Green Chemistry

GREEN
CHEMISTRY

Sustainable Development

United Nations 1987,

"Meeting the needs of the present without compromising the ability of future generations to meet their own needs."

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Sustainable Development

1. Economic sustainability
2. Social sustainability ✓
3. Environmental sustainability

Closely related to Green Chemistry

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Green Chemistry

- During the early 1990s,

  ➔ the US Environmental Protection Agency (EPA) coined the phrase "green chemistry"

  ➔ promote innovative chemical technologies

  ➔ reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products

Green Chemistry

Green chemistry is about the design of chemical products and processes that reduce or eliminate the **use** and **generation** of hazardous substances.

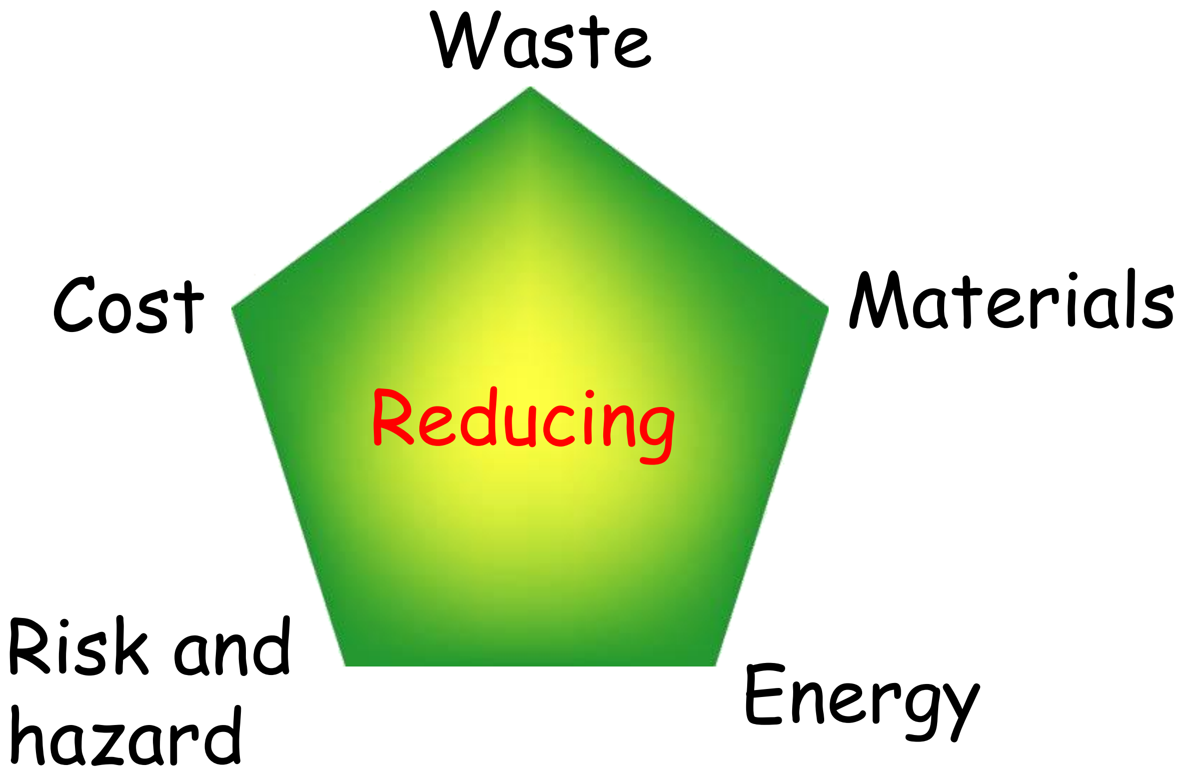
Green chemistry seeks to **reduce** and **prevent pollution** at its **source**.

Green Chemistry

Green Chemistry can also be described as

1. Sustainable chemistry
2. Chemistry that is benign by design
3. Pollution prevention at the molecular level
4. All of the above

Green chemistry can be regarded as a reduction process.



The 12 Principles of Green Chemistry:

1. Waste Prevention
2. Maximizing Atom Economy
3. Using Less Hazardous Chemical Syntheses
4. Producing Safer Chemical Products
5. Using Safer Solvents and Auxiliaries
6. Designing for Energy Efficiency
7. Using Renewable Raw Materials
8. Reducing Derivatives (fewer steps)

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The **12** Principles of Green Chemistry:

9. Using Catalysts
10. Designing Degradable Chemical Products
11. Developing Real-time Analysis for Pollution Prevention
12. Minimizing the Potential for Chemical Accidents

1. Waste prevention

It is better to prevent the formation of waste than to treat or clean up the waste.

Chemical wastes are undesirable products from chemical reactions. They are usually hazardous to the environment.

Industrial processes should be designed to minimize the generation of waste.

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2. Maximizing atom economy

Traditionally, the success of a chemical reaction is judged by the percentage yield of product.

It is possible to achieve **100%** yield but the reaction may generate waste that is far greater in mass and volume than that of the desired product.

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Consider the following reaction:

$$AgNO_3(aq) + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$$

~100% yield

undesirable

Suggest reactions that have no undesirable products.

$Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(s)$

Direct combination

$CH_2{=}CH_2(g) + H_2(g) \rightarrow C_2H_6(g)$

Addition reaction

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Concept of atom economy

$$AE = \frac{\text{Mass of desired product}}{\text{Total mass of all products (or reactants)}} \times 100\%$$

The greater the value of the atom economy, the better is the reaction to convert all the reactant atoms to the desired product.

$\Rightarrow$ Less waste

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Calculate the **atom economy** of each of the following conversions

$$C_4H_9OH + KBr + H_2SO_4 \rightarrow C_4H_9Br + KHSO_4 + H_2O$$

136.9 136.2 18.0

$$AE = \frac{136.9}{136.9 + 136.2 + 18.0} \times 100\% = 47.0\%$$

$$3C_4H_9OH + PBr_3 \rightarrow 3C_4H_9Br + H_3PO_3$$

3×136.9 82.0

$$AE = \frac{3 \times 136.9}{3 \times 136.9 + 82.0} \times 100\% = 83.4\%$$

Greener

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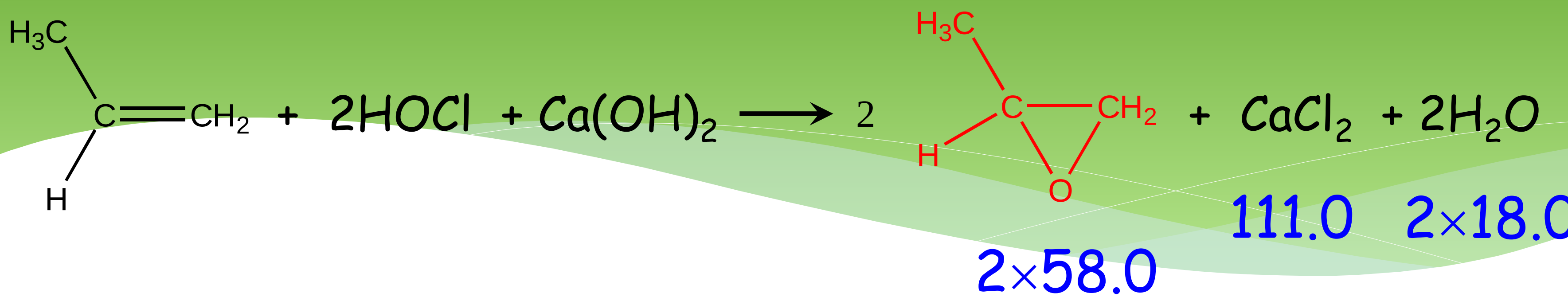
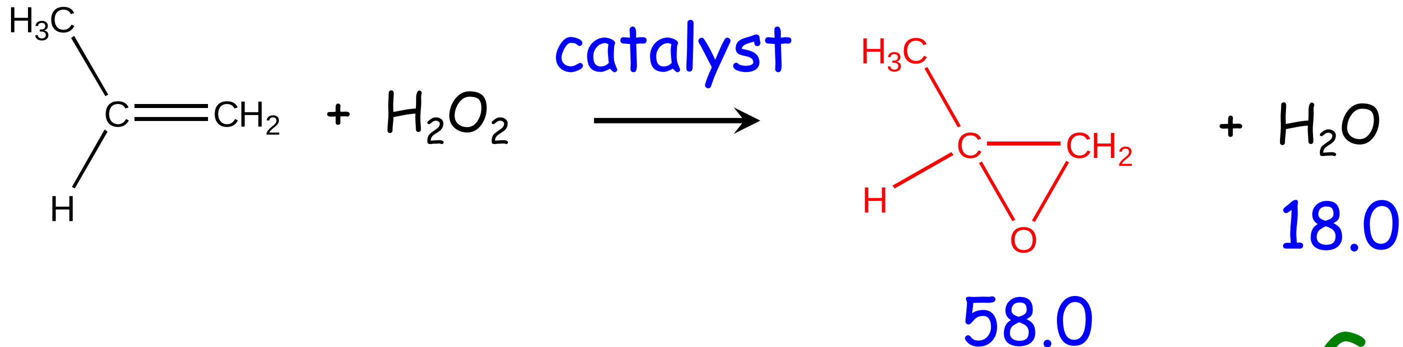


$$AE = \frac{2 \times 58.0}{2 \times 58.0 + 111.0 + 2 \times 18.0} \times 100\% = 44.1\%$$



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$$AE = \frac{58.0}{58.0 + 18.0} \times 100\% = 76.3\%$$

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3. Using less hazardous chemical syntheses

Chemical syntheses should be designed to use or generate substances that possess little or no toxicity to humans and the environment.

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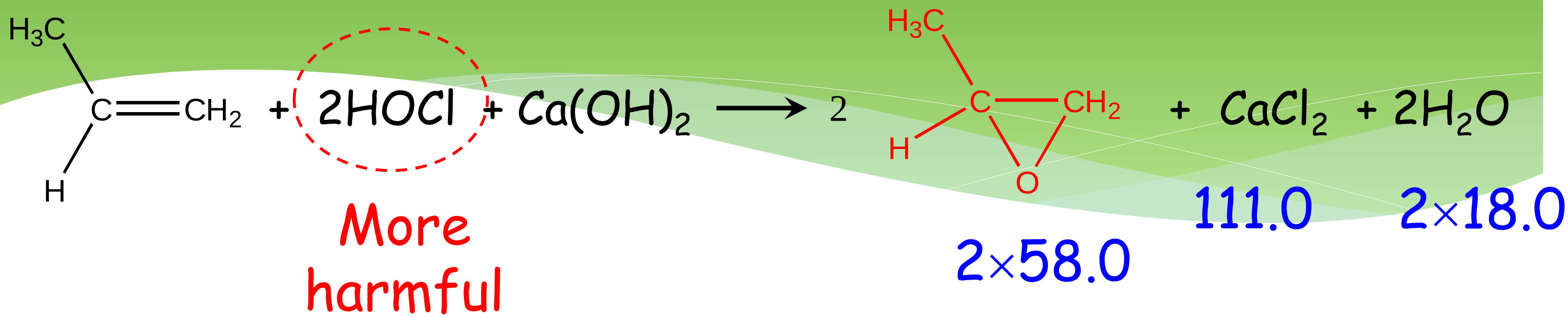

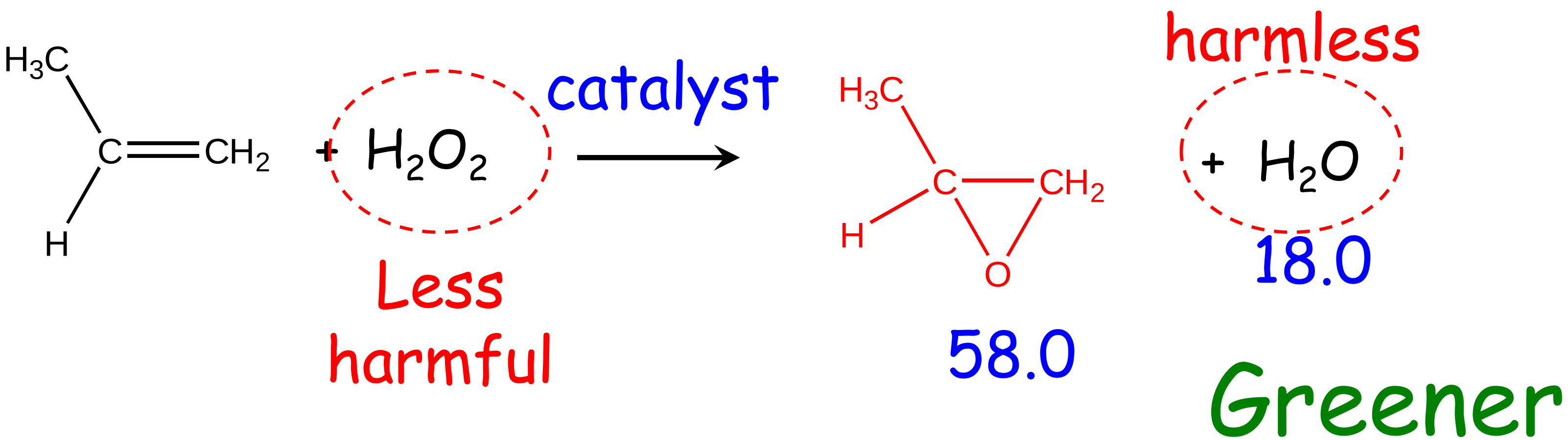

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Another example:

Consider the synthesis of adipic acid ($HOOC(CH_2)_4COOH$).

Adipic acid is the essential feedstock for making synthetic fibres such as nylon.

Traditional method

$$C_6H_6 \longrightarrow HOOC(CH_2)_4COOH$$

benzene

New method

$$C_6H_{12}O_6 \longrightarrow HOOC(CH_2)_4COOH$$

D-glucose

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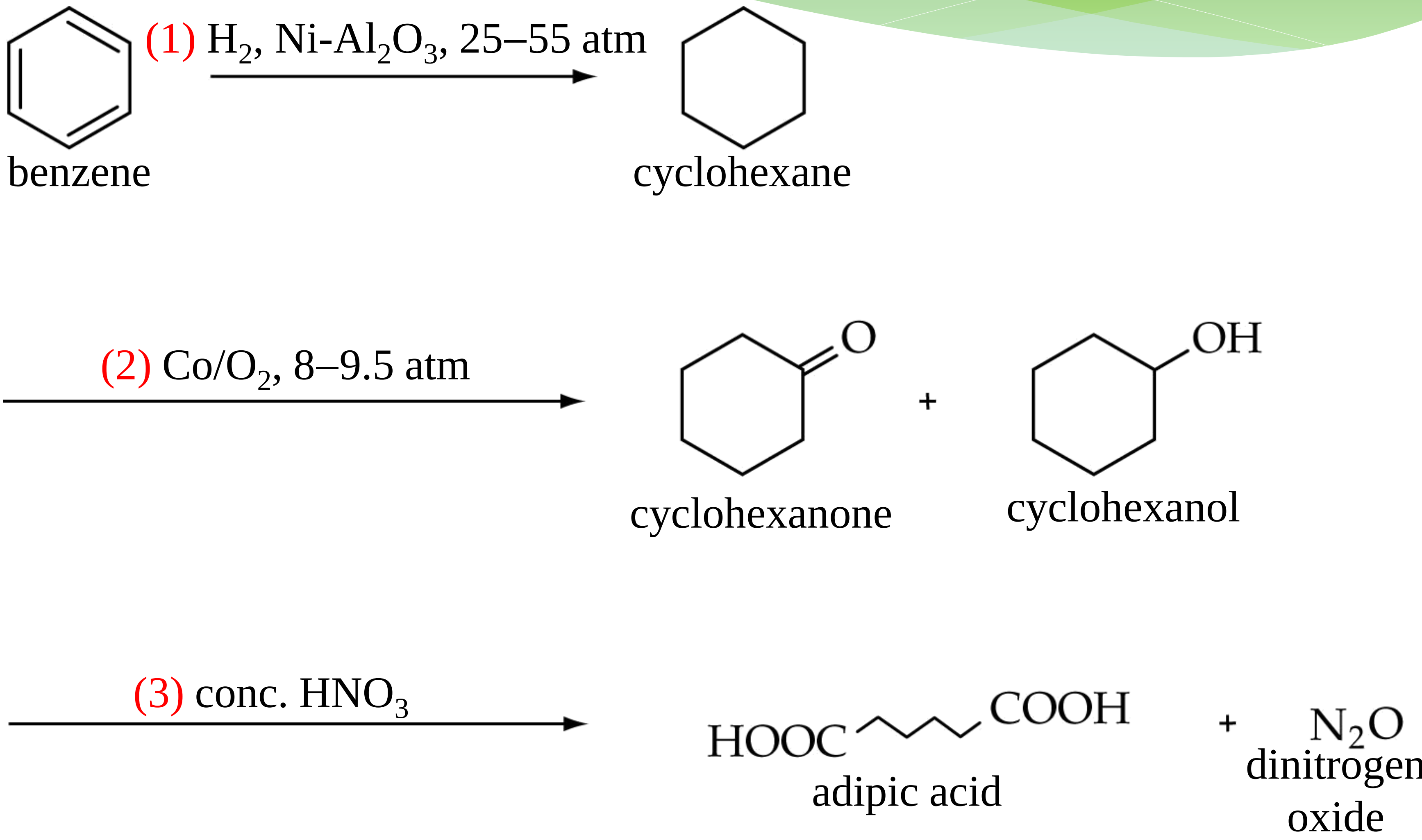
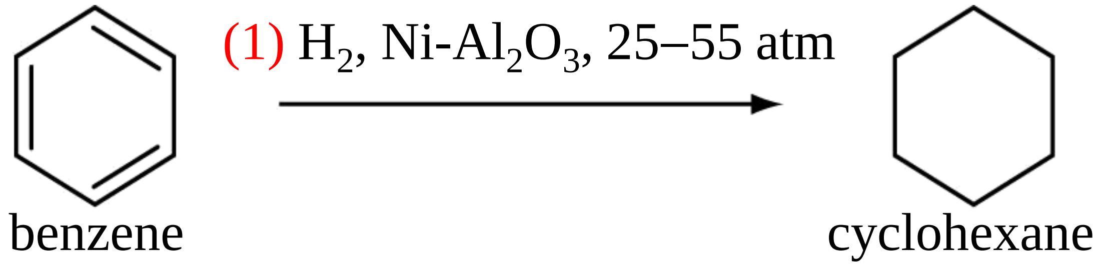
Traditional Method



Traditional Method

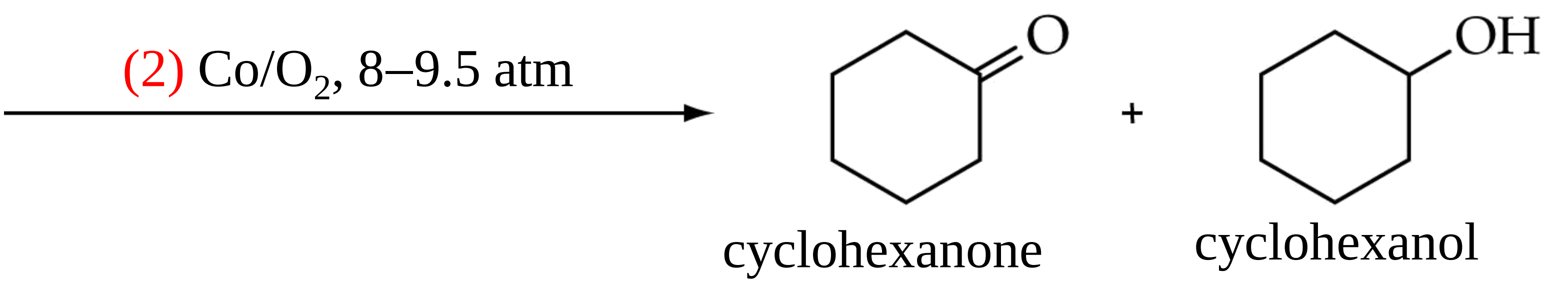
The synthesis has the following **risks** and **hazards**:

In step 1, the starting material for the synthesis is benzene, which is a known carcinogen.



Traditional Method

In step 2, the oxidation of cyclohexane with air may lead to an uncontrolled reaction. It has the **risk** of **explosion**.

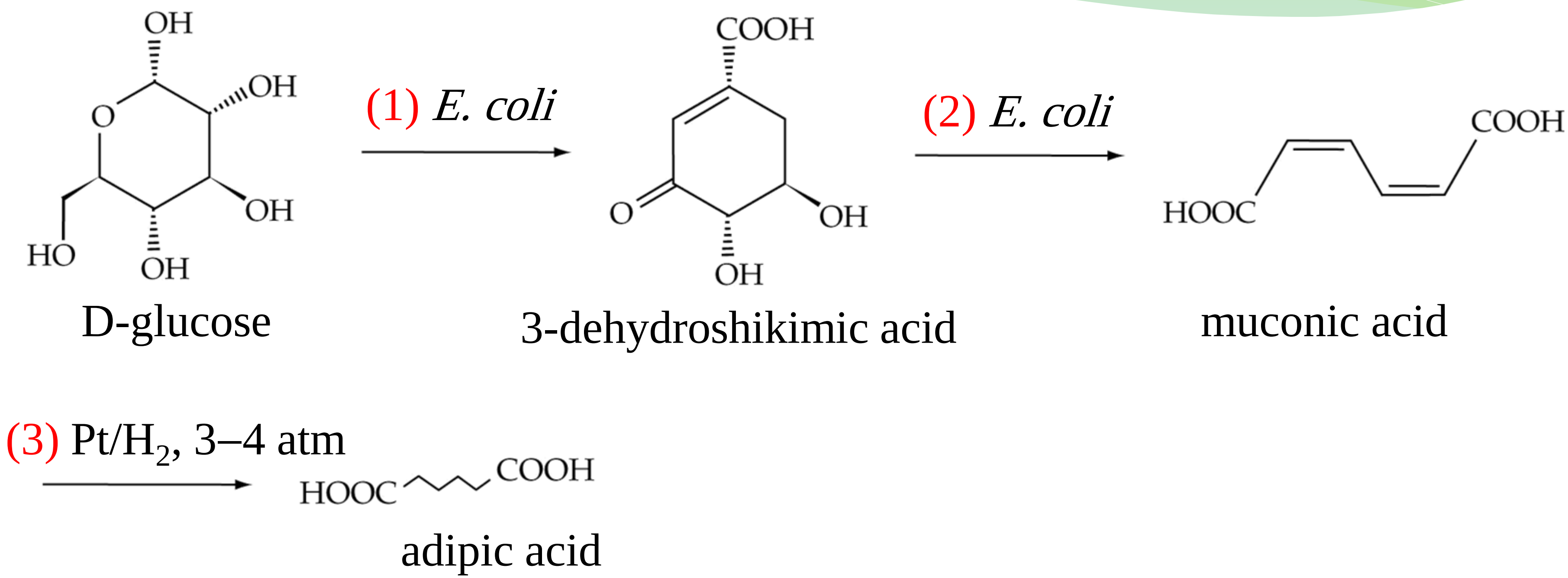


Not all of the cobalt catalysts can be recovered. This may lead to the **disposal** of a heavy metal to the environment.

Traditional Method

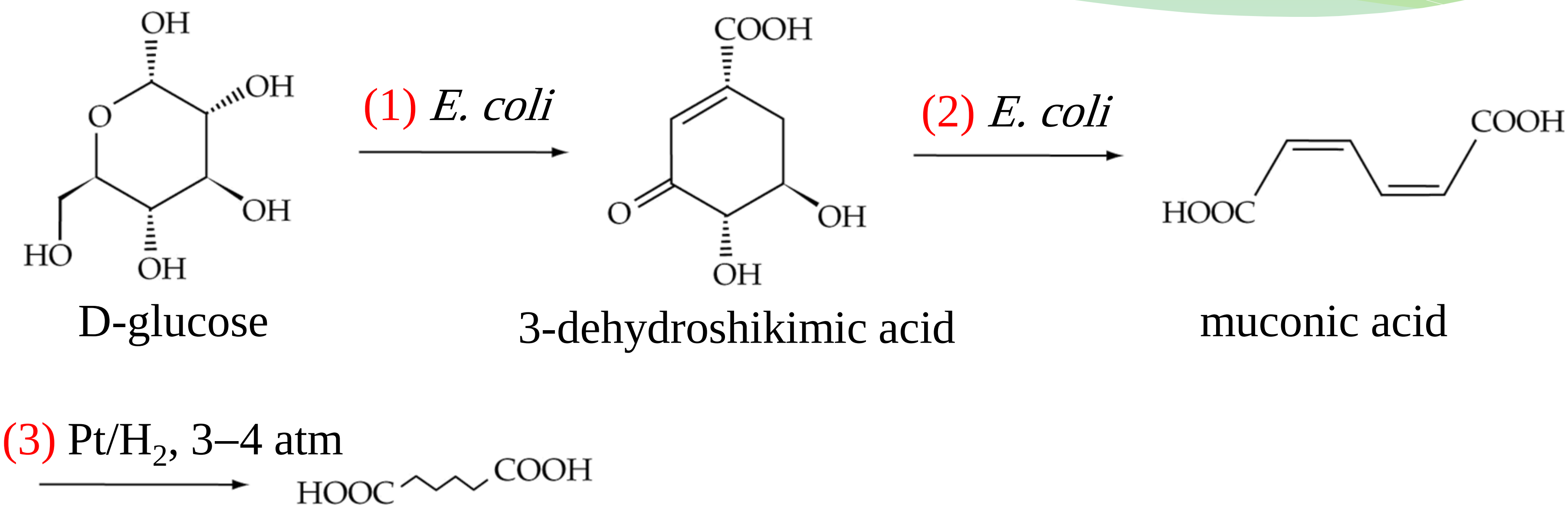
In step 3, dinitrogen oxide or nitrous oxide (N_2O) gas is produced as a by-product. It is a **greenhouse gas** with an effect which is 200 times the effect of carbon dioxide.

biosynthetic pathway



1. the starting material, glucose, is harmless.

biosynthetic pathway



D-glucose
3-dehydroshikimic acid
muconic acid
adipic acid

2. E. coli is used to catalyse two steps of the reaction. This **reduces** the use of certain chemical reagents with significant toxicity.

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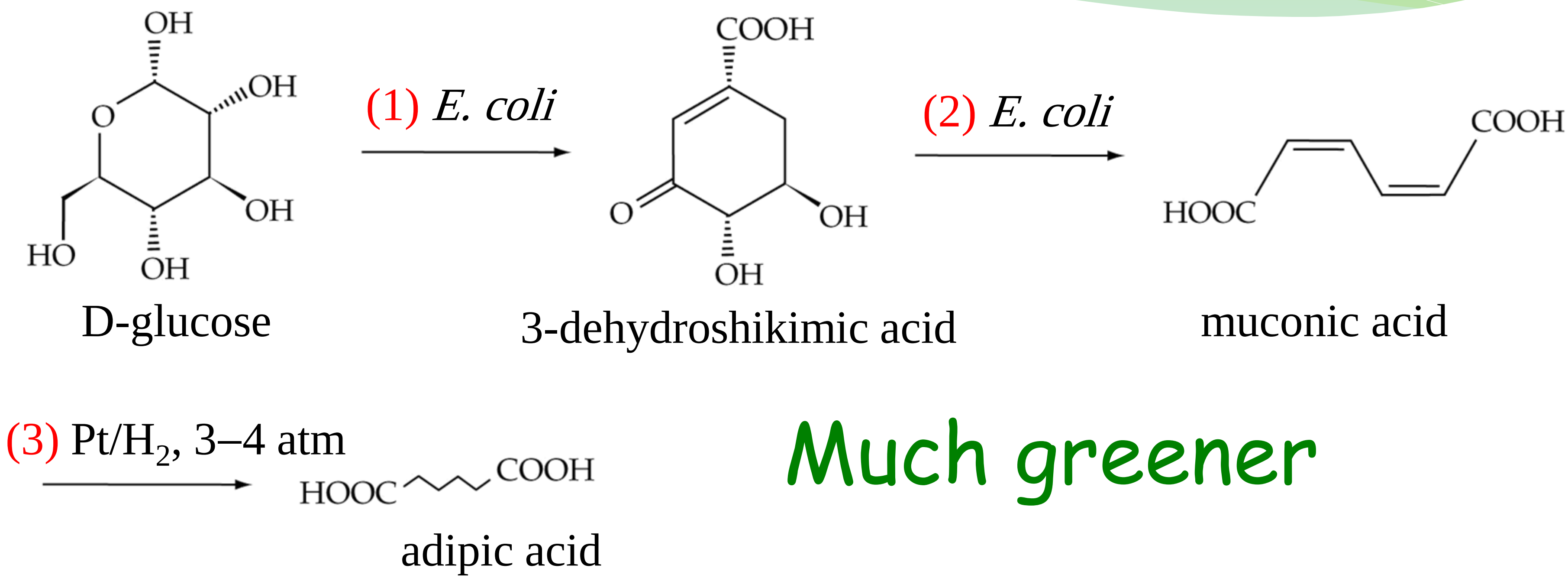
biosynthetic pathway



Much greener

3. there are **no by-products** generated during the synthesis.

4. Producing safer chemical products

The chemical products synthesized should be **safe to use**.

For example, chemicals called organotin compounds (Anti-biofouling agent) were used in large ships to prevent accumulation of barnacles and marine plants traditionally.

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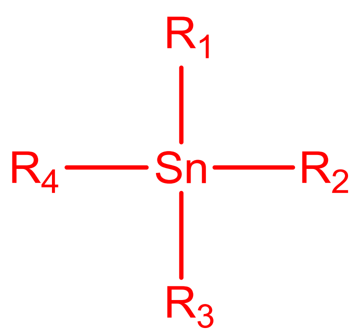

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The accumulation of **barnacles** on the ship may increase the resistance to its movement.

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Microbial Home : Market Applications : Paint and Coatings : Marine Antifouling : Products

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Marine Antifouling Products

SEA-NINE™ 211N Marine Antifouling Agent

TDS

- Recipient of the First Presidential Green Chemistry Challenge Award in 1996 (U.S. EPA)
- Broad spectrum, effective against a broad array of marine fouling organisms
- Active rapidly biodegrades in the environment
- Minimal potential for bio-accumulation
- Excellent safety profile
- Low human health risk
- Excellent eco-toxicological profile
- Effective by itself or in combination with other biocides

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Dow Microbial Control

SEA-NINE™ 211N Marine Antifouling Agent

General

SEA-NINE™ 211N marine antifouling agent is a rapidly biodegradable settlement inhibitor, developed by The Dow Chemical Company for the new generation of environmentally acceptable marine antifouling paints for ships and marine structures.

Physical Properties

The following are typical properties of SEA-NINE 211N; **they are not to be considered product specifications.**

Appearance	clear, yellowish liquid
Flashpoint (closed cup)	28°C (solvent)
Vapour pressure	5.0 mmHg at 16°C
Boiling point	138-144°C
Melting or freezing point	-3°C
Density at 25°C	0.94 g/ml
Viscosity (Brookfield) at 25°C	1.3 mPa.s
Colour, Gardner (VCS)	6

Special Features and Benefits

- Highly effective antifouling agent against bacterial slime, algae, barnacles, tubeworms, hydroids, bryozoa, tunicates and diatoms
- Free from heavy metals
- Excellent long term efficacy
- Stable in all major types of marine coating systems
- Global registrations including BPD notification and support
- Global environmental acceptance and compatibility

Key Environmental Characteristics

- Rapid degradation of the antifouling agent in the environment
- Rapid environmental partitioning, resulting in a limited bioavailability to non-target organisms
- Acceptable risk to non-target organism at concentrations presents in the environment
- Minimal bioaccumulation of toxicologically significant compounds
- Non-hazardous environmental concentrations at recommended use levels

For its environmental properties, SEA-NINE 211N gained the first ever Green Chemistry Challenge Award in the category for Designing Safer Chemical Products awarded by the United States Environmental Protection Agency.

5. Using safer solvents and auxiliaries

The solvents and auxiliaries (e.g. drying agent, blowing agent, etc.) used in chemical syntheses will become part of the wastes.

They may cause environmental pollution and health hazard.

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CFCs ;

unreactive

volatile liquids or easily liquefied gases

low flammability

low toxicity

$\Rightarrow$ Cleaning solvents

Propellants

Refrigerants

Blowing agents

They were eventually banned because they **deplete** the **ozone** layer.

Screening of UV radiations by ozone layer

$$2O_3 \underset{\lambda=250\ nm}{\overset{\lambda=215\text{-}295\ nm}{\rightleftharpoons}} 3O_2$$

~99% of UV radiation from the sun are screened out

$$CFCl_3 \xrightarrow{uv} CFCl_2 + Cl\bullet$$

$$Cl\bullet + O_3 \rightarrow ClO + O_2$$

$$ClO + O_3 \rightarrow Cl\bullet + 2O_2$$

} chain reaction

One Cl• free radical can destroy 100,000 ozone molecules !!

Many solvents currently used in the chemical industry are harmful and volatile.

They are known as **V**olatile **O**rganic **C**ompound**s** (VOCs)

E.g. Propanone, benzene, dichloromethane, dibromomethane, chloroform and carbon tetrachloride.

$$\text{VOCs} + NO_x \xrightarrow{\text{UV}} \text{photochemical smog}$$

Use safer solvents and auxiliaries – **How?**

A. Use of **water** as an environmentally innocuous solvent;

B. Use of liquid or supercritical carbon dioxide;

C. Use of non-volatile solvents such as **ionic liquids**;

D. Use of hybrid solvent systems of the three above;

E. Solvent-less reactions;

A. Aqueous Media as Solvents for Chemical Synthesis and Processes.

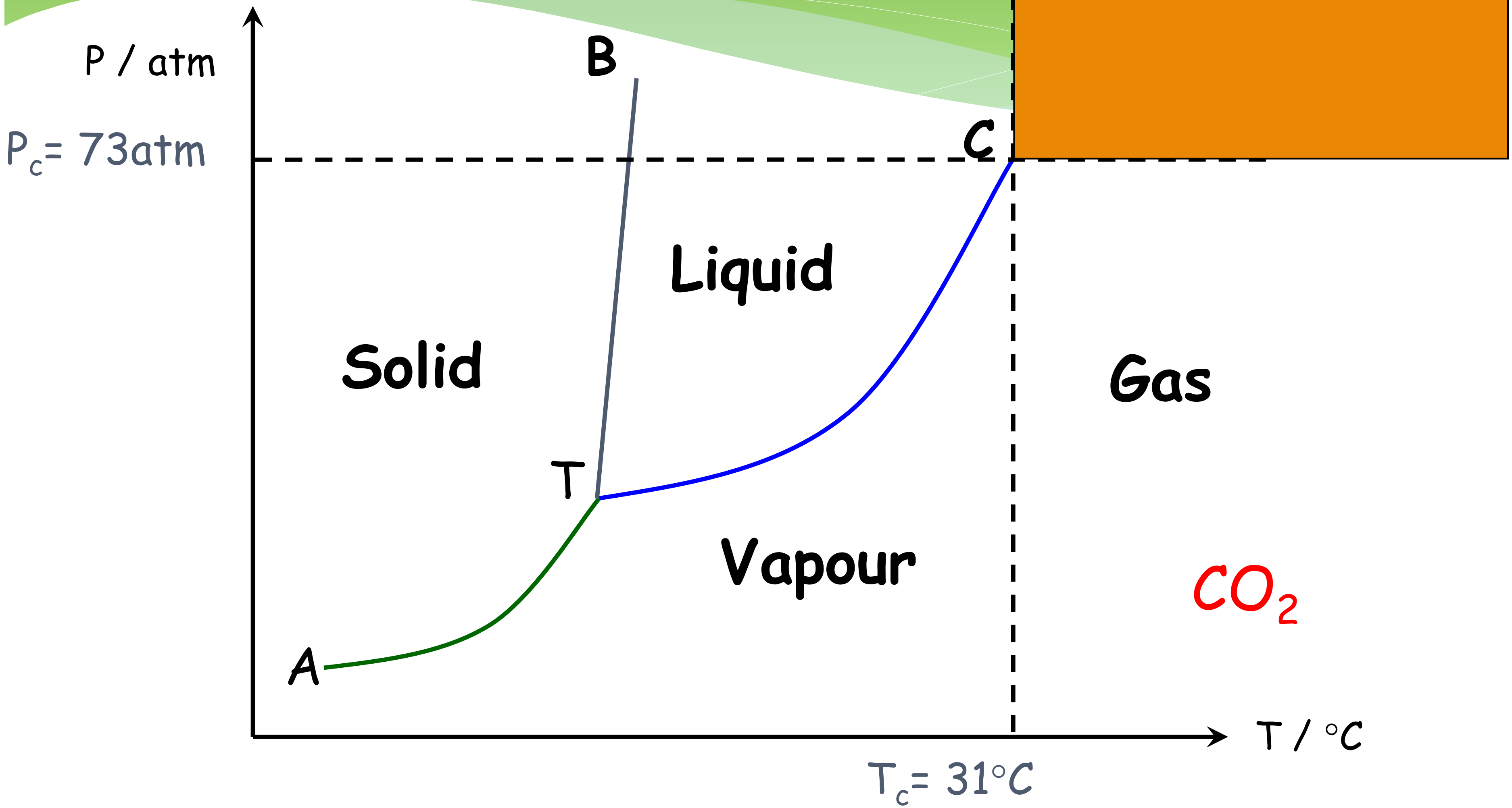
Advantages:

- Non-toxic
- Non-flammable
- Inexpensive
- Environmentally benign

Disadvantages:

- Many organic compounds are not soluble in water

B. Use of liquid or supercritical **carbon dioxide**



Using supercritical CO_2 as solvent in decaffeination

Coffee beans —**decaffeination**→ Coffee beans

with caffeine → without caffeine

In the past, solvents used for decaffeination was harmful to the environment and human beings

E.g. $CHCl_3$, CH_2Cl_2, benzene

Advantages of decaffeination using **scCO_2**

Supercritical CO_2 has :

1. the high diffusion of a **gas** that allows it to penetrate deep into the beans

2. the high density of a **liquid** that dissolves 97-99% of the caffeine

3. Will not reinforce the greenhouse effect since scCO_2 comes from the atmospheric CO_2

Advantages of decaffeination using scCO_2

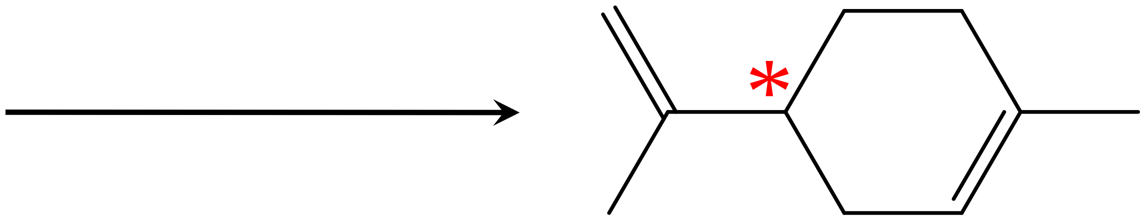
Coffee beans with caffeine $\xrightarrow{\text{Supercritical } CO_2}$ Coffee beans without caffeine

Limitations and disadvantages of decaffeination ?

1. Decaffeination is based on solvent extraction (principle of partition equilibrium).
   $\rightarrow$ complete removal of caffeine is not possible
2. Other compounds are lost during the process.
   $\rightarrow$ the flavor and aroma are changed.

Essential oils are organic compounds that are extracted from natural sources and used in many products such as flavorings, fragrances, and cleaning products.

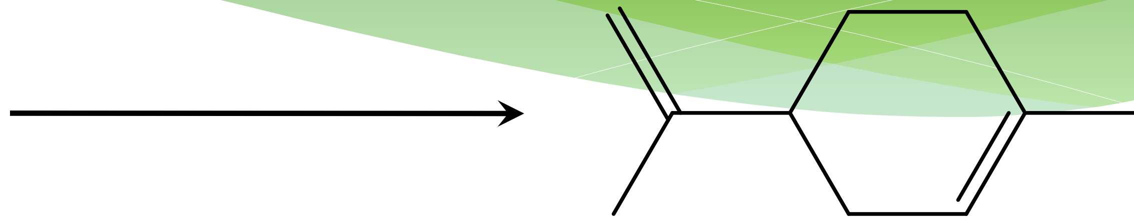
Orange peel



D-limonene

D-limonene : - optically active

- difficult to prepare

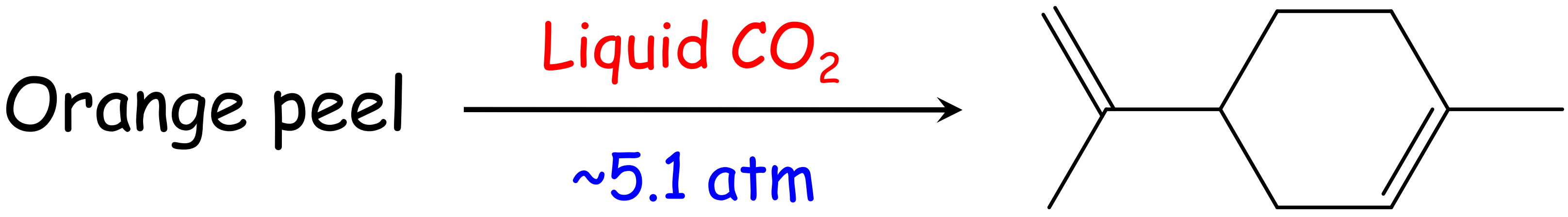
Orange peel 

D-limonene

Traditionally, it was done by organic solvent extraction or steam distillation

Disadvantages :

- VOCs used in solvent extraction are harmful to the environment
- More energy is consumed in steam distillation

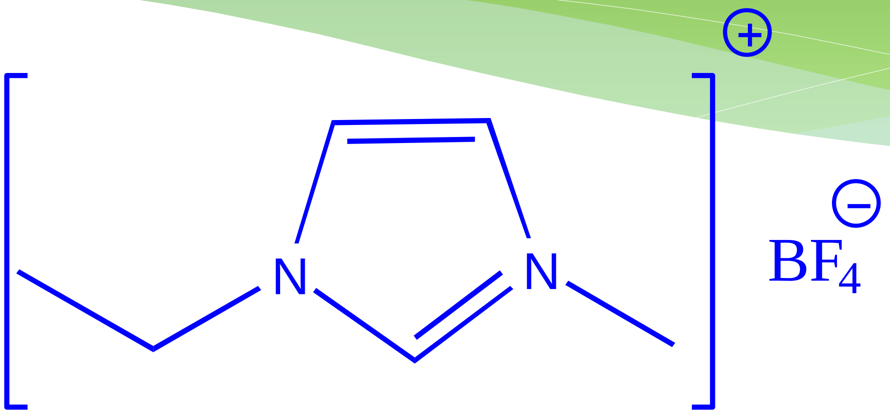


D-limonene

Liquid CO_2 can be obtained easily by allowing dry ice to evaporate in a closed vessel at room temperature.

C. Using ionic liquids as solvents

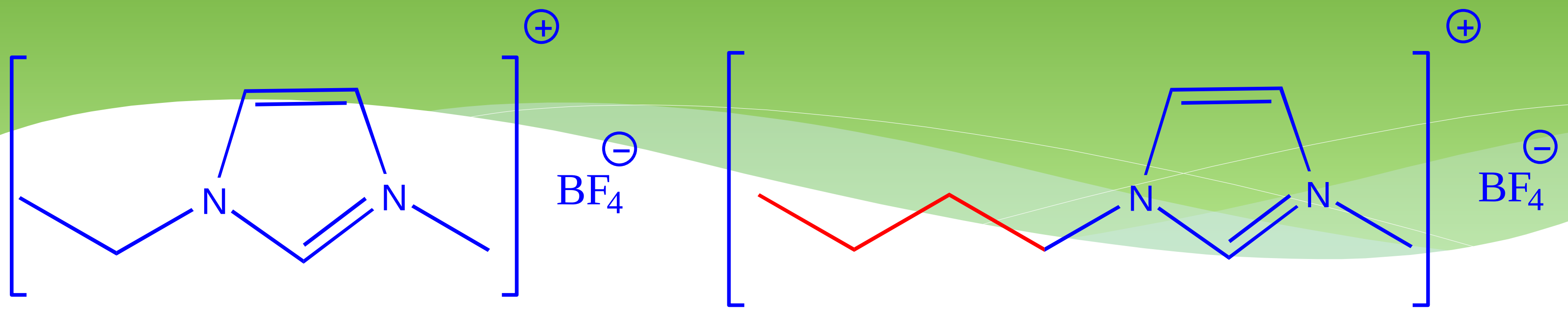
E.g.



Low m.p. due to poor packing between ions of significantly different sizes

High b.p. due to ionic nature

$\Rightarrow$ Low volatility



By modifying the structures and charges of the ions, ionic liquids can exhibit specific properties such as m.p., viscosity, volatility & hydrophobicity to meet the particular needs of a synthesis.

Designer solvents

Advantages of using ionic liquids over using VOCs as solvents (2010 AL Paper 1 Q.6)

1. Tailor-made
2. High b.p.

   Not easily escape to the environment

   Volatile organic reactants/products can be easily removed by simple distillation.

   The solvents can be easily recycled and reused
3. Low flammability due to their low vapor pressure

Advantages of using ionic liquids over using VOCs as solvents

4. Wide liquid range due to low m.p. and high b.p.

   Organic syntheses can occur at higher temperatures

5. Ionic nature can allow organic syntheses involving ionic species.

E. Solvent-less reactions

Not easy for reactions involving heating as heat exchange is difficult without a solvent

Solved by microwave heating
Suitable only for polar reactants which are active to microwave.

6. Designing for energy efficiency

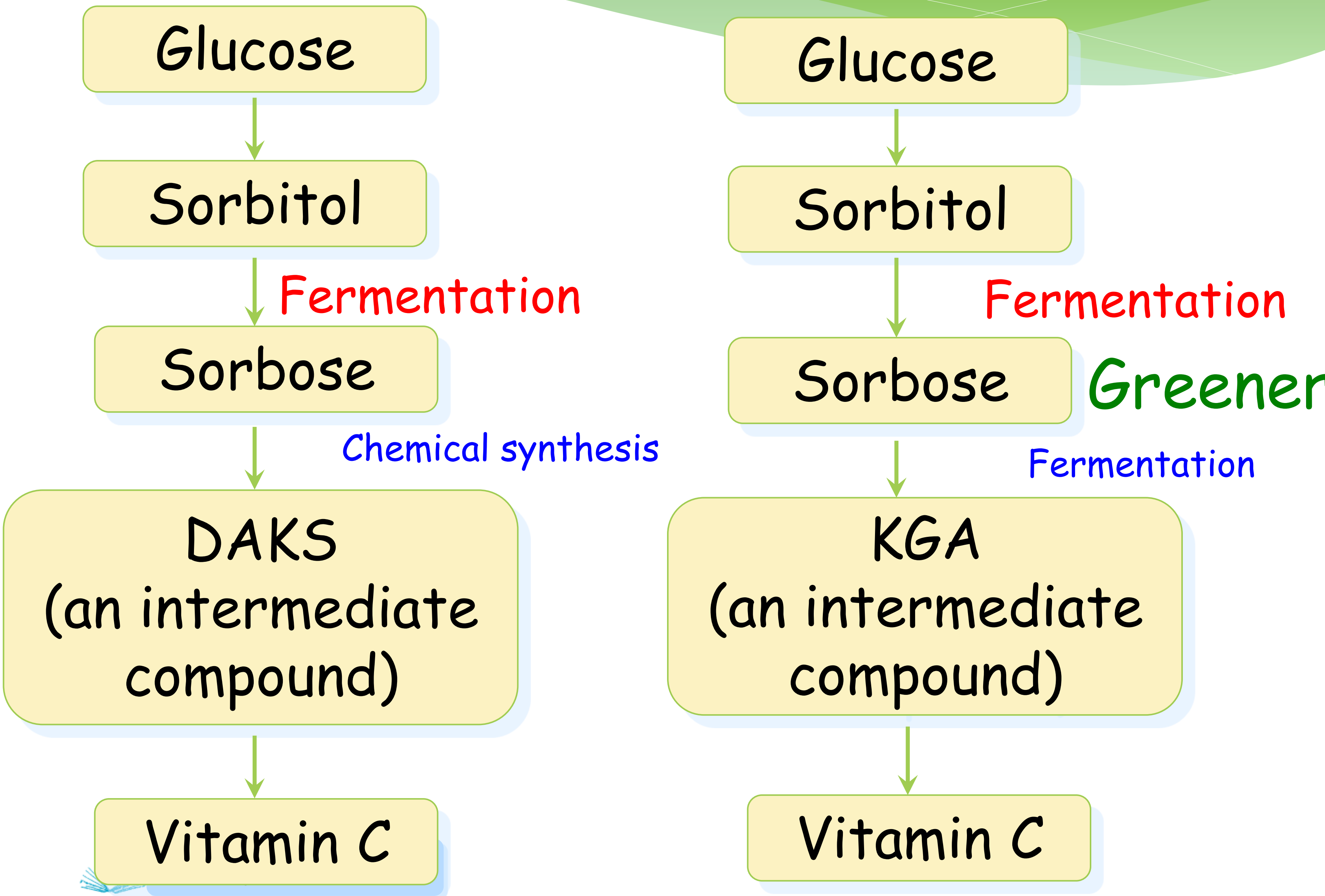
- Chemical syntheses should be designed to minimize the use of energy.

- Energy is used to
  - raise the temperature of reactants so that a reaction starts or goes on.
  - heat liquid mixtures for separating and purifying products by distillation.

Ways to conserve energy:

- Using catalysts
  - reactions at lower T & P
- Using microwave heating
  - more efficient
- Using biosynthetic pathways
  - reaction at ambient T & P

Reichstein process | **2-stage fermentation process**



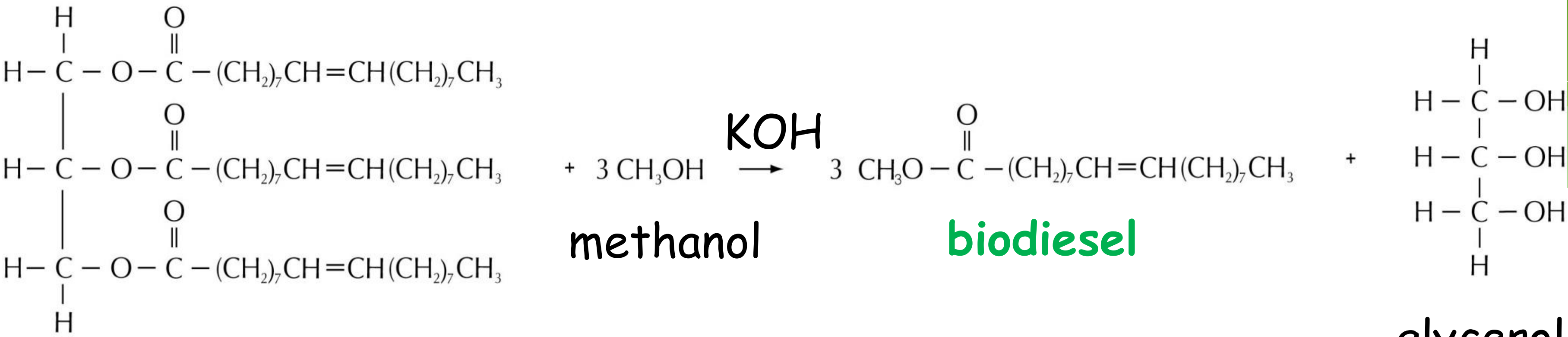
7. Using renewable raw materials

Renewable raw materials

- They are often made from agricultural products.

  E.g. glucose for making adipic acid and vitamin C

  biodiesel for motor vehicles



glycerol

vegetable oil

renewable

Diesel comes from petroleum which is non-renewable

Biodiesel Burns more completely than diesel due to its higher oxygen.

- In the production of synthesis gas, natural gas is used as the raw material for the steam-methane reforming process.

$$CH_4(g) + H_2O(g) \underset{\text{NiO}}{\overset{700\text{–}1000^\circ C,\ 10\text{–}20\ \text{atm}}{\rightleftharpoons}} 3H_2(g) + CO(g)$$

From natural gas

Synthesis gas (or **syngas**)

$$CH_4(g) + H_2O(g) \underset{\text{NiO}}{\overset{\text{700–1000°C, 10–20 atm}}{\rightleftharpoons}} 3H_2(g) + CO(g)$$

From natural gas

Synthesis gas (or **syngas**)

$$N_2(g) + 3H_2(g) \underset{\text{Finely divided Fe}}{\overset{\text{450°C, 200 atm}}{\rightleftharpoons}} 2NH_3(g)$$

$$2H_2(g) + CO(g) \underset{Cu/ZnO/Al_2O_3}{\overset{\text{250°C, 50-100 atm}}{\rightleftharpoons}} CH_3OH(g)$$

$$CH_3OH(g) + CO(g) \underset{\text{Cativa process}}{\overset{\text{Ir based catalyst, HI}}{\rightleftharpoons}} CH_3COOH(g)$$

Renewable raw materials

Landfill methane gas

Non-renewable raw material

Pig's manure

Replaced by

Natural gas

Paper & wood waste

Seaweed

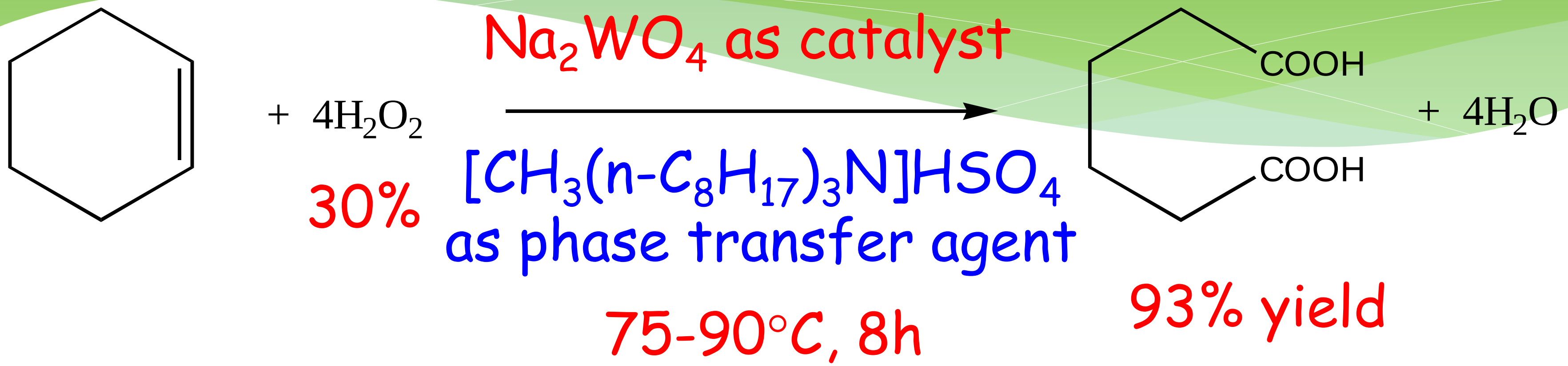
Shredded paper (left) and seaweed (right) can be used as the raw materials for the production of synthesis gas

8. Reducing derivatives

- We should avoid unnecessary use of synthetic steps in order to reduce the **derivatives** of the desired product.

- Otherwise, more reagents are needed and more waste will be generated.

A "Greener" Route to Adipic Acid.



1. One-step synthesis with high yield
2. Proceeds in aqueous medium at relatively low T
3. Reagents and by-product are environmentally benign

9. Using catalysts

Bleaching of wood pulp in paper manufacturing

1. H_2O_2 + dye $\longrightarrow$ H_2O + (dye + O)

2. OCl^- + dye $\longrightarrow$ Cl^- + (dye + O)

Reaction 1 is greener because

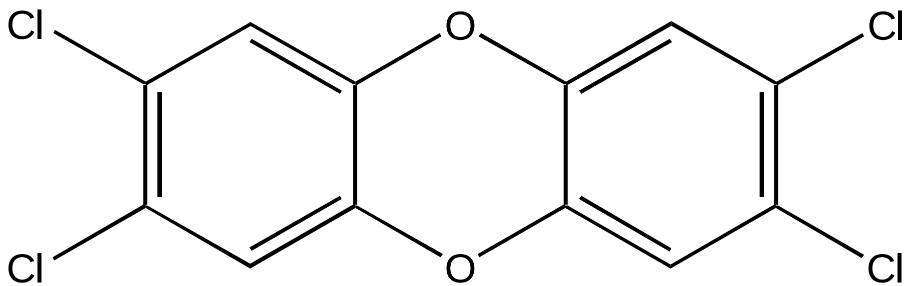
- it involves less harmful chemicals

Bleaching of wood pulp in paper manufacturing

1. H_2O_2 + dye $\longrightarrow$ H_2O + (dye + O)

2. OCl^- + dye $\longrightarrow$ Cl^- + (dye + O)

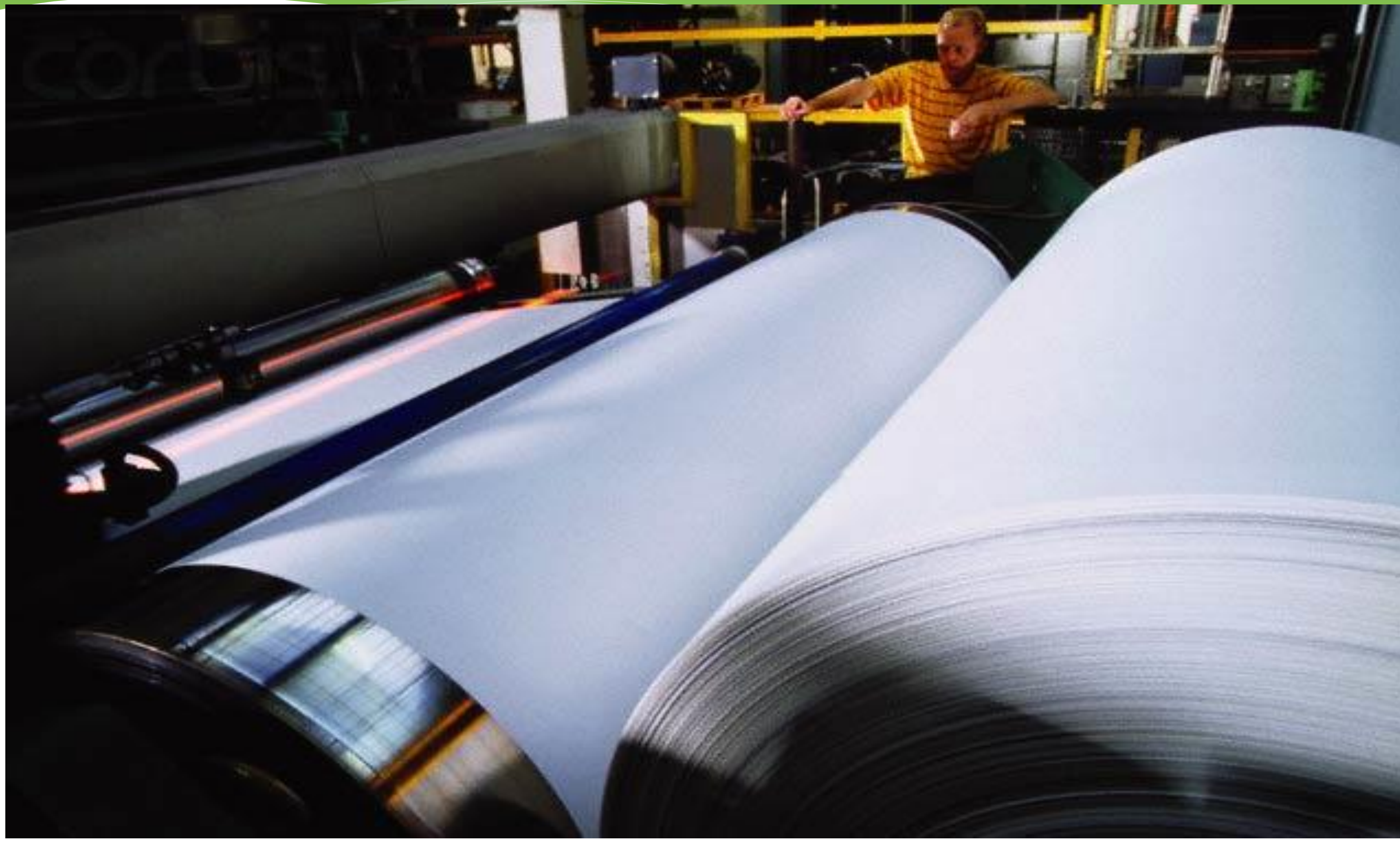
Bleaching with Cl_2 may lead to the formation of dioxin which is an accumulative carcinogen



$$H_2O_2 + \text{dye} \xrightarrow{\text{TAML}^{\text{TM}}\text{ catalyst}} H_2O + (\text{dye} + O)$$

Tetra-Amido Macrocyclic Ligand (TAML)

- non-toxic iron-based 'green' catalysts.
- promote the conversion of hydrogen peroxide into hydroxyl radicals that are involved in the bleaching process
- catalyse the oxidation of organic substances in wastewater.



TAML™ catalysts can be used to clean up wastewater streams in the pulp and paper industry

Environmental benefits of using TAML™ catalysts in wastewater treatment

Decrease in energy requirements

Elimination of chlorinated organic substances

Reduction in water usage

Degradable catalysts

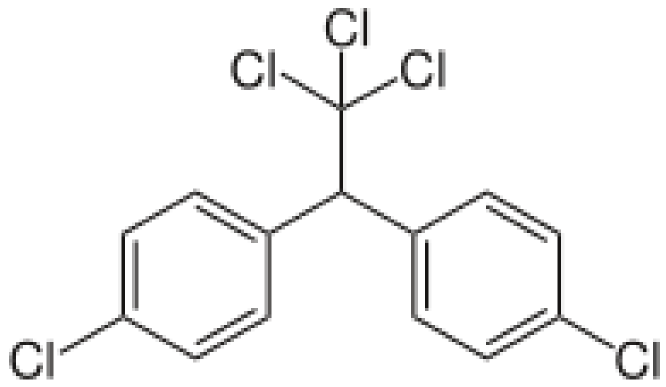
10. Designing degradable chemical products

- Many chemical products persist in the environment after use.

  - They should be designed so that they can be broken down into **harmless** substances.

Pesticides

- E.g. DDT, they accumulate in plants and animals, causing damage to the final consumers — humans.



- Designing degradable pesticides that can be decomposed by water, sunlight or micro-organisms.

Degradable Plastics

- Several types of degradable plastics:
  - ➔ biopolymers
  - ➔ photodegradable plastics
  - ➔ synthetic biodegradable plastics

Biodegradable plastic utensils.

Photodegradable plastic bag.

11. Developing real-time analysis for pollution prevention

Real-time monitoring system for monitoring sulphur dioxide (SO_2) level

When coal is burnt in industrial boilers, SO_2 (a pollutant) is formed.

If the temperature of the boilers is too high, a large amount of SO_2 will be generated.

Real-time monitoring system for monitoring sulphur dioxide (SO_2) level

Using real-time monitoring, the amount of SO_2 generated can be measured all the time.

Once it reaches an unacceptable level, an alarming signal will be generated. Then the temperature will be lowered immediately.

12. Minimizing the potential for chemical accidents

Chemical accidents include leakages, explosions and fires.

Minimize the use of volatile liquids or gases which are associated with the majority of chemical accidents.

If possible, allow reactions to proceed under ambient T & P.