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APPLIED CHEMISTRY

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Lecture 32

VIPS
Technical Campus
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IN PURSUIT OF PERFECTION

SCHOOL OF ENGINEERING AND TECHNOLOGY

Twelve principles of green chemistry:

1. **Prevention:** It is better to prevent waste than to treat or clean up waste after it has been created.
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:** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.
4. **Designing Safer Chemicals:** Chemical products should be designed to effect their desired £unction while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries :** The use of auxiliary substances *(e.g.,* solvents or separation agents) should be made unnecessary whenever possible and innocuous when used
6. **Design for Energy Efficiency:** Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimized· If possible, synthetic methods should be conducted at ambient temperature and pressure
7. **Use of Renewable Feedstocks A** raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce derivatives: Unnecessary derivatization (use of blocking groups and temporary modification of physical chemical processes) should be minimized because such steps need additional reagents and generate waste.

9. **Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

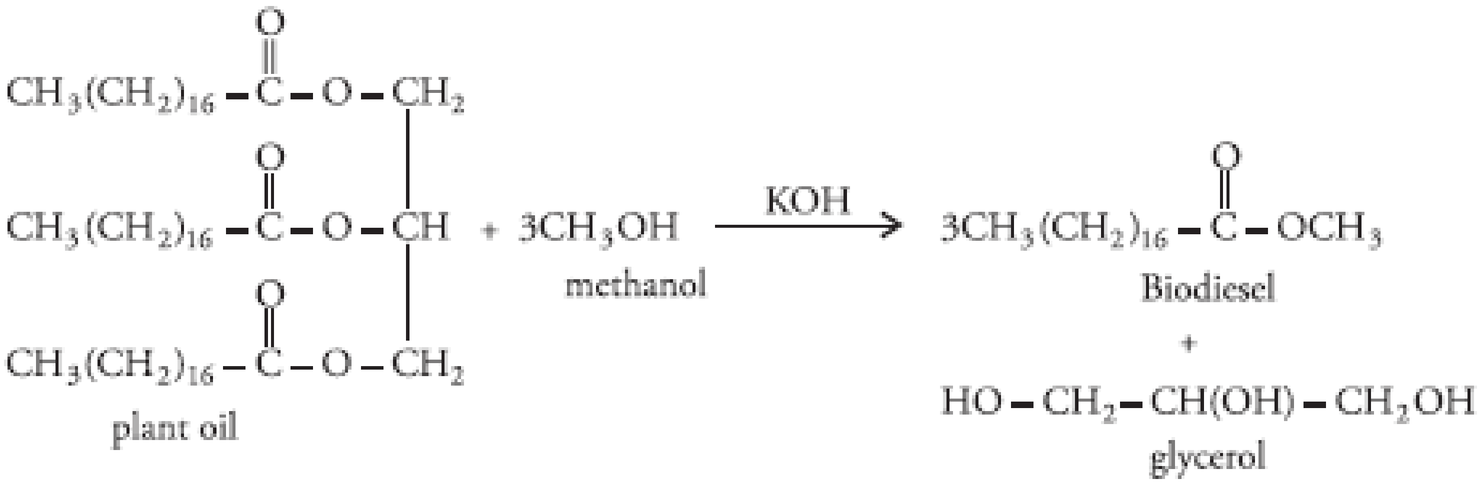
10. **Design for Degradation:** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11· **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.

12· **Inherently Safer Chemistry for Accident Prevention :** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

USE OF ALTERNATIVE FEEDSTOCKS (BIO FUELS)

- Feedstock is defined as any renewable, biological material that can be used directly as a fuel, or converted to another form of fuel or energy product.
- For energy use there are several options including wind, water, solar and nuclear as well as biomass. For organic chemical production the only non-fossil option is biomass.
- Green chemistry tries to utilize benign, renewable feedstocks as raw materials. The production of biodiesel oil is thus a promising possibility
- biodiesel oil is produced from cultivated plants oil, mainly vegetable oils such as soybean, sunflower, palm and rapeseed.
- The main constituents of vegetable oils are triglycerides, which are esters of glycerol with long-chain saturated and unsaturated fatty acids
- To convert raw oils into useful material, transesterification technology is used . The oil is reacted with a low molecular weight alcohol, commonly methanol, in the presence of a catalyst to form the fatty acid ester and glycerol. The ester is subsequently separated from the glycerol and used as biodiesel,



The advantages of using biodiesel oil are many.

- It is a fuel from renewable resources
- contrary to normal diesel oil, the combustion of biodiesel does not generate sulphur compounds
- and generally does not increase the amount of carbon dioxide in the atmosphere.

USE OF ALTERNATIVE SOLVENTS

- Solvents are used in almost all areas of chemistry
- Many of the commonly used solvents are volatile organic compounds (VOCs), hazardous air pollutants (HAPs), flammable,and/or toxic. They also pose serious environmental, health, and safety (EHS) concerns
- The main environmental issue concerned with VOCs is their ability to form low-level ozone and smog through free radical air oxidation processes.
- alternatives to organic solvents are needed to decrease the negative environmental impact of these substances.
- Some of the more common alternatives to using organic solvents are:

→use of safer/green solvents,

→use of water as solvent,

→solvent-free processes

→use of supercritical liquids (supercritical carbon dioxide (31.1°C, 73 atm),and water (374°C, 218 atm),

→Room-temperature ionic liquids

(a) Use of safer solvents

- Many of the commonly used solvents (benzene, chlorinated organic solvents, etc.) are known carcinogens, and many others pose hazardous threats to the environment.
- Solvents that are stable, inexpensive, and readily available, with an acceptable environment impact, are the most suitable.
- **Examples:** Isoamyl alcohol, 2-Ethylhexanol, 2-Butanol, 1-Butanol, t-Butyl acetate
- Green solvents are environmentally friendly solvents, or biosolvents, which are derived from the processing of agricultural crops.
- **Example:** →Ethyl lactate, for example, is a green solvent derived from processing corn.

→ Ethyl lactate is the ester of lactic acid. Lactate ester solvents are commonly used solvents in the paints and coatings industry and have numerous attractive advantages such as 100% biodegradable, easy to recycle, noncorrosive, noncarcinogenic, and nonozone-depleting

(b) Use of supercritical liquids

- The term "supercritical fluids" comprises the liquid and gases at temperatures and pressures higher than their critical temperatures and pressures
- Above the critical point the liquid-vapour phase boundary disappears and the supercritical liquid exhibits properties between those of gas and liquid.
- High compressibility of supercritical fluids in the vicinity of the critical point makes it easy to adjust density and solution ability by a small change of temperature or pressure. Due to this; the supercritical fluids are able to dissolve many compounds with different polarity and molecular mass.
- **Examples:**

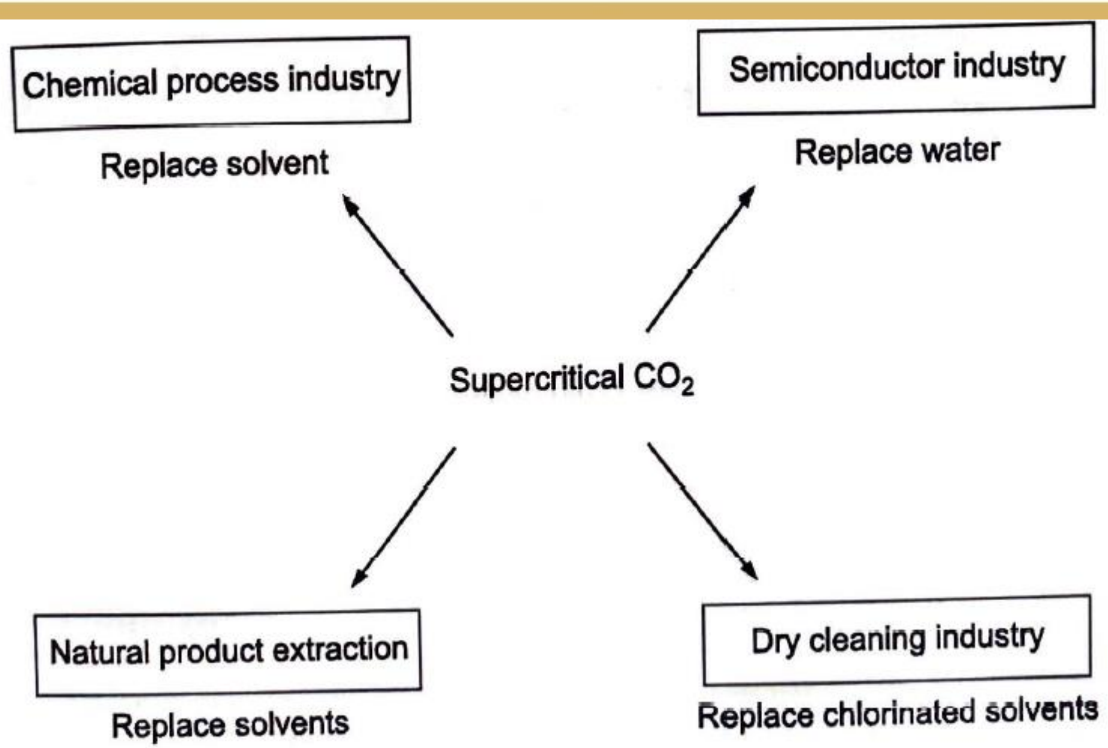
(i) Supercritical carbondioxide (SCCO_2)

→Carbon dioxide has a low critical temperature of 304 K and a moderate critical pressure of 73 bar. Carbon dioxide as a supercritical fluid is most frequently used as medium for reactions.

→It is inflammable, easily available and cheap.

→Its application gives considerable energy savings because the critical point is easy to reach

→ Carbon dioxide as a supercritical fluid dissolves non-polar compounds and some polar (e.g. methanol, acetone) like fluorocarbon solvents.



(ii) Supercritical water (SCH_2O):

→ Water has a critical temperature of 647 K and a critical pressure of 220 bar due to its high polarity

→ At this temperature, water loses many peculiar properties it has in its liquid state, such as hydrogen bonding and insolubility of non-polar substances in it.

→ When hydrogen bonds are broken, water molecules can dissolve chemicals that were previously insoluble. Thus the character of water at supercritical conditions changes from one that dissolves only ionic species at normal conditions to one that dissolves paraffins, aromatics, gases and salts.

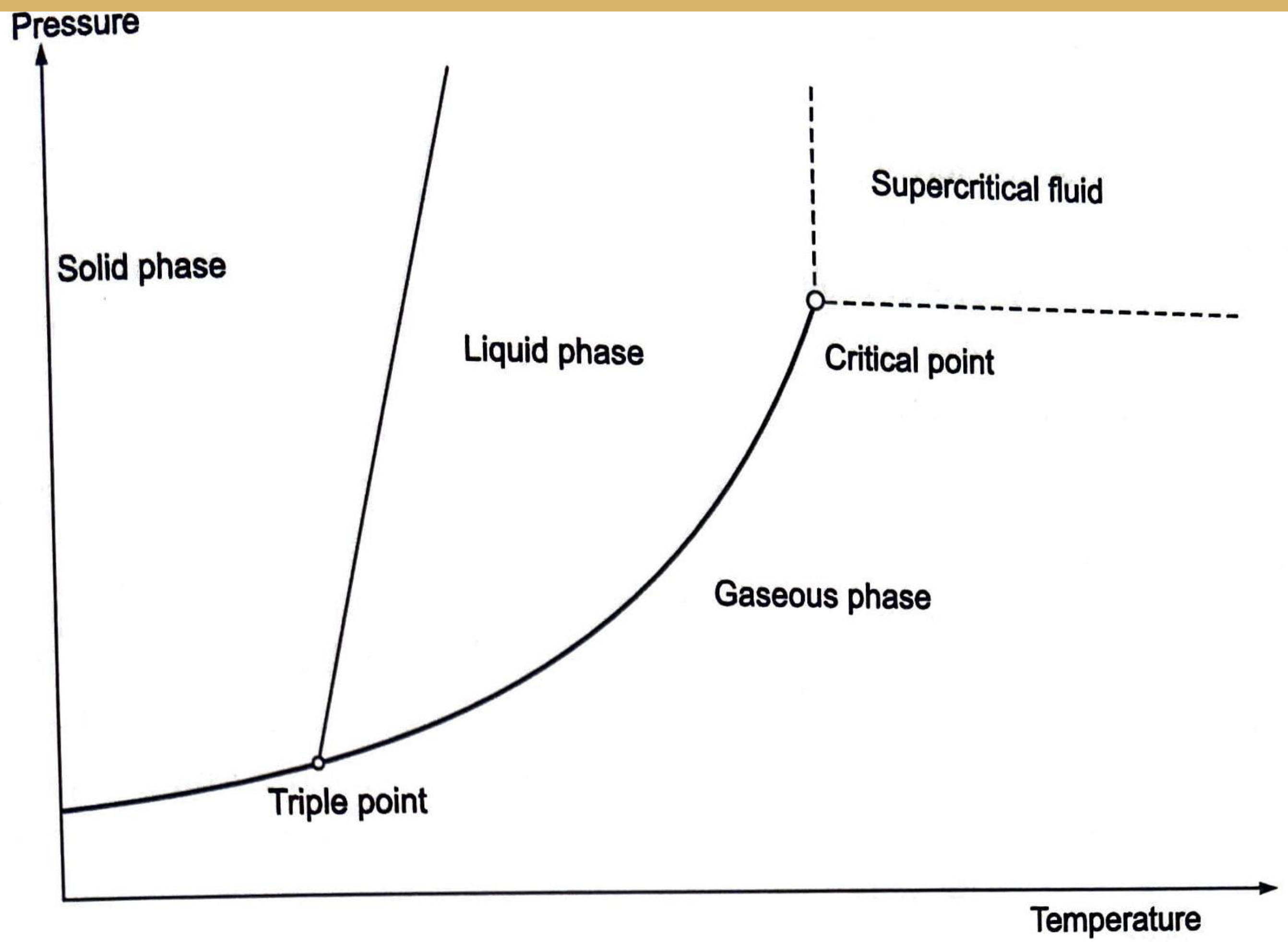


Fig 10.1 *Phase diagram showing supercritical fluid region*

(c) Room-temperature ionic liquids

→Ionic liquids are composed entirely of ions.

→An ionic liquid is a salt in which ions are poorly coordinated.

→By making simple changes in the structure of their ions, their properties like melting point, viscosity, density and hydrophobicity can be varied.

→Exhibit high thermal stability and high thermal conductivity, absence of volatility and lower toxicity

→The first room-temperature ionic liquid $(EtNH_3)(NO_3)$ was discovered in 1914, and later . on binary ionic liquids from mixtures of aluminium (III) chloride and N-alkylpyridinium or dialkylimidazolium chloride were discovered.

→Ionic liquids have been found useful for a wide range of chemical reactions and processes, including hydrogenation reactions, biocatalysis reactions such as transesterification and hydrolysis, and electrochemical applications such as battery electrolytes

(d) Water as Solvent

- The use of water as solvent for organic reactions is one of the finest solutions to the problem of solvent toxicity and disposal.
- The chemistry in natural systems is based on water.
- The use of water as solvent for synthetic chemistry holds great promise for the cheaper and less hazardous production of chemicals.

(e) Solvent free conditions

- **Advantages of solvent free conditions**:

→ There is no reaction media to collect, dispose of, or purify and recycle.

→ On a laboratory's preparative scale there is often no need for specialized equipment.

→ Extensive and expensive purification procedures such as chromatography can often be avoided due to the formation of sufficiently pure compounds.

→ Greater selectivity is often observed.

→ Reaction times can be rapid, often with increased yields and lower energy usage.

DESIGN OF ALTERNATIVE REACTIVE METHODOLOGY

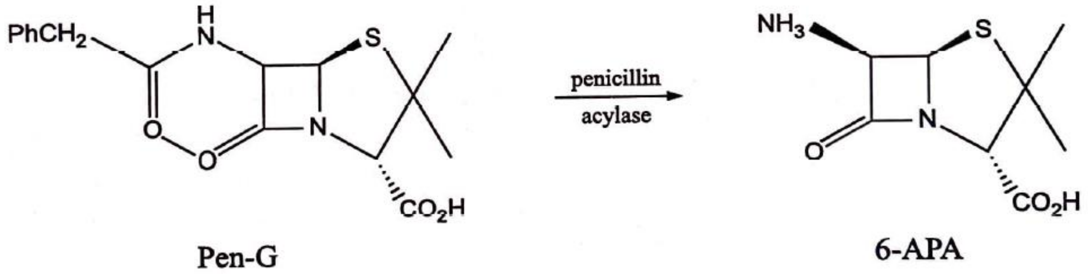
- Industries have resorted to alternative methodologies such as heterogeneous catalytic, biocatalytic, and fermentation routes to improve process efficiency, reduce energy usage, and decrease raw material usage.
- The **key points** are:

→Replacement of the chemical step with a biocatalytic step, which is followed by replacing the entire multiple-step process with a single fermentation process

→Developing atom-economical processes

→Use of enzyme technology has become the focus of many pharmaceutical, food, and specialty industries.

- **Example: 1**. In the pharmaceutical industry, the largest scale biocatalytic process is the conversion of the fermentation product penicillin G into 6-aminopenicillanic acid by the enzyme penicillin acylase

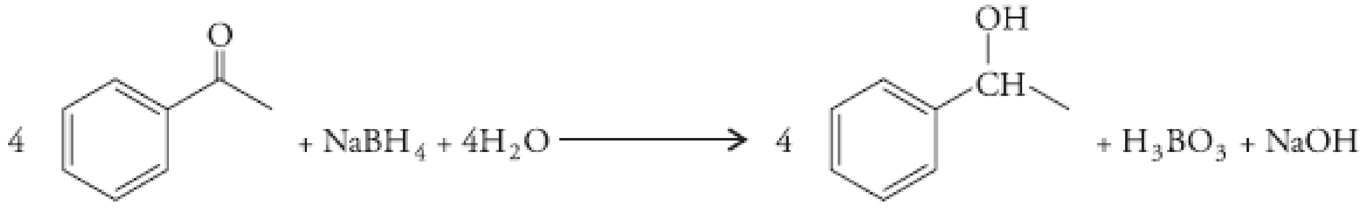


2. The leather industry is developing processes that use lipase instead of harsh chemicals for dehairing, while the semiconductor industry is using SO_3 and SC-CO_2 for cleaning printed circuit boards.

- **Atom Economy:** One of the major areas of reactive methodology is "Atom Economy": Atom economy is a method of determining the efficiency with which raw materials (reactants or feedstocks) are used regardless o/the percentage yield obtained in the reaction.
- Atom economy is a measure of the percentage of reactant atoms leading to product formation. Most reactions have a yield of about 70–90%. The atoms that are not incorporated in the product result in the generation of waste.

$$\text{Percentage atom economy} = \frac{\text{Formula weight (FW) of the desired product}}{\text{Formula weight (FW) of all reactants}} \times 100$$

- Example: Consider the reduction of ketone to secondary alcohol using sodium boron hydride as the reductant



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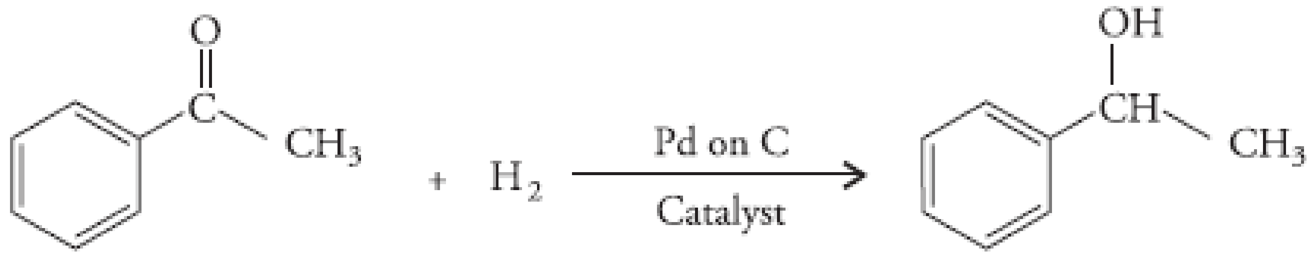
Reagent formula	Reagent FW	Utilised atoms
1. C_8H_8O	$120 \times 4 = 480$	$C_8H_{10}O$
2. $NaBH_4$	38	
3. H_2O	$18 \times 4 = 72$	
Total	590	$122 \times 4 = 488$

$$\text{Percentage atom economy} = \frac{488}{590} \times 100 = 82.70\%$$

- Nearly 17.3% of the reactant atoms is wasted in unwanted side products. Green chemistry envisages a better atom economy which can be achieved by an alternative reaction pathway.
- If molecular hydrogen is used as a reducing agent in the presence of palladium and charcoal as a catalyst, then the atom economy rises to 100% and there is no generation of waste.



Weight of all the reactants = 120 + 2 = 122

Weight of utilised atom = 122

$$\text{Atom economy} = \frac{122}{122} \times 100 = 100\%$$

USE OF INNOCUOUS REAGENTS

- Principles of Green Chemistry guide us to make use of reagents that are inherently less hazardous and are catalytic whenever feasible.
- **Example:** → Water is generally disinfected by a municipality using potentially hazardous chlorine gas. The reaction occurs as follows.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

→ HOCl is a good disinfecting agent as it kills bacteria and virus by inactivating their enzymes. However, the use of chlorine gas poses a danger by the formation of undesirable trihalomethanes.

→ This problem is overcome by the use of ClO_2 which although a very good disinfectant, is at the same time, dangerously reactive and unsafe to store and transport. Hence, it is prepared in small quantities on the site.

$$2NaClO_2\,(s) + Cl_2\,(g) \rightarrow 2ClO_2\,(g) + 2NaCl(s)$$

Minimizing Energy Consumption

- Chemical reactions generally use thermal sources of energy derived from fossil fuels. This energy is non-specific and does not directly attack the bonds or chemicals undergoing the reaction.
- A large portion of the energy goes into heating the reactor, solvents or is dissipated into the environment.
- In order to reduce the hazards caused by the use of conventional sources of energy, these days microwave and ultrasonic radiation assisted chemical reactions are carried out. These methods are safe, energy-efficient, clean and increase the rate of the reaction.

a) Ultrasound radiation

- Ultrasound refers to sound waves with frequencies higher than those detectable by the human ear, *i.e.* around 18 kHz.
- Ultrasound is known to induce new reactions, leading to the formation of unexpected chemical species.
- The term sonochemistry is used to denote reactions initiated by ultrasound.
- . Ultrasound is known to enhance the reaction rate, thus minimizing the duration of a reaction. The real benefit of using ultrasound lies in its unique selectivity and reactivity enhancement.

- The type of reactions that can be carried out under sonochemical conditions:

→oxidation, which can often be carried out more rapidly at lower temperatures

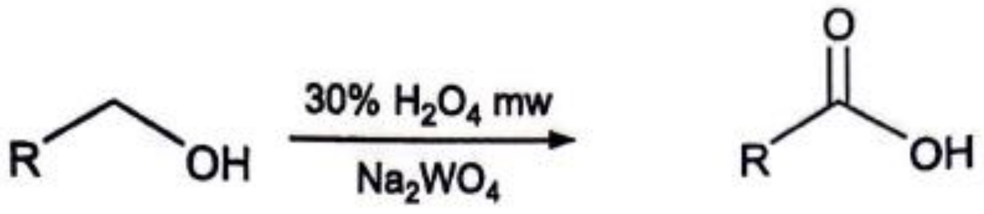
→radical reactions, with the radicals being generated under mild conditions

→Synthesis of nanoparticles

→Ultrasound has uses in industry, such as welding, cutting, emulsification, cell disruption, and atomization

b) **Use of microwave synthesis**

- Microwaves have wavelengths between 1 mm and 1 m and hence have similar frequencies to radar and telecommunication devices
- Microwave assisted synthesis requires less energy, generates less waste and avoids the use of solvent.
- They are cleaner and eco-friendly with a high product yield and minimum waste. The reaction occurs at a very fast rate.
- Microwave cooking is replacing cooking using conventional fuels because it is fast and saves time and energy.
- **Example:** A range of primary alcohols have been oxidized to the corresponding carboxylic acids using sodium tungstate as catalyst in 30% aqueous hydrogen peroxide. Yields, although variable, of up to 85% have been achieved in a rapid, clean, safe and atom efficient reaction



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