Department of Humanities and Applied Sciences

APPLIED CHEMISTRY(Semester I)

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Green Chemistry

CONTENTS

A)	Comparative study of synthesis of following industrially important molecules by conventional and green route:- i) Indigo dye ii) Adipic acid iii) Carbaryl
B)	Green Solvents: - characteristics and applications of Supercritical solvents and ionic liquids
C)	Green Fuels:- Synthesis and Advantages of: i) Biodiesel ii) Ethanol

- Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical product.

- The term was coined by Paul Anastas.

SOME WELL-PUBLICIZED INCIDENTS FROM THE PAST FEW DECADES…

- The Cuyahoga River in Ohio became so polluted with chemicals it caught fire.
- A plant accident in Bhopal, India, released methyl isocyanate. Nearly 4000 people died.

12 Principles of Green Chemistry

1. Prevention of waste

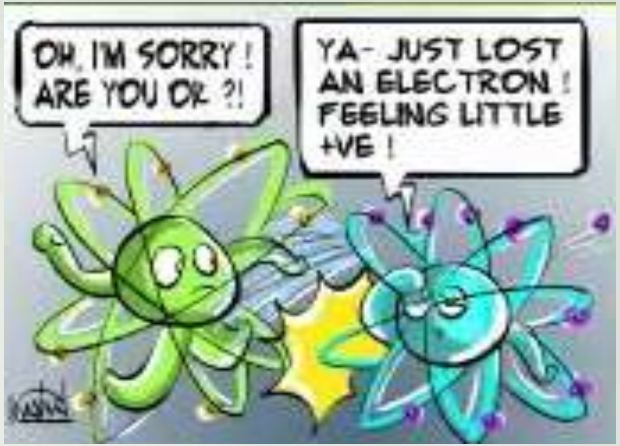
"It is better to prevent waste than to treat or clean up waste after it is formed"

- Manufacturing processes can be designed so as not to produce waste products,

– OR –

- Waste products to be recycled or biodegradable.

2. ATOM ECONOMY



- **% Atom Economy =** $\dfrac{\textbf{Molecular weight of products}}{\textbf{Molecular weight of reactants}} \times 100$

- Concept developed by Barry Frost
- Evaluates the efficiency of a chemical
- Choose transformations that incorporate most of the starting materials into the product increases the efficiency and minimizes waste

3. Non –Hazardous Chemical Synthesis

Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

LEAD POLLUTION HAS BEEN DECREASED BY…

- Replacing lead in paint with safe alternatives, and
- Replacing tetraethyl lead with less toxic additives (e.g., “lead-free” gasoline).

4. Designing Safer Chemicals and products

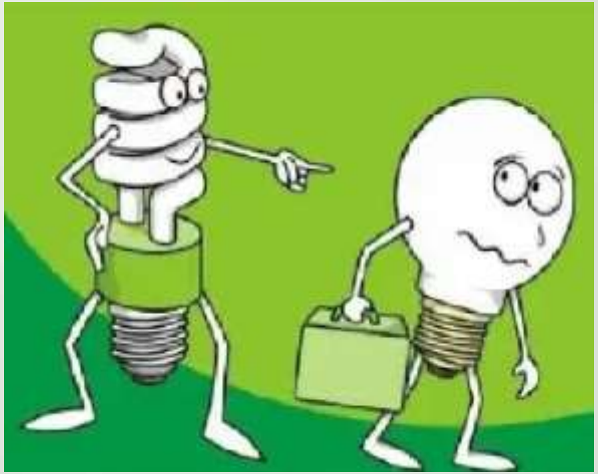
- Chemical products should be designed to preserve efficiency of the function while reducing toxicity.
- Use of biological pesticides in place of DDT, gamaxane, aldrin ,etc. which are toxic to humans.

5. Safer Solvents and Auxiliaries

- The use of auxiliary substances (solvents, separation agents, etc.) should be made only when necessary .Solvent Substitution
- Water as a solvent
- New solvents:
  Ionic liquids
  Supercritical fluids

6. Design for Energy Efficiency

- Energy requirements should be recognized for their environmental and economic impacts and should be minimized.
- Minimal wastage of energy during the process.



7. Use of Renewable Feedstocks

- A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

8. Avoid Chemical Derivatives

- Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
- The use of derivatives increases the steps of the process.

9. Use catalysts ,not Stoichiometric reagents

- Catalytic reagents (as selective as possible) are superior to stoichiometric reagents
- Readily regenerated, separated
- Recyclable
- Mild conditions

10. Design for Degradation

- Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products
- CFCs, DDT
- Biodegradable polymers

11. Real-time Analysis for Pollution Prevention

- Real time analysis for a chemist is the process of “checking the progress of chemical reactions as it happens.”

- Knowing when your product is “done” can save a lot of waste, time and energy!

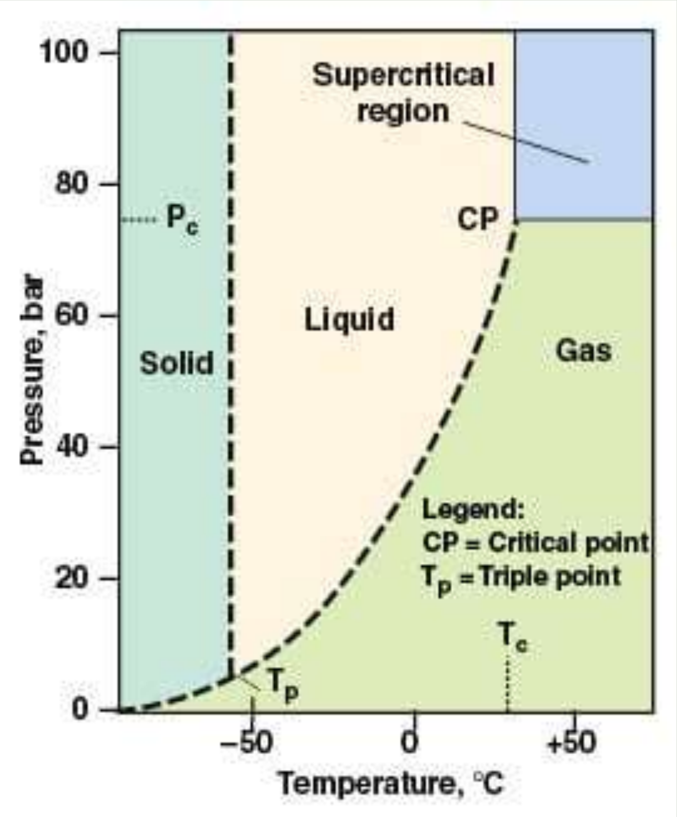
12. Minimize the potential for Accidents

- Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires
- Various industrial accidents
- Eg: Bhopal gas tragedy

Supercritical Solvents

Supercritical Fluid is any substance at a temperature and pressure above its Critical point, where distinct liquid and gas phases do not exist, but below the pressure required to compress it into a solid.

Example: Commonly used Supercritical fluids are CO_2 & H_2O.



Characteristics of Supercritical Solvents

- Can penetrate solids like gas
- Dissolves materials like liquid.
- There is no surface tension in SCF.
- It has a very good solvent property.
- In supercritical environment only one phase exists and hence no liquid-gas phase boundary.
- Close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties to be "fine-tuned”.

Supercritical Solvents

- Supercritical CO_2 is simply carbon dioxide that is pressurized and heated above its critical point .
- Natural,cheap,plentiful
- Available in 99.9 % pure form.
- The fluid has many useful properties including low viscosity, high density, very low cost and leaves no residual solvents.

Advantages of CO2

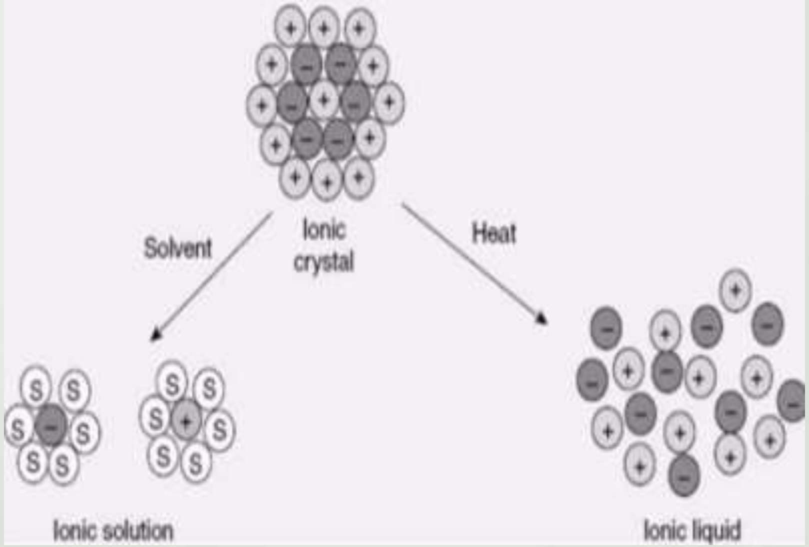
- **Handling**
  With critical points at 31 ℃ and 22 MPa, CO_2 becomes a supercritical fluid under modest conditions.
- **Safety**
  CO_2 is not flammable and has minimal risk of explosion even if used compressed. CO_2 offers intrinsically low toxicity, when compared to other organic solvents.
- **Cost**
  CO_2 is mainly sold as a liquid stored in high-pressure cylinders and in most cases can be acquired at a low cost.
- **Environmental Friendliness**
  Other organic solvents are incinerated for disposal, which emits large amounts of energy and CO_2. However, liquified carbon dioxide gas is collected as a byproduct of fermentation processes or chemical plants. That means using liquified CO_2 causes minimal environmental impact.

Applications

- Separation of essential and its derivatives for use in food, cosmetics and pharmaceutical industry.
- Supercritical CO_2 coupled with HPLC to extract and characterize antimicrobial compounds and food preservatives.
- The liquid like density of SCF promotes solubility of many substances in supercritical fluids.
- It shows significantly small surface tension ,allowing for highly efficient and harmless drying conditions.
- It can be used for prolong preservation of biological products.

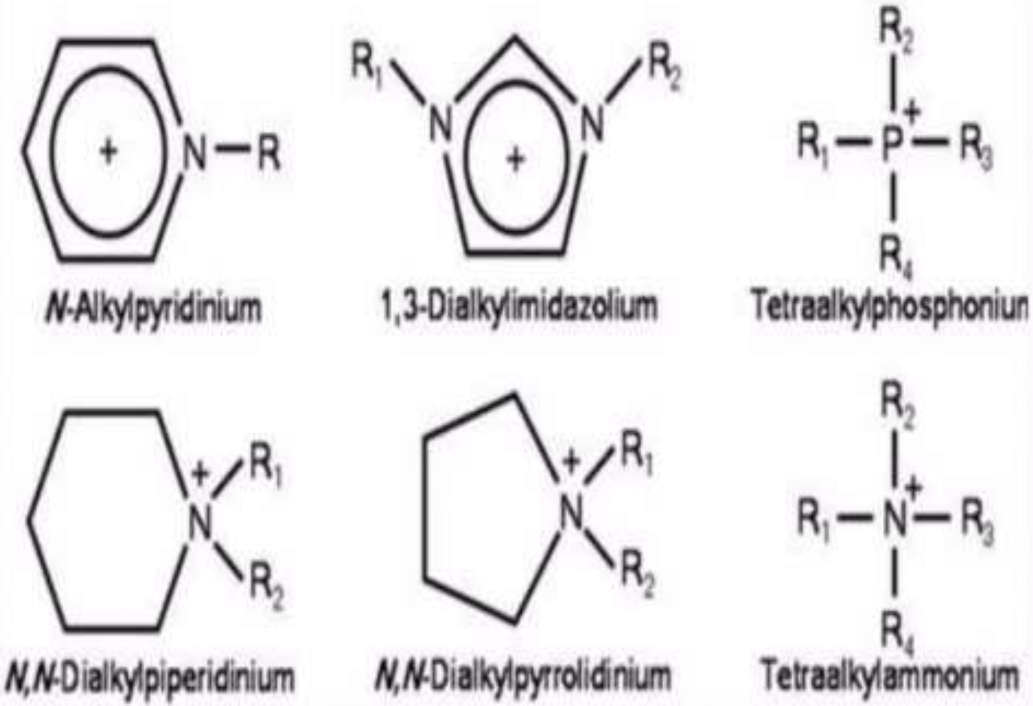
Ionic liquids

- An **ionic liquid** (**IL**) is a salt in the liquid state at ambient conditions.
- In some contexts, the term has been restricted to salts whose melting point is below a specific temperature, such as 100 °C
- These substances are variously called **liquid electrolytes**, **ionic melts**, **ionic fluids**, **fused salts**, **liquid salts**, or **ionic glasses.**



Typical cations and anions

Cations



Anions

Cl^-	$C(CN)_3^-$
Br^-	CH_3COO^-
I^-	$(CF_3SO_2)_2N^-$
BF_4^-	$(CF_3SO_2)_3C^-$
PF_6^-	NO_3^-
$N(SO_2F)_2^-$	$HCOO^-$
$CF_3SO_3^-$	$AlCl_4^-$

Properties of Ionic Liquids

- Zero or no vapour pressure ,they do not evaporate easily.
- Non-flammable
- High thermal stability
- Immiscible in majority of organic solvents
- Have good solubility of gases
- Large electrochemical window
- Good ionic conductors
- Viscous
- Volatile Organic Compounds Emissions
- Recyclability and Waste Reduction

Applications of Ionic Liquids

- Green Solvents in Chemistry
- Catalysis and Synthesis
- Extraction and Separation Processes
- Electrochemical Applications
- Gas Absorption and Storage
- Biocatalysis and Biotechnology
- Lubricants and Lubricant Additives
- Nanostructure Synthesis
- Drug Delivery

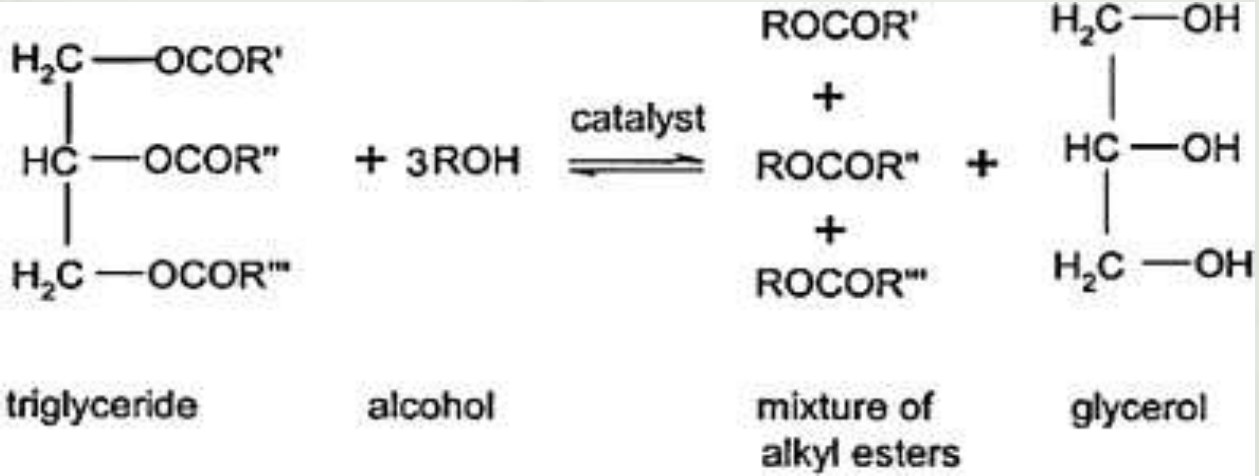
Green Fuels

What are green fuels

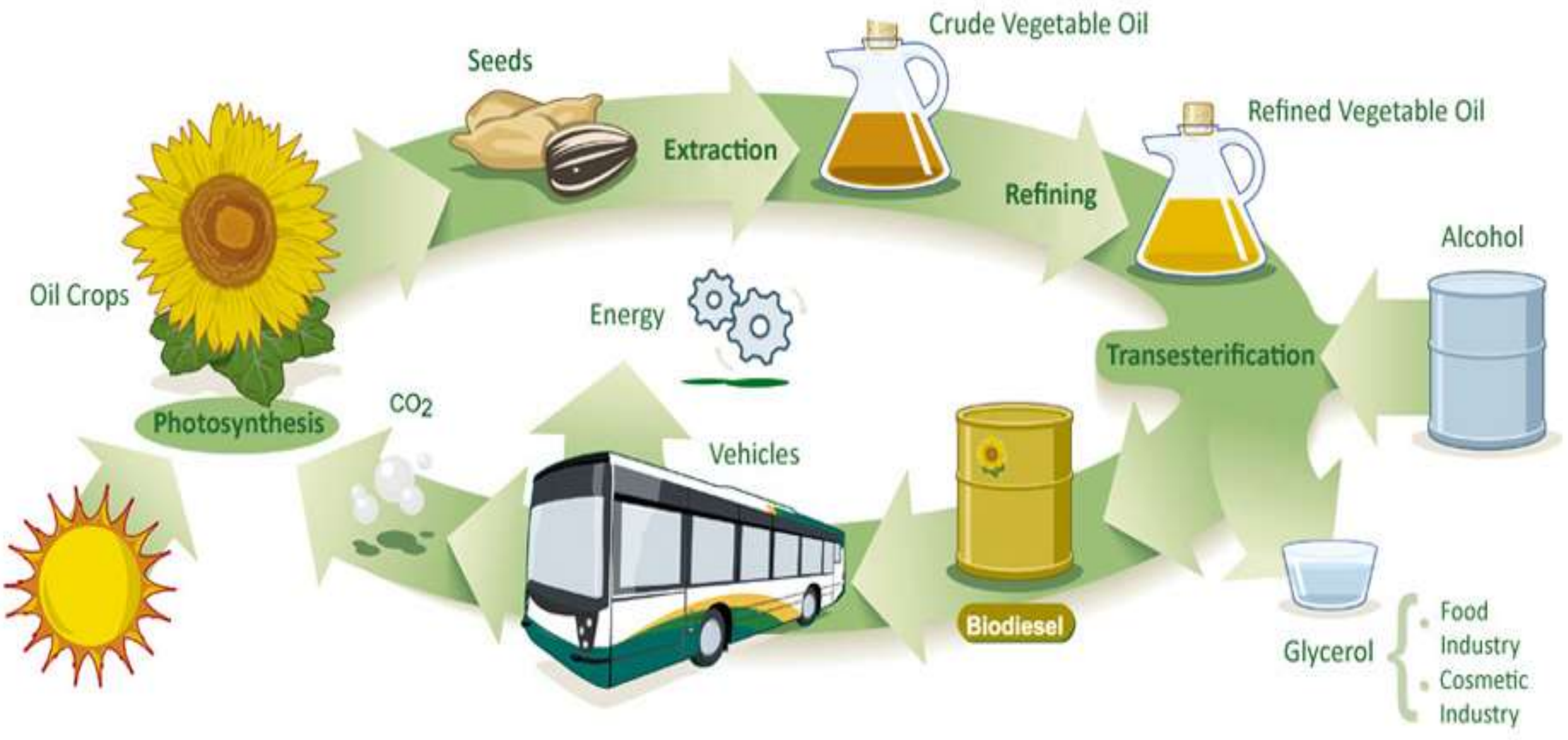
- Green fuel, also known as biofuel, is a type of fuel distilled from plants and animal materials, believed by some to be more environmentally friendly than the widely-used fossil fuels that power most of the world.

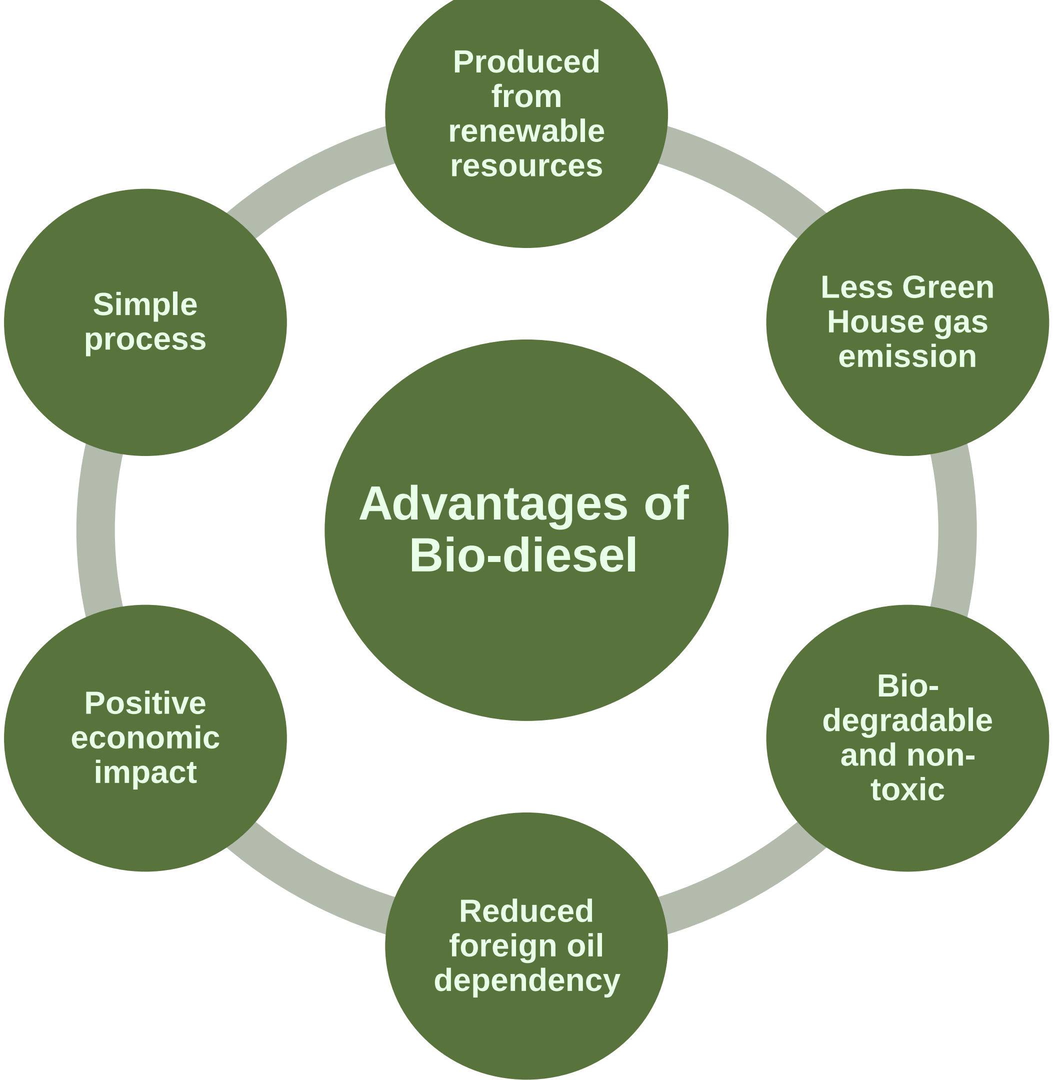
Bio-diesel : Synthesis

- A triglyceride source, typically vegetable oil, animal fat, or waste cooking oil is taken.
- Alcohol (usually methanol or ethanol) is added.
- A catalyst, sodium hydroxide (NaOH) or potassium hydroxide (KOH).
- It converts triglycerides into biodiesel.
- Separate the biodiesel from the glycerol.



The Biodiesel Cycle




Produced from renewable resources
Less Green House gas emission
Bio-degradable and non-toxic
Reduced foreign oil dependency
Positive economic impact
Simple process
Advantages of Bio-diesel

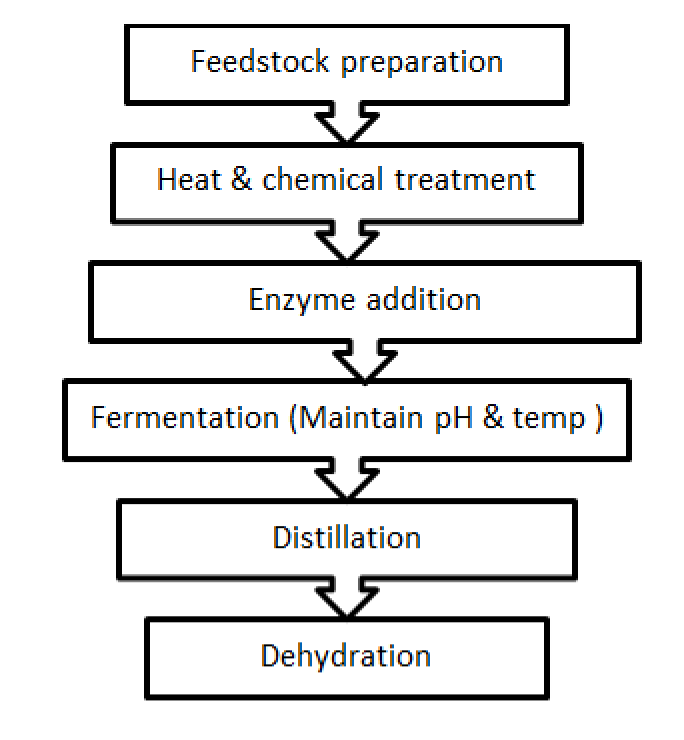

Food-fuel conflict
Land security
High production cost
High Viscosity pour point
Expensive
Choking of engines
Disadvantages of Bio-diesel

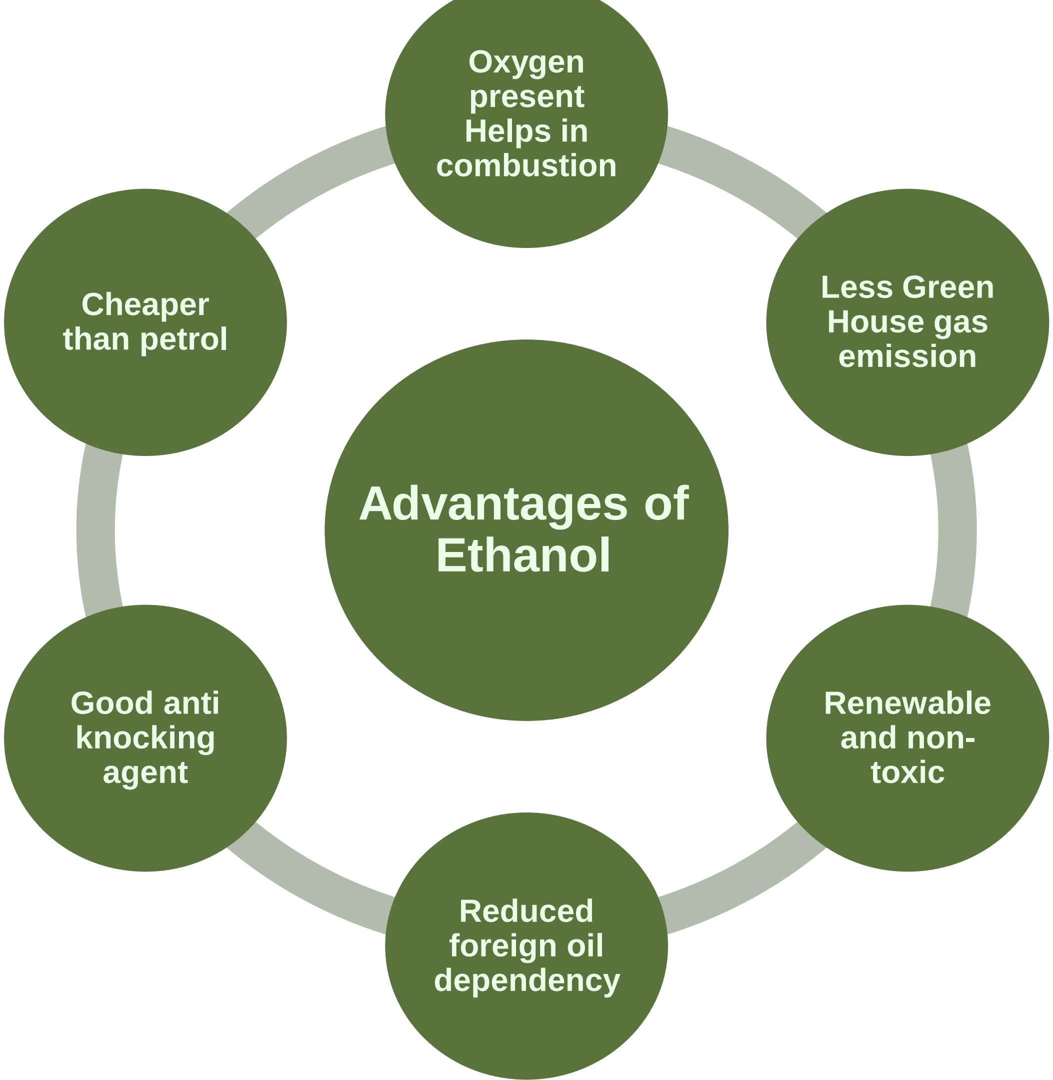
Ethanol : Synthesis

Ethanol can be manufactured by using molasses as raw material

$$C_{12}H_{22}O_{11} \xrightarrow{\text{invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$$




Advantages of Ethanol
Oxygen present Helps in combustion
Less Green House gas emission
Renewable and non-toxic
Reduced foreign oil dependency
Good anti knocking agent
Cheaper than petrol

THANK YOU