undesirable*

A Catalytic Route

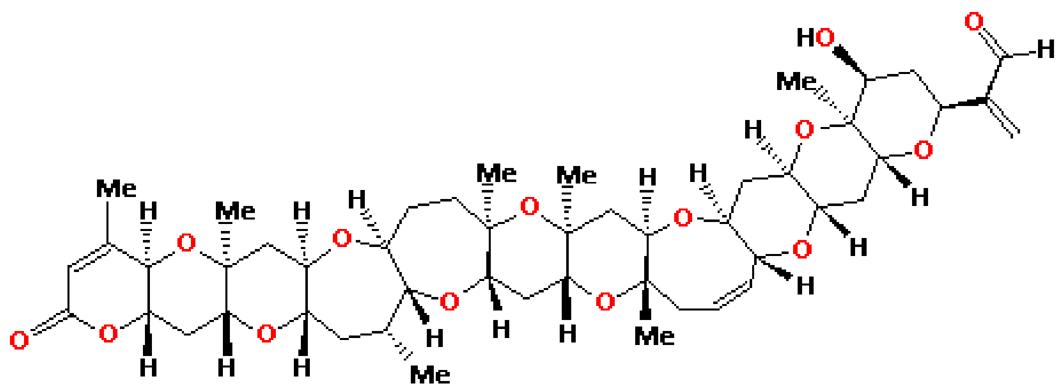
$$PhCH(OH)CH_3 + 1/2O_2 \xrightarrow{\text{Catalyst}} PhCOCH_3 + H_2O$$

Atom Economy = (120/138) × 100 = 87%

Byproduct = H_2O *innocuous*

Principle 6:

Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.



Brevetoxin B

Principle 7:

Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.

E-Factor

***E*-factor defined by the mass ratio of waste to desired product.**

$$E\text{-factor} = \frac{\text{Kilogram of byproducts}}{\text{Kilogram of products}}$$

The *E*-Factor

Industry segment	Product tonnage	kg byproduct / kg product
Bulk chemicals	10^4 - 10^6	< 1 - 5
Fine chemicals	10^2 - 10^4	5 - > 50
Pharmaceuticals	10 - 10^3	25 - > 100

WHERE DOES ALL THIS WASTE ORIGINATE?

1. STOICHIOMETRIC BRONSTED ACIDS & BASES
   - Aromatic nitrations with H_2SO_4 / HNO_3
   - Acid promoted rearrangements, e.g. Beckmann (H_2SO_4)
   - Base promoted condensations, e.g. Aldol (NaOH, NaOMe)
2. STOICHIOMETRIC LEWIS ACIDS
   - Friedel-Crafts acylation ($AlCl_3$, $ZnCl_2$, BF_3)
3. STOICHIOMETRIC OXIDANTS & REDUCTANTS
   - $Na_2Cr_2O_7$, $KMnO_4$, MnO_2
   - $LiAlH_4$, $NaBH_4$, Zn, Fe/HCl
4. HALOGENATION & HALOGEN REPLACEMENT
   - Nucleophilic substitutions
5. SOLVENT LOSSES
   - Air emissions & aqueous effluent

TUDelft

Atom economy

The concept of Atom Economy was developed by Trost of Stanford University (US), for which he received the Presidential Green Chemistry Challenge Award in 1998.

It is a method of expressing how efficiently a particular reaction makes use of the reactant atoms.

Calculation of Atom Economy

$$\text{Atom economy} = \frac{\text{mass of atoms in desired product}}{\text{mass of atoms in reactants}} \times 100\ \%$$

$$\%\ \text{Yield} = \frac{\text{Actual yield of product}}{\text{Theoretical yield of product}} \times 100$$

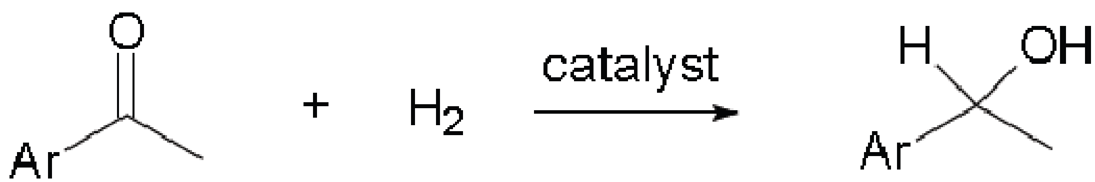
Inherent Atom Economy

Some Atom Economic Reactions	Some Atom Un-Economic Reactions
Rearrangement	Substitution
Addition	Elimination
Diels-Alder	Wittig
Other concerted reactions	Grignard

Note that atom economy can be poor even when chemical yield is near 100%

Examples of Atom Efficient Reactions

Hydrogenation:

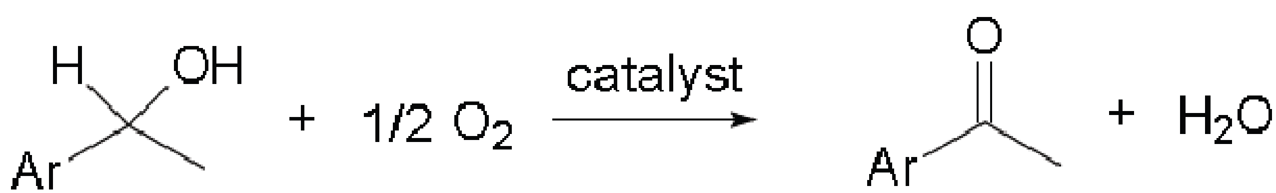


100% atom efficient

Carbonylation:

100% atom efficient

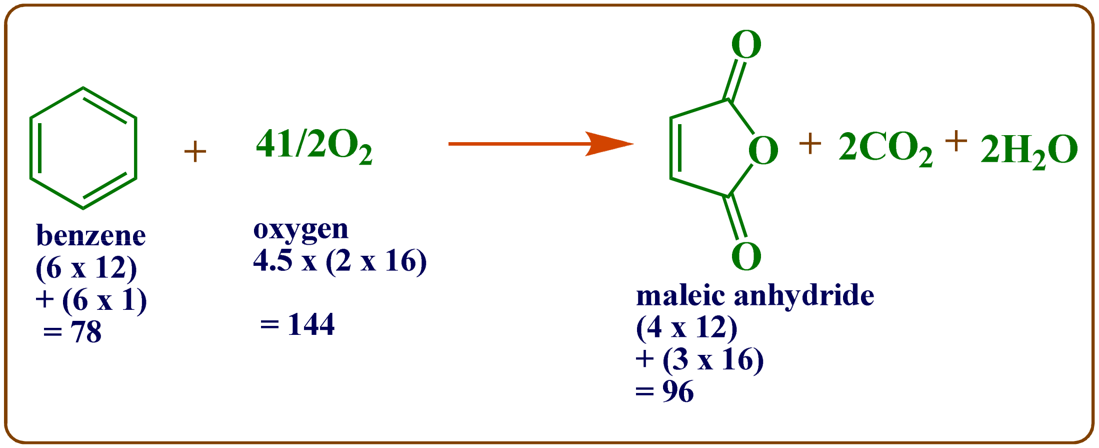
Oxidation:



87% atom efficient

Atom Economy

Oxidation of benzene to maleic anhydride, an important intermediate chemical



$$\text{Atom economy} = \frac{96}{(78 + 144)} \times 100\ \%$$

$$= 43\ \%$$

Principle 8:

Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals. If a solvent is necessary, water is a good medium as well as certain eco-friendly solvents that do not contribute to smog formation or destroy the ozone.

Disadvantage of Organic Solvents

* **Toxicity**
* **High volatality**
* **Fire hazard**
* **Cost**

Solvent Selection Guide

Preferred	Usable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane
Ethanol	Toluene	Di-isopropyl ether
2-propanol	Methylcyclohexane	Diethyl ether
Ethyl acetate	Methyl t-butyl ether	Dichloromethane
Isopropyl acetate	Isooctane	Dichloroethane
Methanol	Acetonitrile	Chloroform
Metyl ethyl ketone	2-MethylTHF	Dimethyl formamide
1-Butanol	Tetrahydrofuran	N-Methylpyrrolidinone
t-Butanol	Xylenes	Pyridine
	Dimethyl sulphoxide	Dimethyl acetate
	Acetic acid	Dioxane
	Ethylene glycol	Dimethoxyethane
		Benzene
		Carbone tetrachloride

MORE HAZARDOUS

Green Chem., **2008**, *10*, 31-36

Solvent Replacement Table

Undesirable solvents	Better Alternative
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or tert-butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or tert-butyl methyl ether
Pyridine	Triethyl amine (base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

Non-organic Alternative Green Reaction Medium

i) Water

ii) Supercritical Fluids

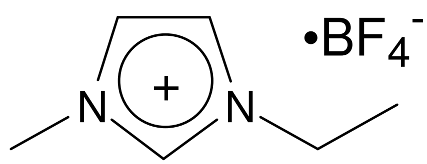
iii) Ionic Liquids

iv) Solid Surface

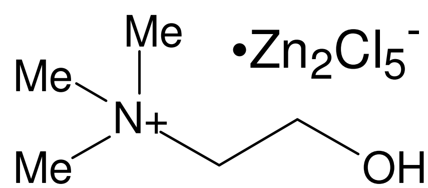
v) Neat

Ionic liquids (IL’s)

- Typically consist of organic cation (often ammonium or phosphonium salt) and inorganic anion



1. Ethylmethylimidazolium tetrafluoroborate, [emim][BF_4]



2.Choline chloride/Zinc chloride ionic liquid

- Usually only consider IL’s which are liquid at room temperature
- Great variety of structures possible
- Very low vapour pressure – attractive alternative to VOCs.

Principle 9:

Increase energy efficiency: **Run chemical reactions at ambient temperature and pressure whenever possible.**

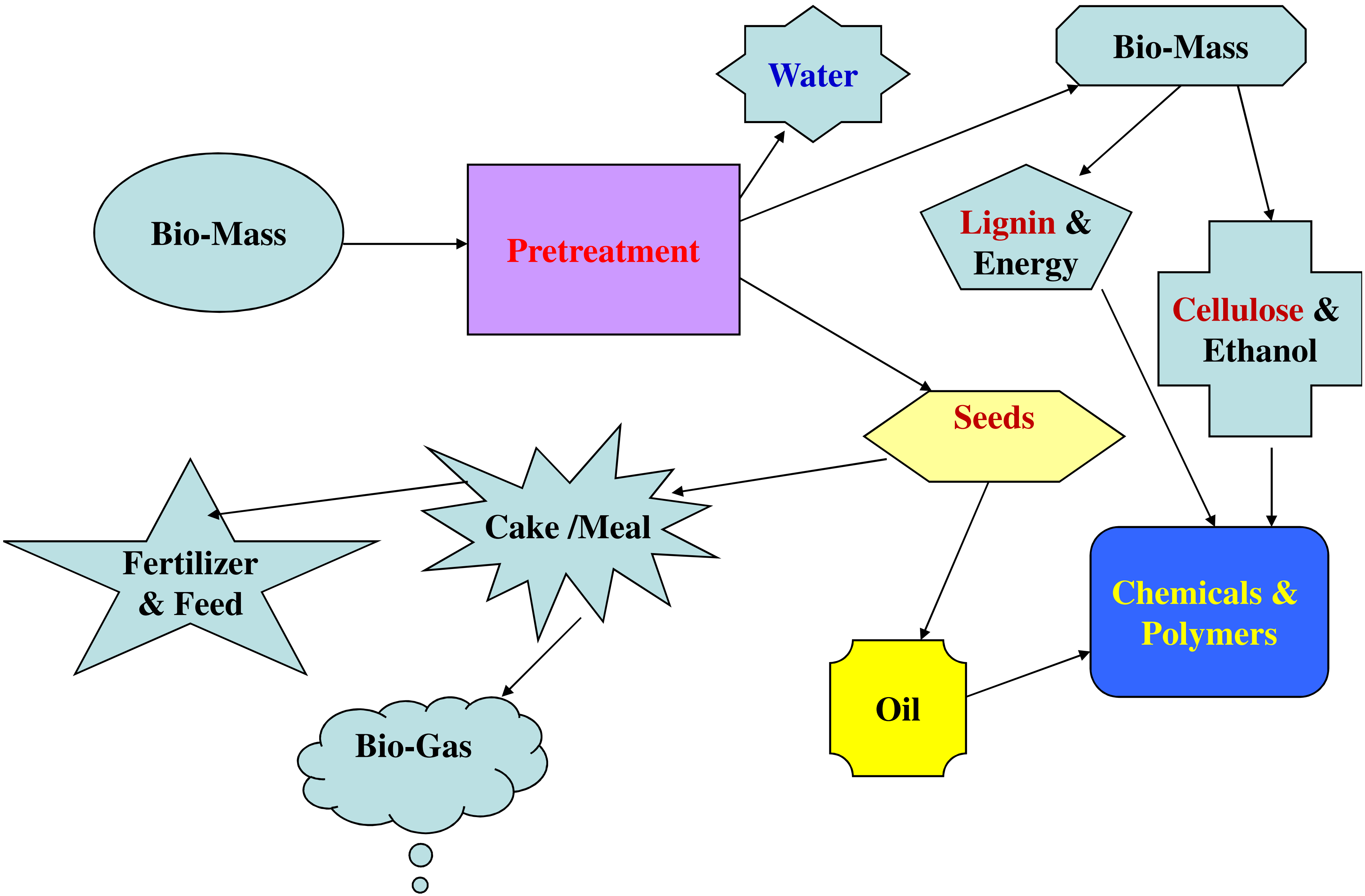
Principle 10:

Design chemicals and products to degrade after use: **Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.**

WHY BIOREFINERY?

- **Biorefinery converts Biomass into Fuels, Chemicals & Materials, Energy, Feed, etc.**
- **Depleting Oil & Gas Resources & Increasing Costs to discover & Use these.**
- **National Energy Security.**
- **Need for Environmental Sustainability.**
- **Growing Aspiration of Developing Countries.**

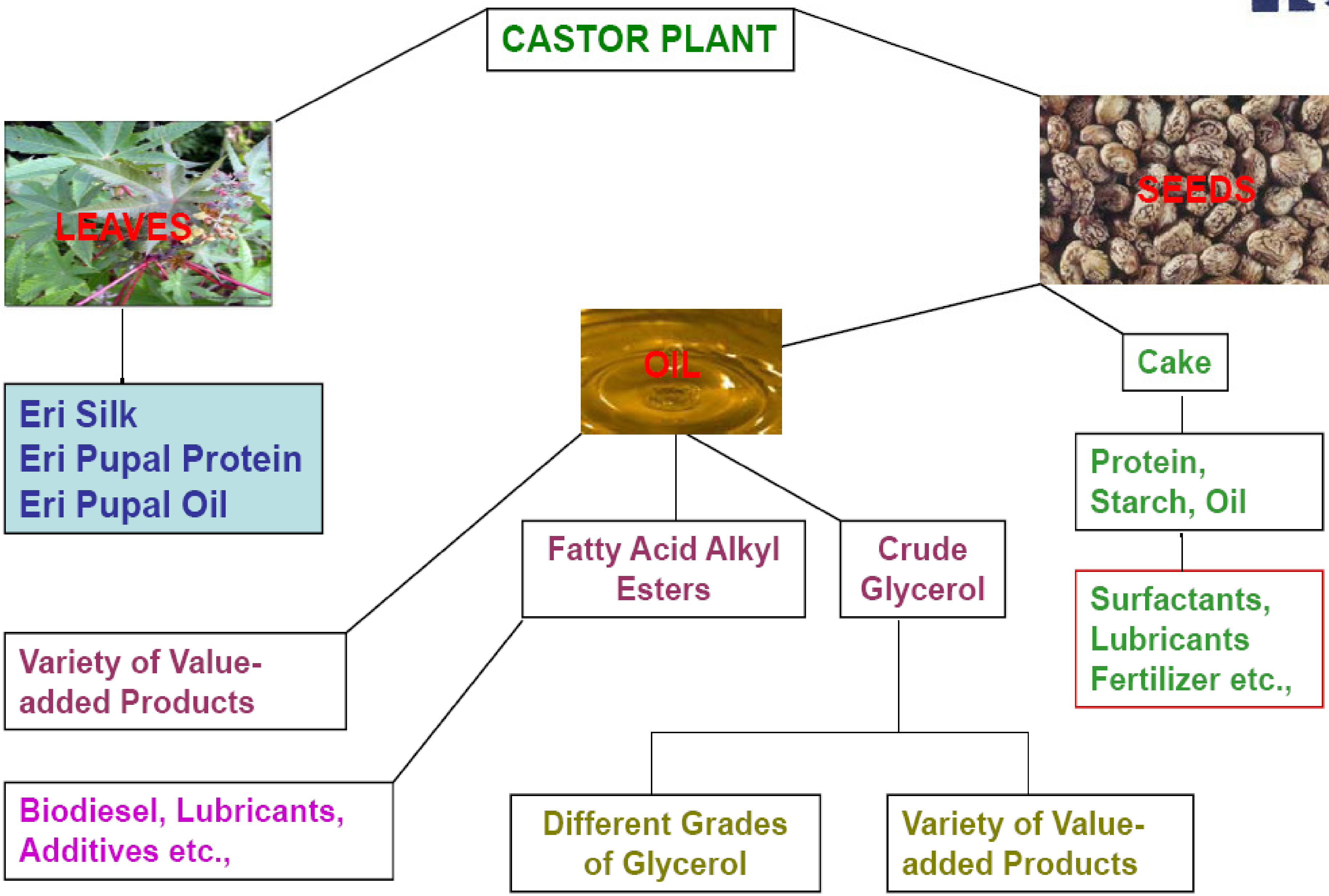
BIO-REFINERY PROCESS



FOUR TYPES OF BIO-REFINERY

- 1^{ST} Generation: Ethanol from sugar cane, beat root, etc.
- 2^{nd} Generation: Plant Oil based.
- 3^{rd} Generation: Ethanol from Cellulosics.
- 4^{th} Generation: Ethanol, Polymers from Algae & Microbes.

CASTOR BIOREFINERY



Principle 11:

Analyze in real time to prevent pollution: **Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.**

Principle 12:

Minimize the potential for accidents: **Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.**

A carbon footprint is the total amount of carbon dioxide a person contributes to the environment

Reducing Carbon Foot print

- Planting a Tree
- Ceiling fans instead of AC
- Read online newspaper
- Eat in season (veg.) produce
- Use energy efficient appliances
- Use microwave heating
- Use hybrid vehicle
- Use rechargeable batteries
- Take Shower
- Cold water bath
- Create wormery
- Switch to renewable energy
- Take a train than flight
- Shifting gear sooner
- Replace CFL bulbs
- Filter your own water
- Carpool
- Plant an Organic garden
- Unplug phone charger
- Use laptop and not desktop