Progresso Umano e Sviluppo Sostenibile

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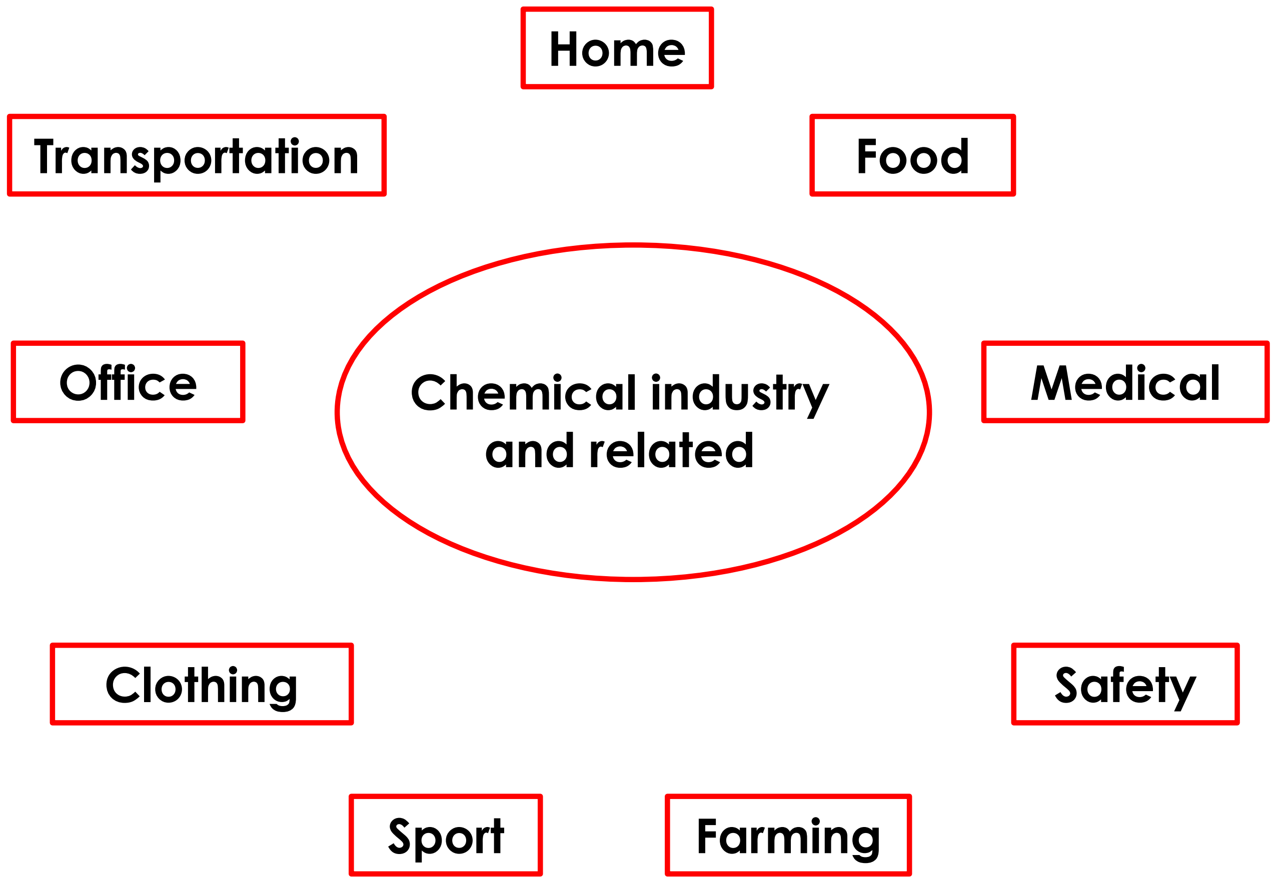
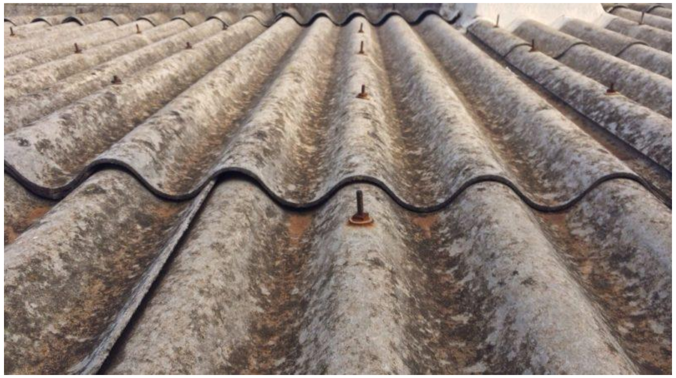
Introduction

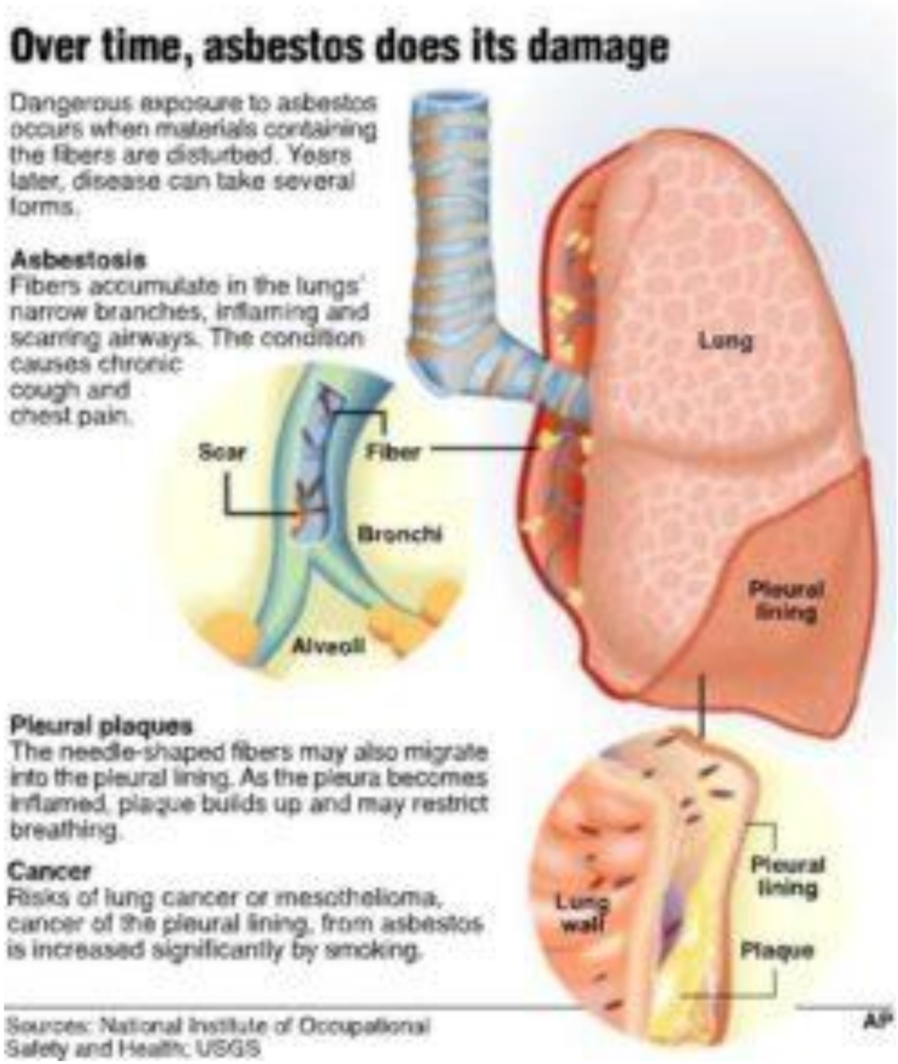


Introduction

Asbestos

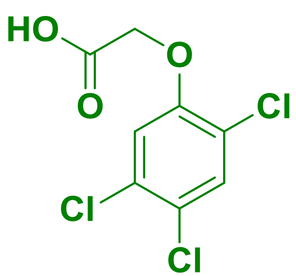


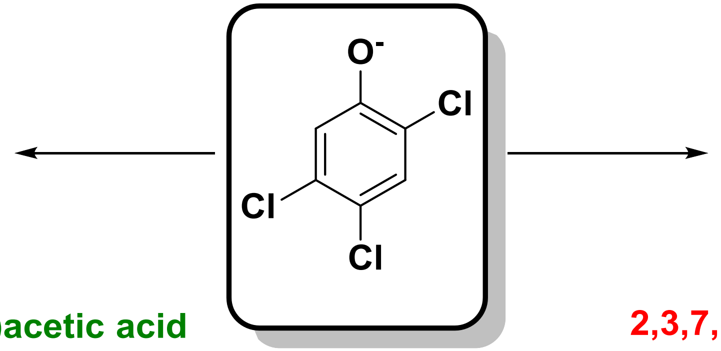
- Naturally occurring fibrous minerals
- Good tensile strength
- Flexibility
- Heat resistant
- Electrical resistance
- Good insulation
- Chemical resistant

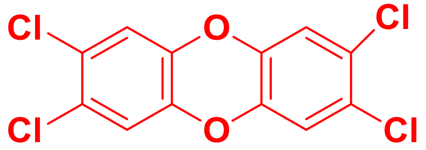


Introduction

Seveso



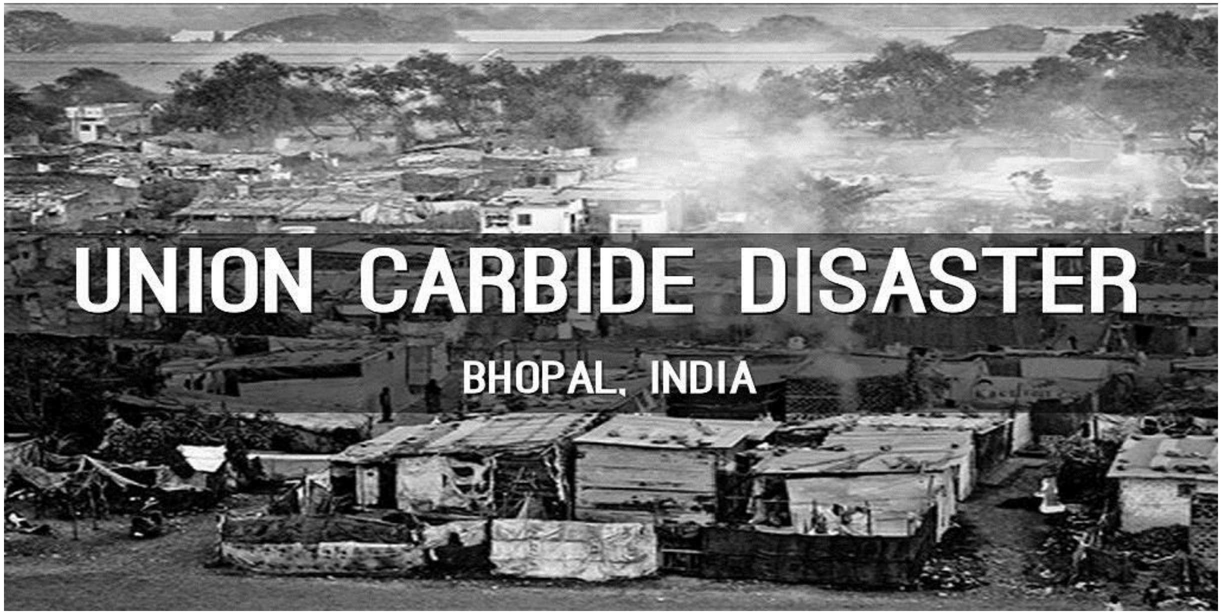


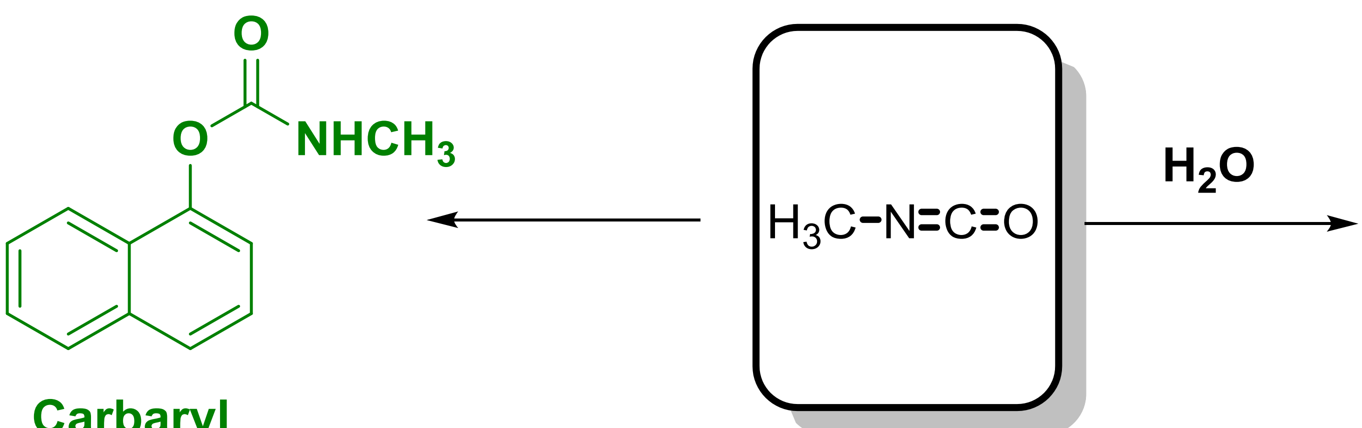


2-(2,4,5-trichlorophenoxy)acetic acid
(Agent Orange)

2,3,7,8-tetrachlorodibenzo[*b*,*e*][1,4]dioxine
(TCDD)

Introduction





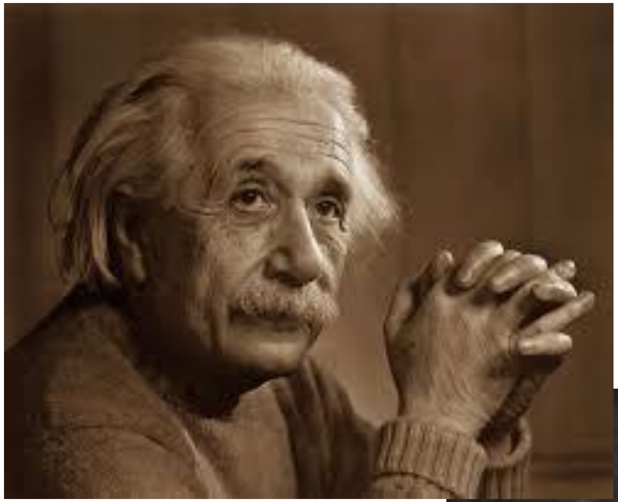
Carbaryl

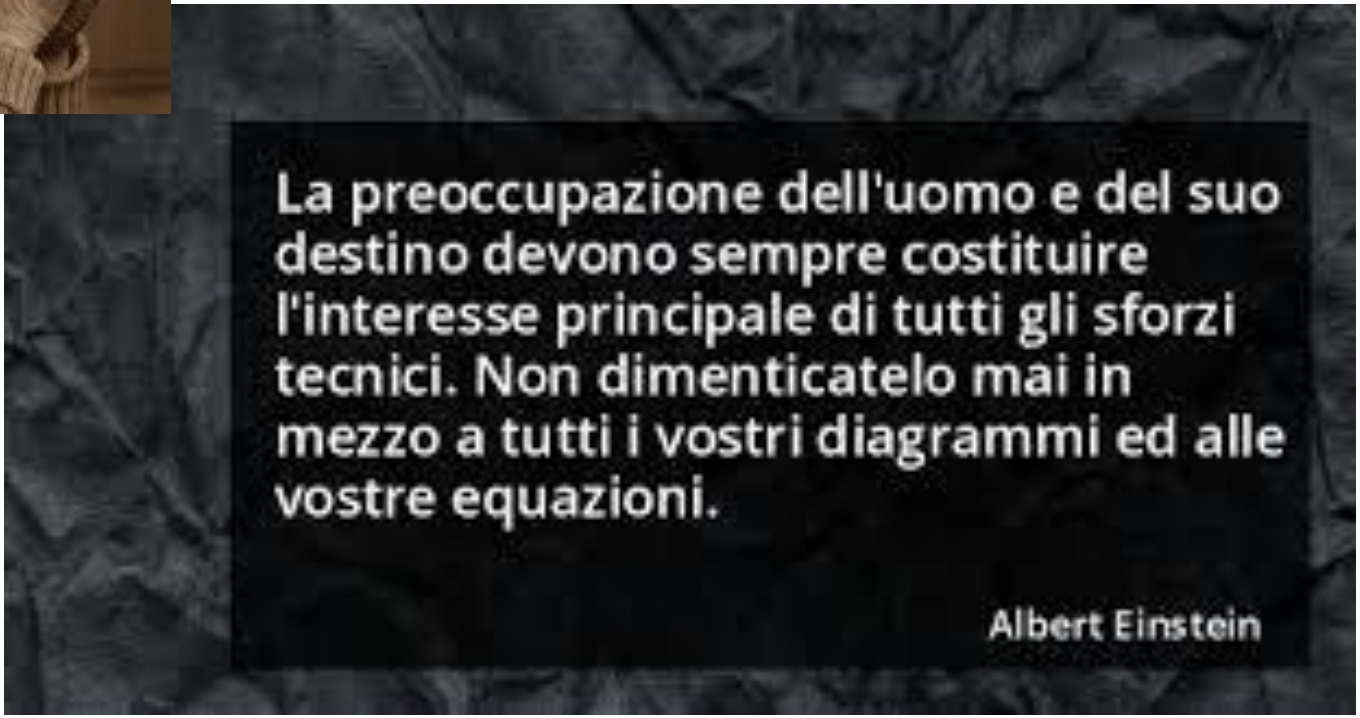
Methyl Isocyanate

$CH_3NH_2 + CO_2$

Exothermic Reaction

Introduction





Sustainable Development

"**Sustainable development** is development that **meets the needs of the present without compromising** the ability of future generations to meet their own needs".

(Brundtland Report, 1987)

Gro Harlem Brundtland

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

(US EPA, Early 1990s)

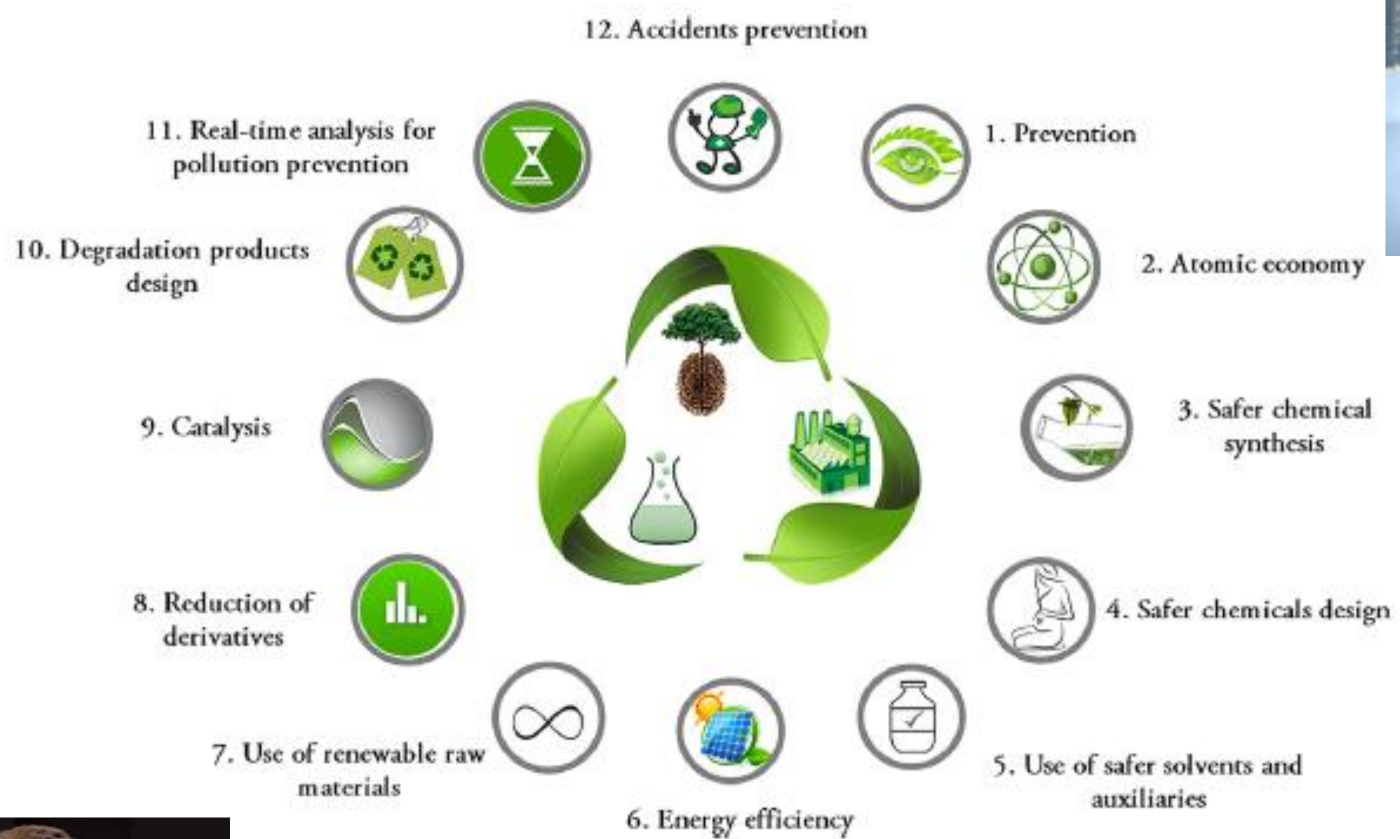
Sustainable Development

Sezione II, capitolo 19. A substantial use of chemicals is essential to meet the **social and economic goals of the world community** and today's best practice demonstrates that they can be used widely in a cost-effective manner and with a high degree of safety.

1992

The 12 Principles of Green Chemistry

John Warner



Green Chemistry: Theory and Practice, 1998

Paul Anastas

The 12 Principles of Green Chemistry

R1 + R2 ⟶	**P1 + P2 + W**	**R1 e R2 : reagents** **P1 e P2: products** **W: waste**

1) It is better to prevent waste than to treat or clean up waste after it has been created.

$$E\text{-factor} = \frac{\text{Total waste}(\text{kg})}{\text{Product}(\text{kg})}$$

2) Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product. (**Atom Economy**)

The 12 Principles of Green Chemistry

2)

R1 + R2 ⟶ P1 + P2 + W		**R1 e R2 : reagents** **P1 e P2: products** **W: waste**

$$\textbf{Yield (P1)(\%)} = \frac{\textit{actual quantity of products achived (P1)}}{\textit{theoretical quantity of products achievable (P1)}} * 100$$

Es. actual quantity of products achived *(P1)= 60g*

theoretical quantity of products achievable*(P1) = 80g* $\text{Yield} = \frac{60g}{80g} * 100 = 75\%$

$$\textbf{Selectivity (P1)(\%)} = \frac{\textit{yield of desidered product (\%P1)}}{\textit{yields of all products (\%P1+\%P2)}} * 100$$

Es. yield of desidered product *(%P1)= 75%*

amount of substrate converted *(%P1+ %P2)= 75% + 10%*

$$\text{Selectivity(P1)} = \frac{75}{(75+10)} * 100 = 88\%$$

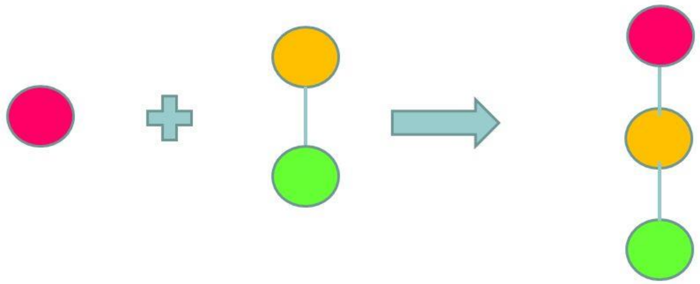
Both parameters do not take into account

N.B. Both parameters do not take into account *W* .

The 12 Principles of Green Chemistry

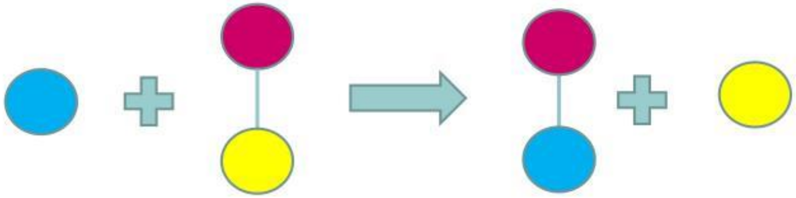
2) **Atom economy (A.E.) =** $\frac{Molecular\ Mass\ of\ desidered\ poducts}{Molecular\ Mass\ of\ all\ reactants}$ $*100$

High atom economy



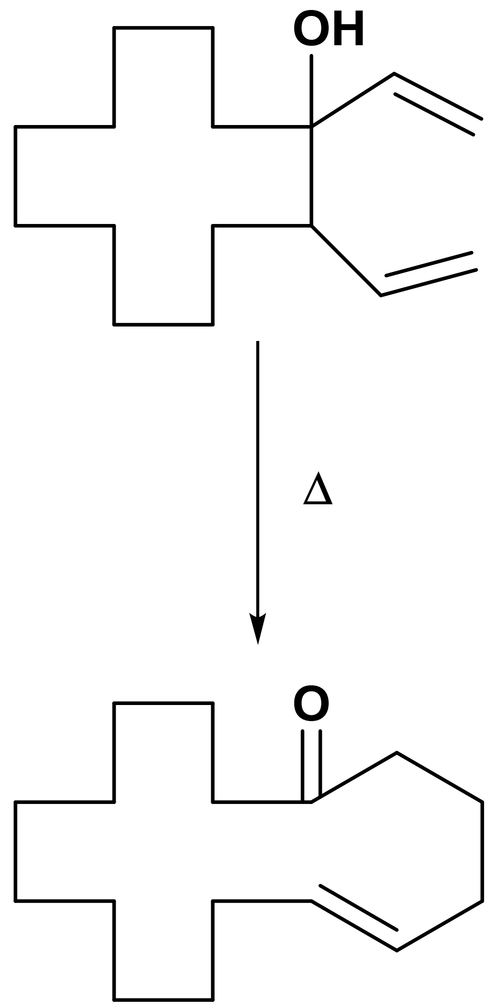
All reactant atoms included in the desired product.

Low atom economy



Some reactant atoms not included in the desired product.

The 12 Principles of Green Chemistry



Ambretone® (Toray)

The 12 Principles of Green Chemistry

3) Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4) Chemical products should be designed to preserve efficacy of function while reducing toxicity.

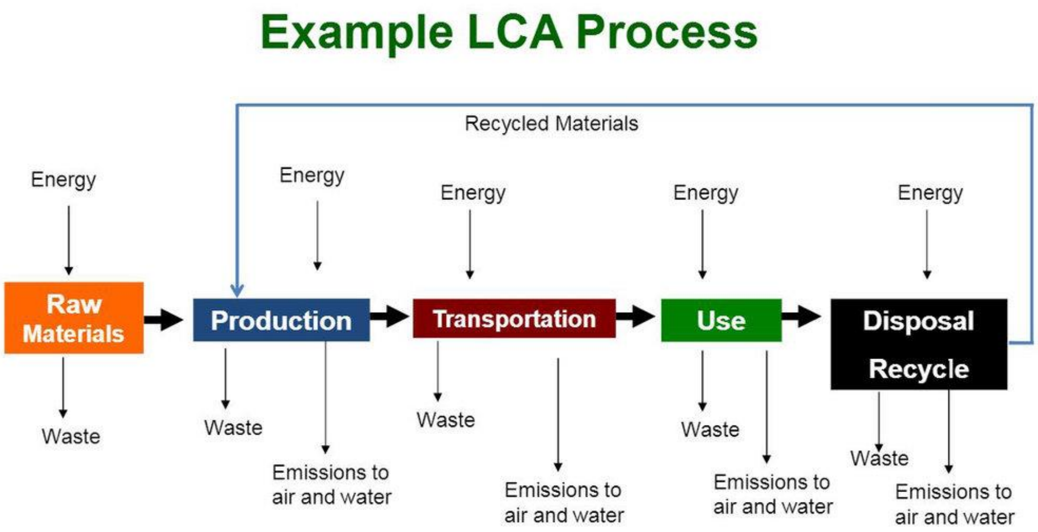
5) The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used. (**Process Mass Intensity**)

(Process) Mass intensity $$\mathrm{PMI} = \frac{\textit{total mass in a process or process step}}{\textit{mass of product}}$$

6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

The 12 Principles of Green Chemistry

Life Cycle Assessment (LCA): from cradle to grave



The 12 Principles of green chemistry

7) A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8) Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

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

10) 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.

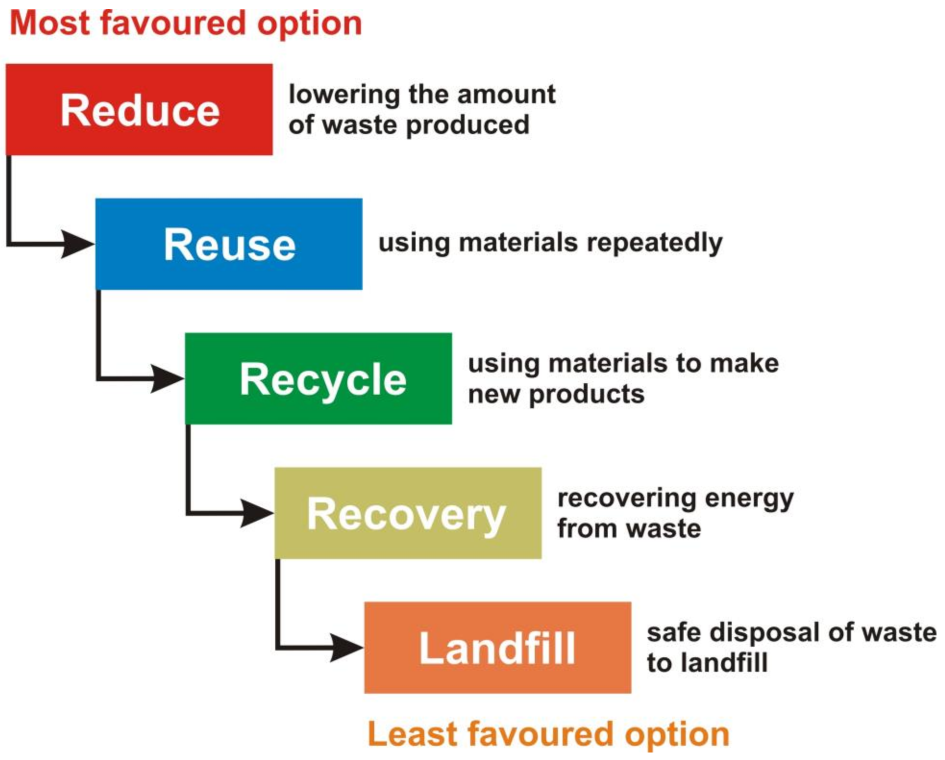
11) Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12) 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.

1) It is better to prevent waste than to treat or clean up waste after it has been created

" In a ideal chemical factory there is, strictly speaking, no waste but only products. The better a real factory make use of its waste, the closer it gets to its ideal, the bigger is the profit“.

R. W. Hofmann, 1848



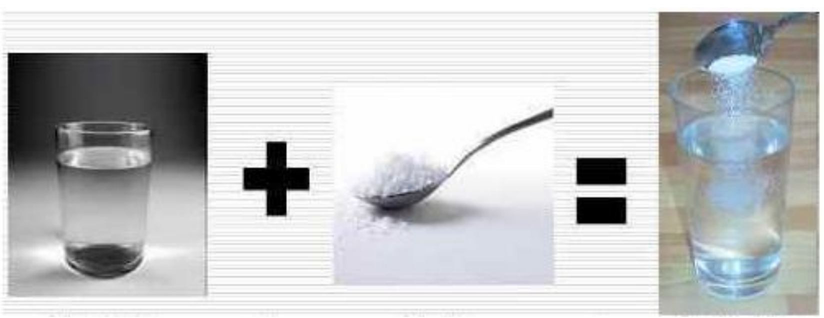
5) The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used. (Process Mass Intensity)

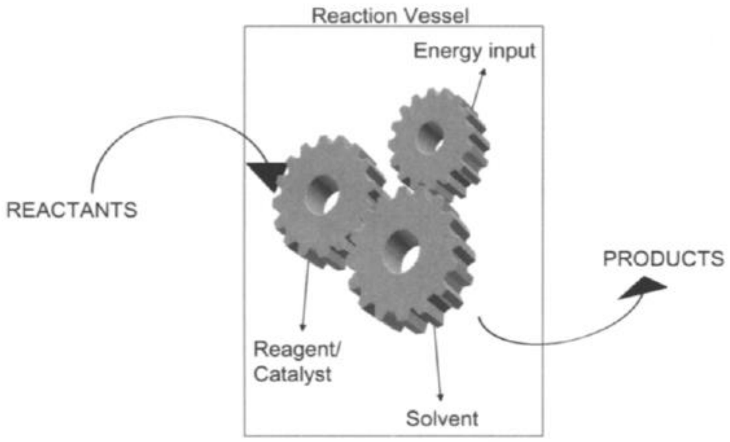
Chemical Reactions: reagents, solvents, energy

Solvents

- they represent, in terms of mass, the majority of the materials introduced into the chemical reaction system;

- they are not incorporated in the final product (auxiliary substances)and must be recovered and treated as waste.





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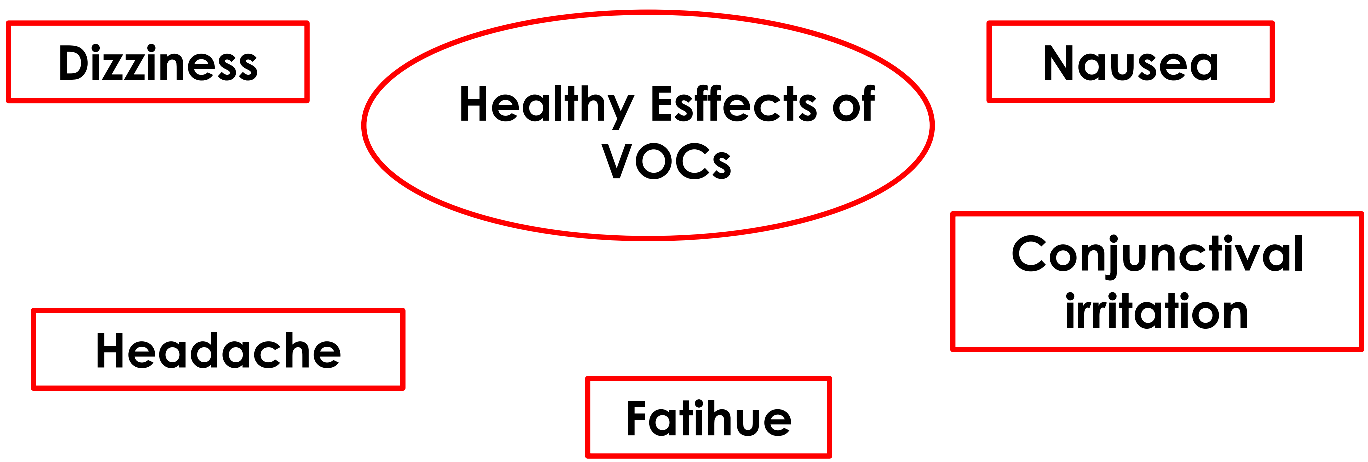
Volatile Organic Solvents (VOCs)

VOCs are easy to remove (significant vapor presssure at room temperature and relatively low boiling point (<250°C)).



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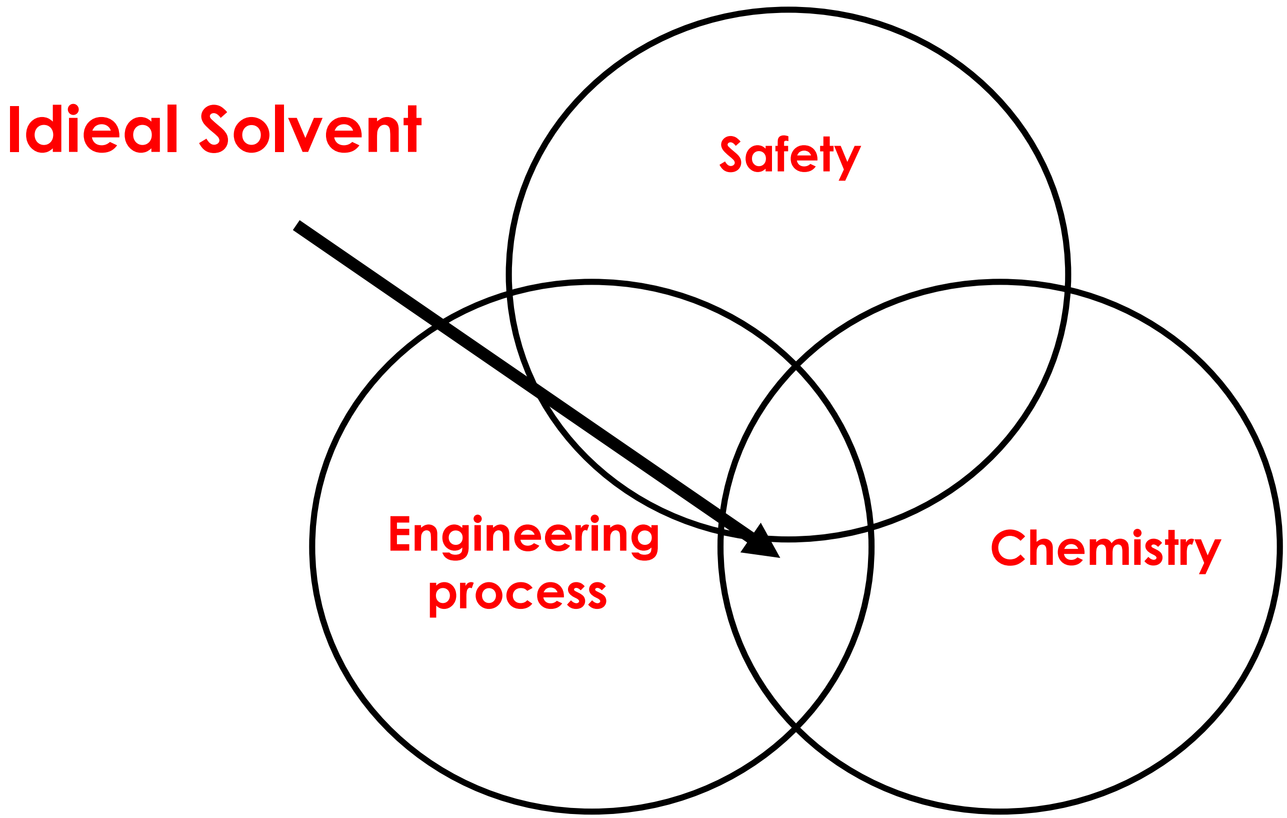

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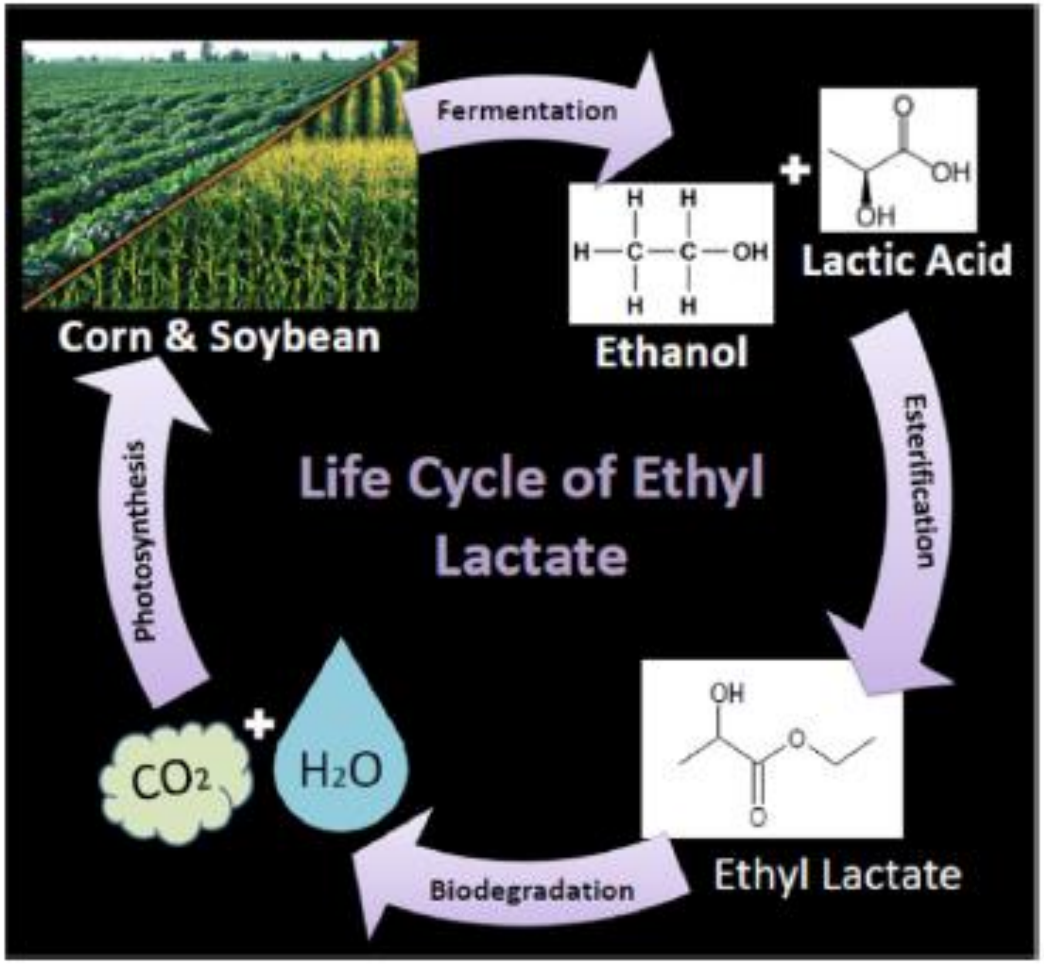
Alternative Solvents 1 : benign non-volatile organic solvents (e.g. **ethyl lactate**)



5) The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used. (Process Mass Intensity)

Table 3
Principles fulfilled by ethyl lactate in the 12 Principles of Green Chemistry (Pereira et al., 2011).

Principles	Description	Reasons
1st	Waste should be avoided instead of treated after generation	Ethyl lactate production could be carried out without any extra waste of reactants. The excess reactant will be recycled until the reaction completes.
3rd	Synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and environment	Water is the only by-product generated during ethyl lactate production.
4th	Chemical products should be designed to preserve efficacy while reducing toxicity	Ethyl lactate has high solvency power, non-carcinogenic and non-toxic. It was reported to pose lesser harm as compared to other solvents at a wide concentration range.
7th	Raw material or feedstock should be renewable rather than depleting	Ethanol and lactic acid are required for ethyl lactate production. They are obtained from plant biomass through fermentation.
9th	Selective catalytic reagents are superior to stoichiometric reagents	Heterogeneous acid catalyst is used to improve the reaction kinetics of ethyl lactate production.
10th	The chemical products do not persist in the environment but break down into innocuous degradation products	Under aerobic condition, 85% of ethyl lactate is readily biodegrade to water and carbon dioxide, which are not harmful or toxic to the environment.
12th	Substance used should be safe from chemical accidents such as release, explosion and fire	Ethyl lactate has low volatility and high flash point, creating safer working environment.

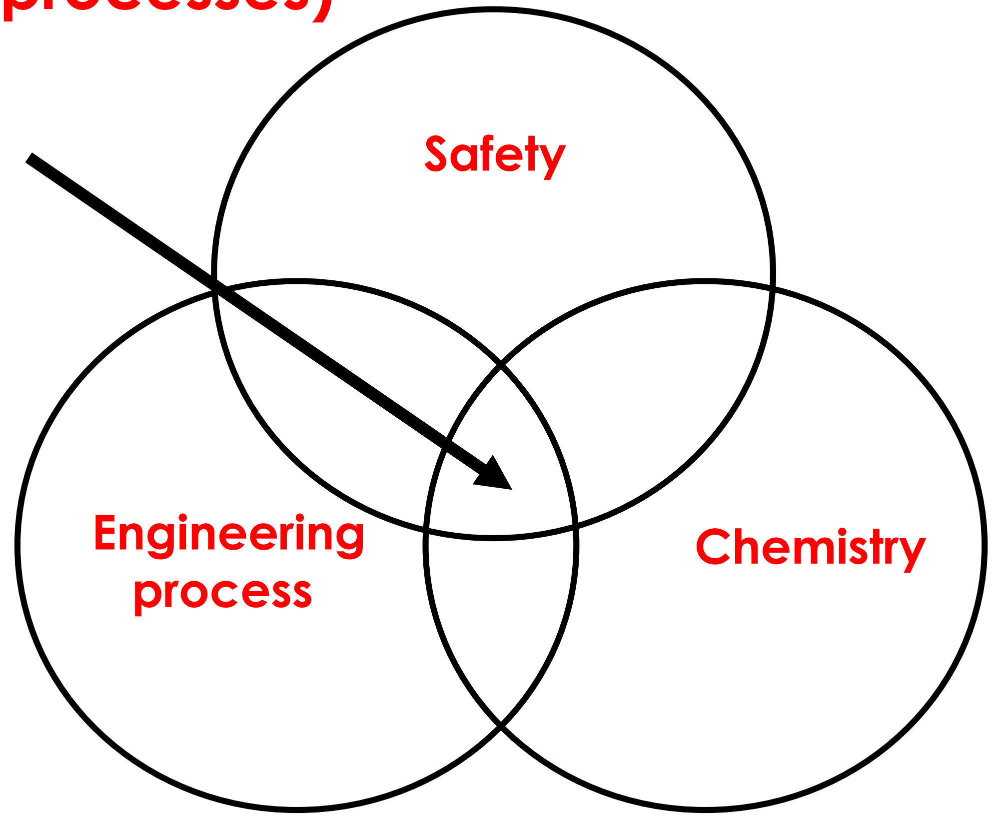
5) The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used. (Process Mass Intensity)

Alternative Solvents 2 : Water based processes

Advantages	***Disadvantages***
Non-toxic	Distillation is energy intensive
Naturally occurring	Poor solvent capacity properties for organic molecules
Inexpensive	Contaminated waste streams may be difficult to treat
Non-flamable	Incompatible with some compounds
High specific heat capacity-exothermic reactions can be more safely controlled	High specific heat capacity-difficult to heat and cool rapidly
Opportunity for replacing VOCs	

5) The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used. (Process Mass Intensity)

Idieal Solvent = No Solvent (Solvent-Free processes)



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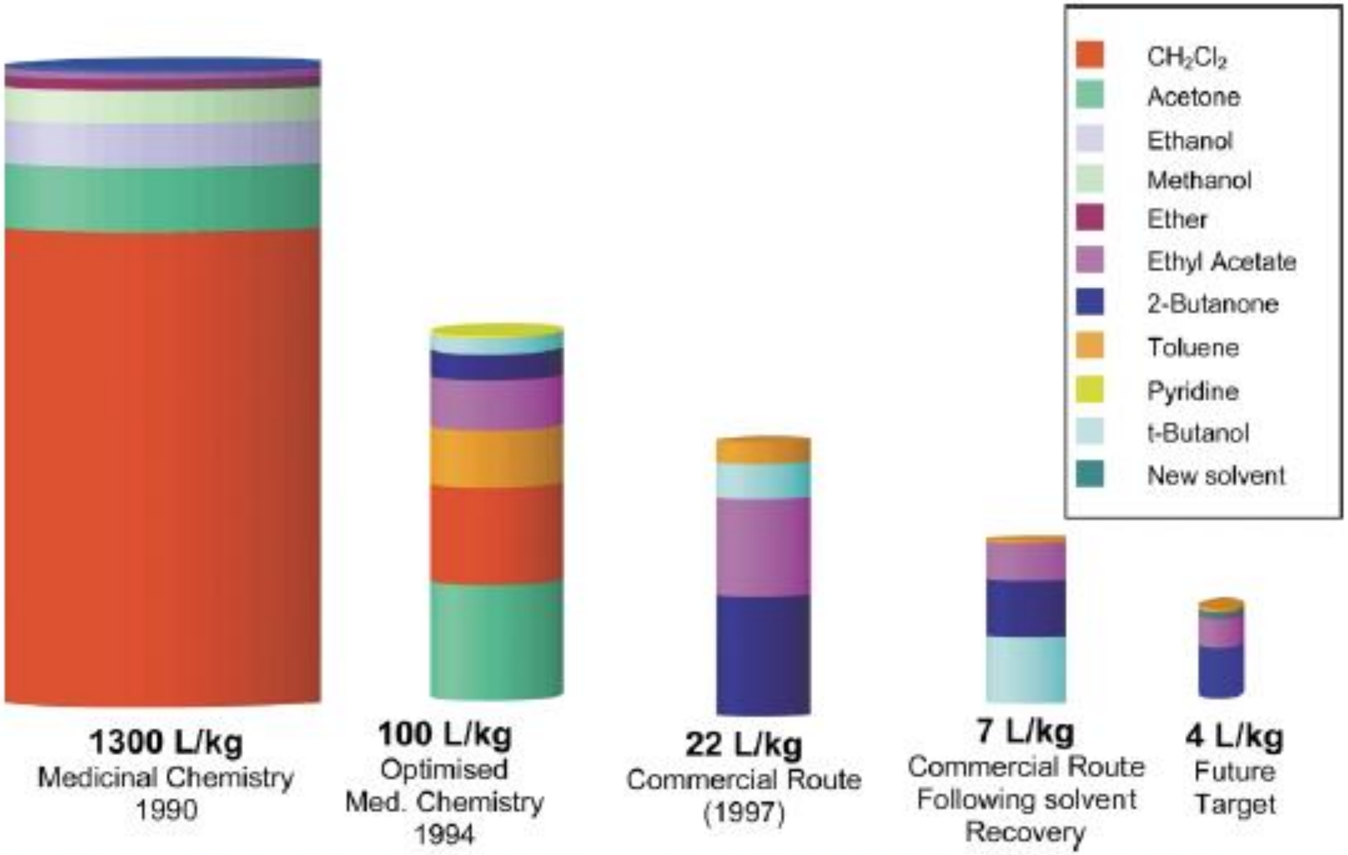
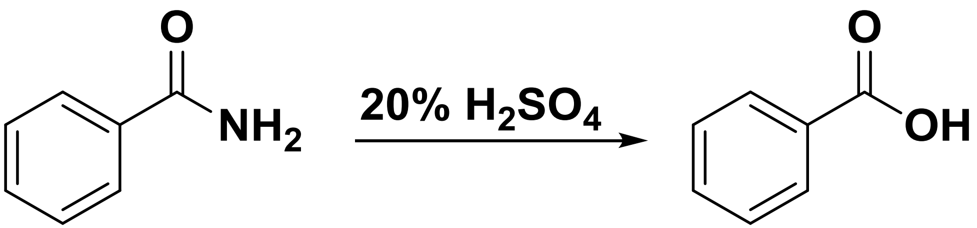


Fig. 1 The amount of organic waste produced by the sildenafil citrate processes at various time points.

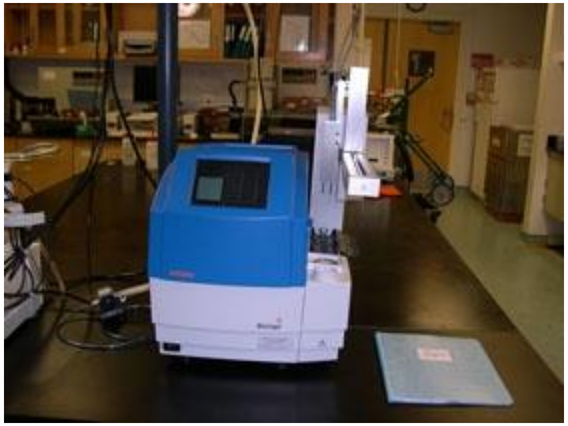
Green. Chem. ***2004***, *43*

6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

<u>Alternative Forms of energy 1:</u> Microwave assisted organic synthesis (MAOS)



Reflux 1hr 90% conv.
Microwave 140°C 7 min. > 99% conv



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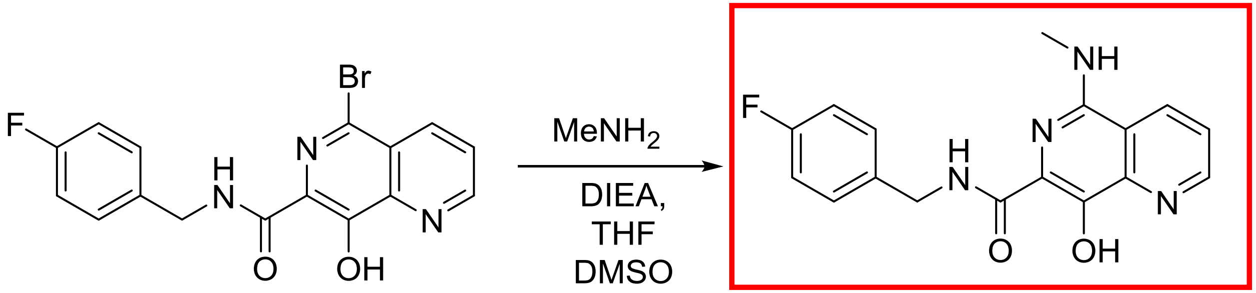
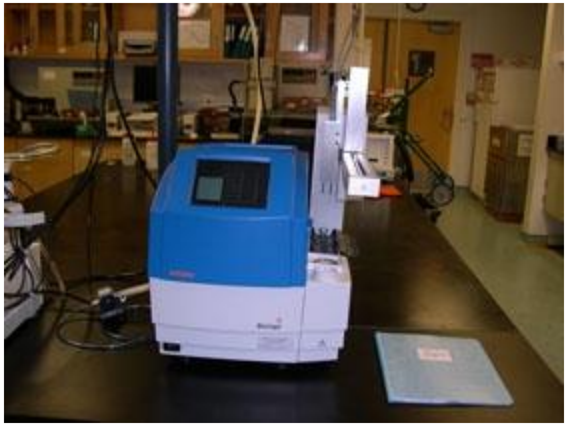
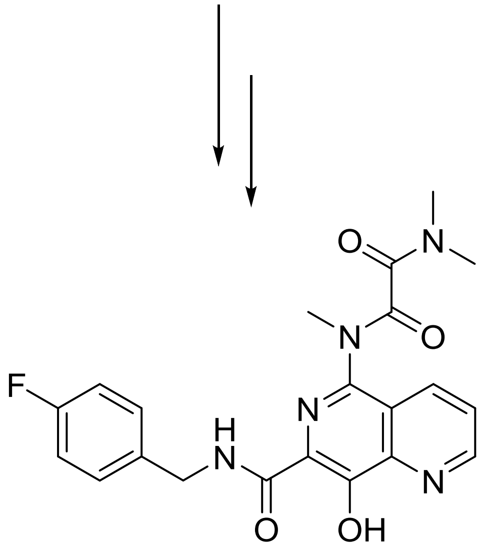
Alternative Forms of energy 1: Microwave assisted organic synthesis (MAOS)



Reflux: 120 g/synthesis (72 h)
Microwave:35 g/synthesis (1h)
1200 g of product in 35 h





HIV Treatment

6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

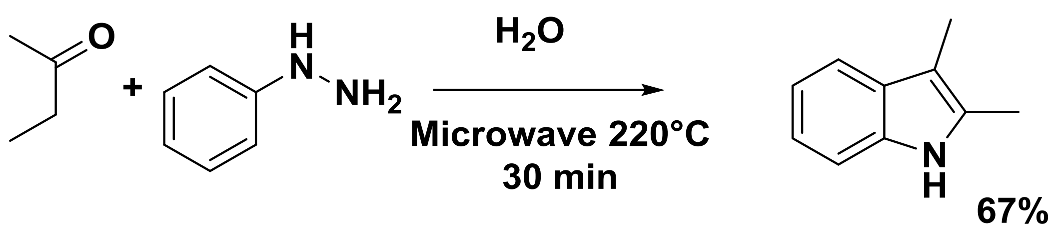
Solvent-free Microwave assisted organic synthesis

Radiation is absorbed by the reactants, giving enhanced energy efficency

$$CH_4 + NH_3 \xrightarrow[\text{Microwave 1200°C}]{\text{Pt/allumina}} HCN + 3H_2$$

Dupont Process

Microwave assisted reactions in water



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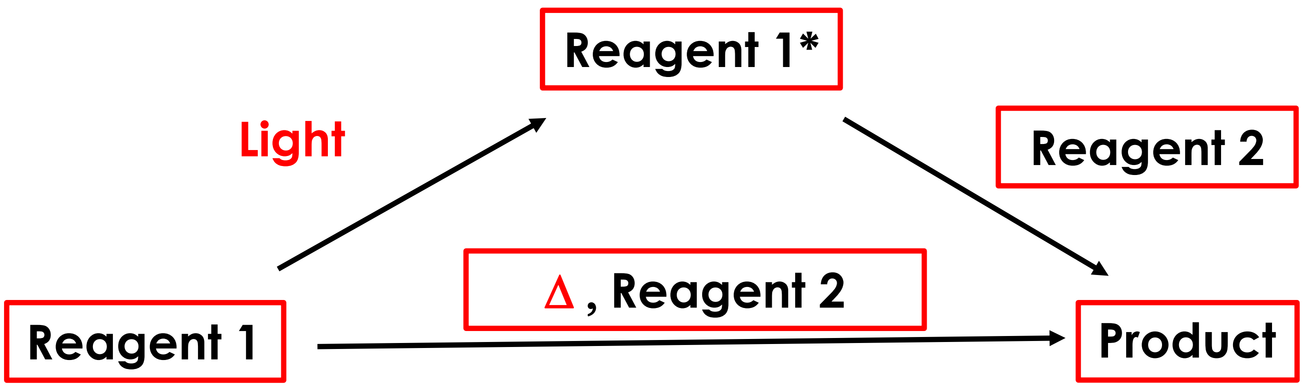
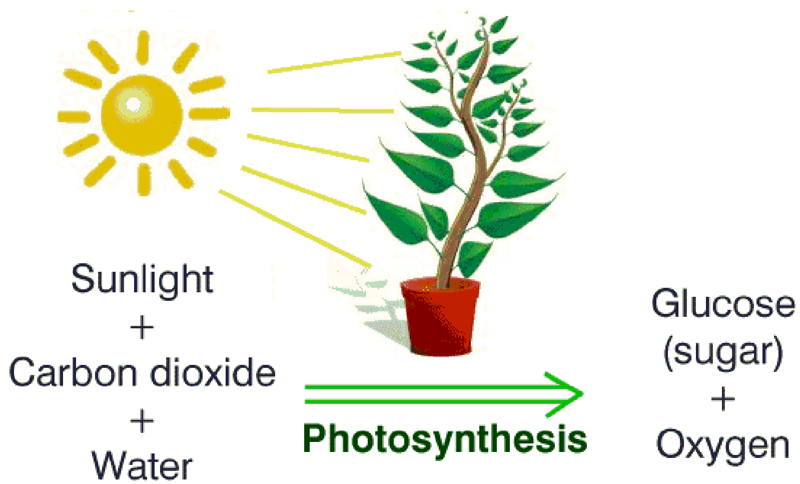
Alternative Forms of energy 2 : Photochemical Reactions





6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

Over the last few decades, the call for sustainable and environmentally friendly technologies has led to an increasing interest in green chemistry [1]. Among the known *green chemical* approaches, organic photochemistry can serve as a valuable application since light is regarded as a *clean* and *traceless reagent* [2]. Despite this advantage, however, synthetic organic photochemistry has been widely ignored by the chemical industry. The main reason for this neglect is the high energy demand of most artificial light sources.

- ✓ Light is a clean and traceless reagent;
- ✓ mild reactions conditions.

- ✓ High energy demand of most articial light source.

Pure Appl. Chem. **2007**, 1939

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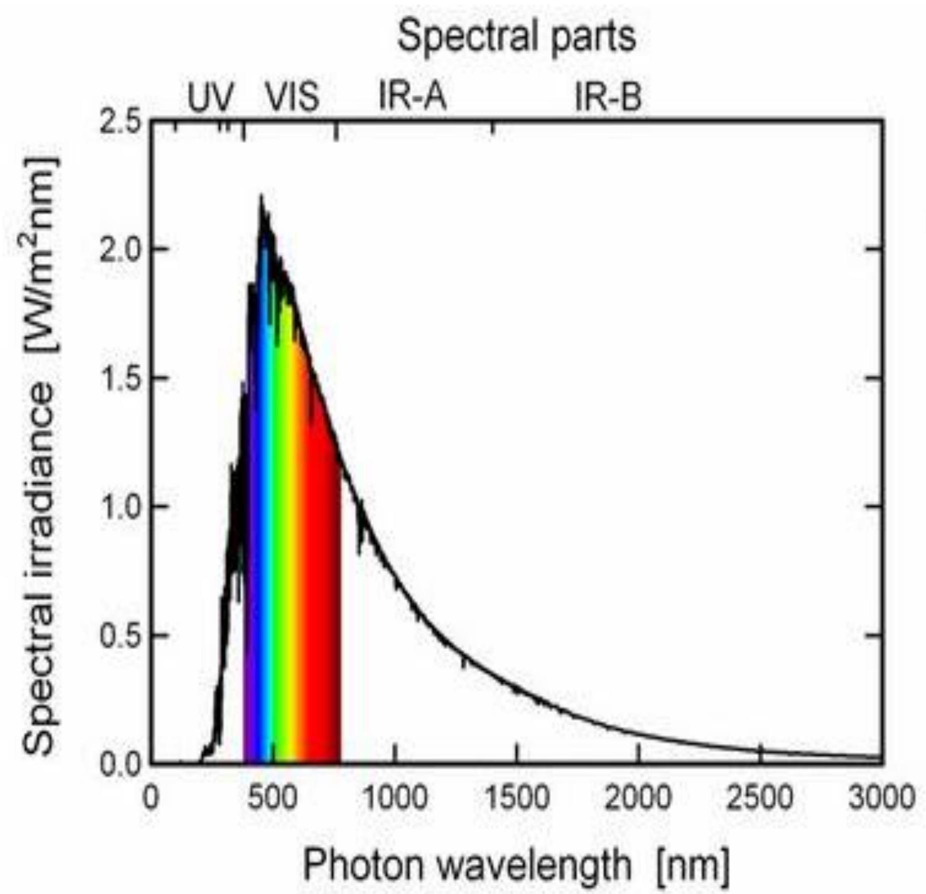
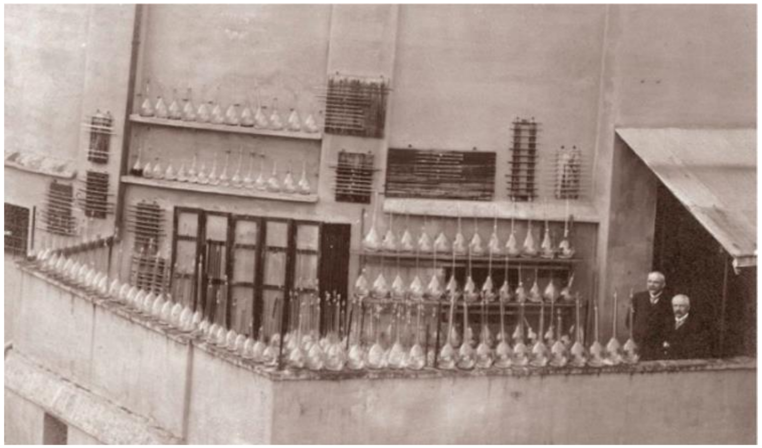
Sunlight



- ✓ Naturally occurring (available in large quantity);
- ✓ free energy source;
- ✓ fully renewable and zero emissions;
- ✓ broad energy spectrum.

6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

Window ledge chemistry



- ✓ Discontinuous intensity;
- ✓ small amount of material can be treated for day.

"On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."

Giacomo Ciamician
Science **36**, 385 (1912)

Giacomo Ciamician, University of Bologna

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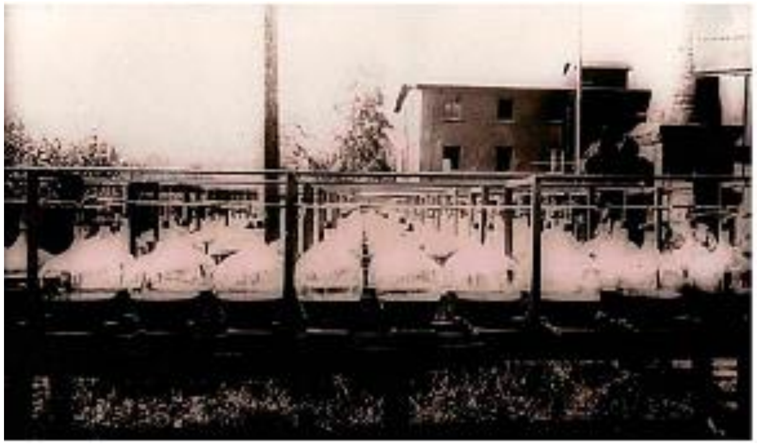
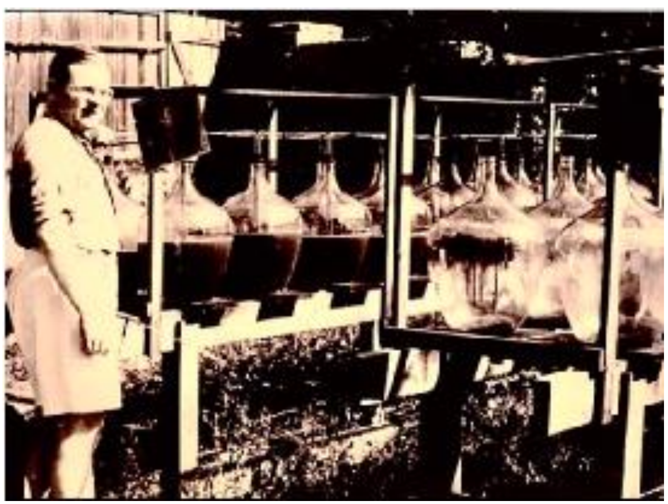
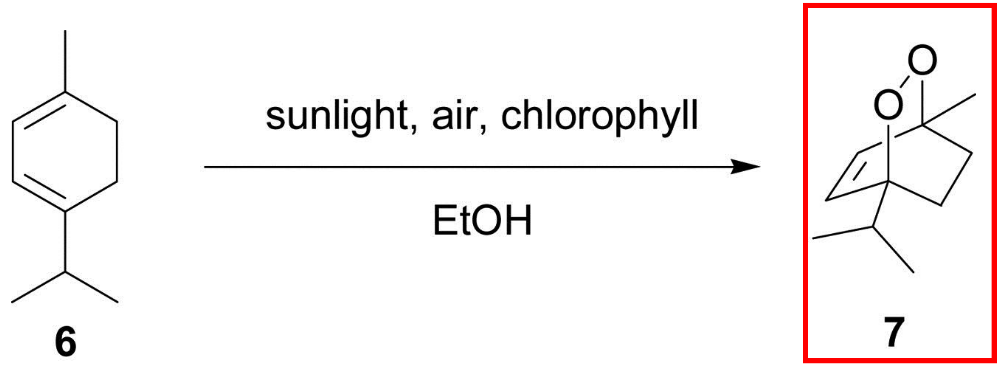
Solar Photoreactors



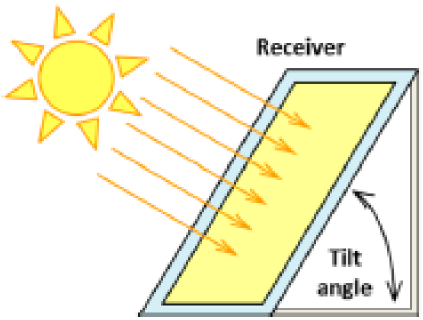


Ascaridole synthesis

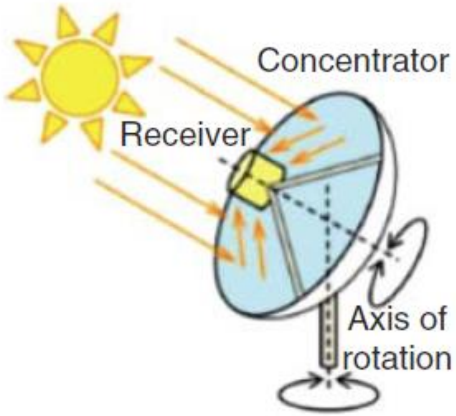


40 g of **6** in 5 l air-saturated EtOH
100-200 g of stinging-nettle leaves (chlorophyll)
ca. 10 g (ca. 20%) of **7** in 2 sunny days (summer)
ca. 2 kg of **7** for the whole plant (200 bottles)

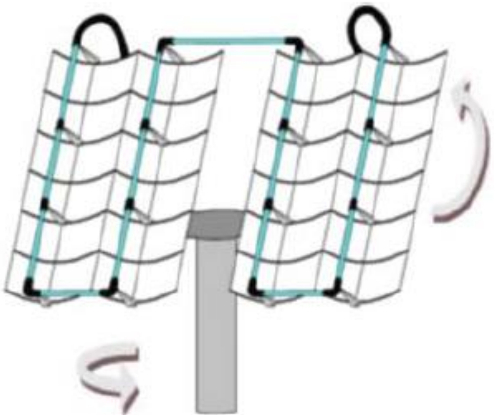
6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.



Flatbed reactor, Università James Cook (JCU) Australia, 2014



Parabolic Dish Solar Concentrator, Ege University, Turkey, 2004



PROPHIS Parabolic tRough collector for Organic PHotochemical syntheses In Solar light

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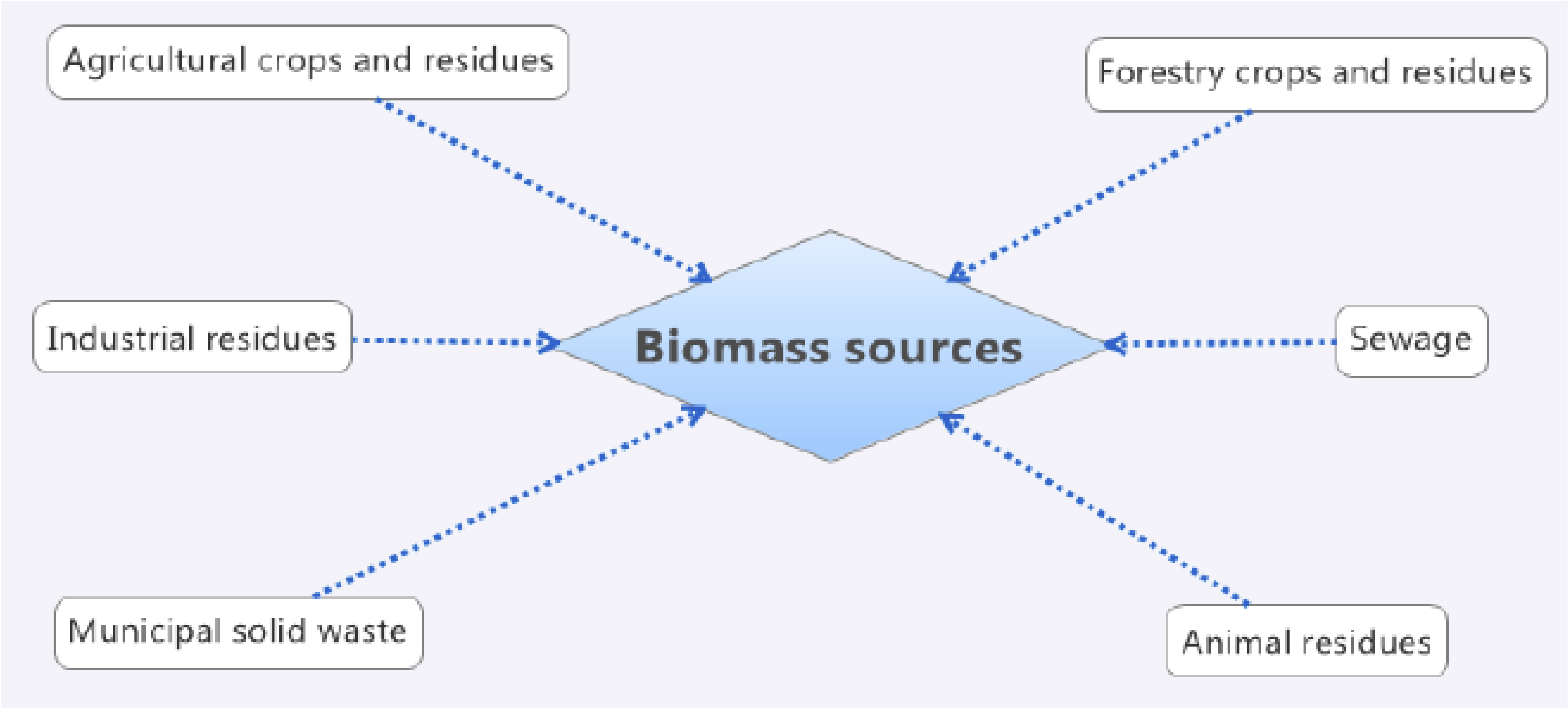
Window ledge chemistry

Solarbox

7) A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Biomass: all living material may be considered as biomass but, commonly, only non-animal renewable resources tend to be referred to as biomass.



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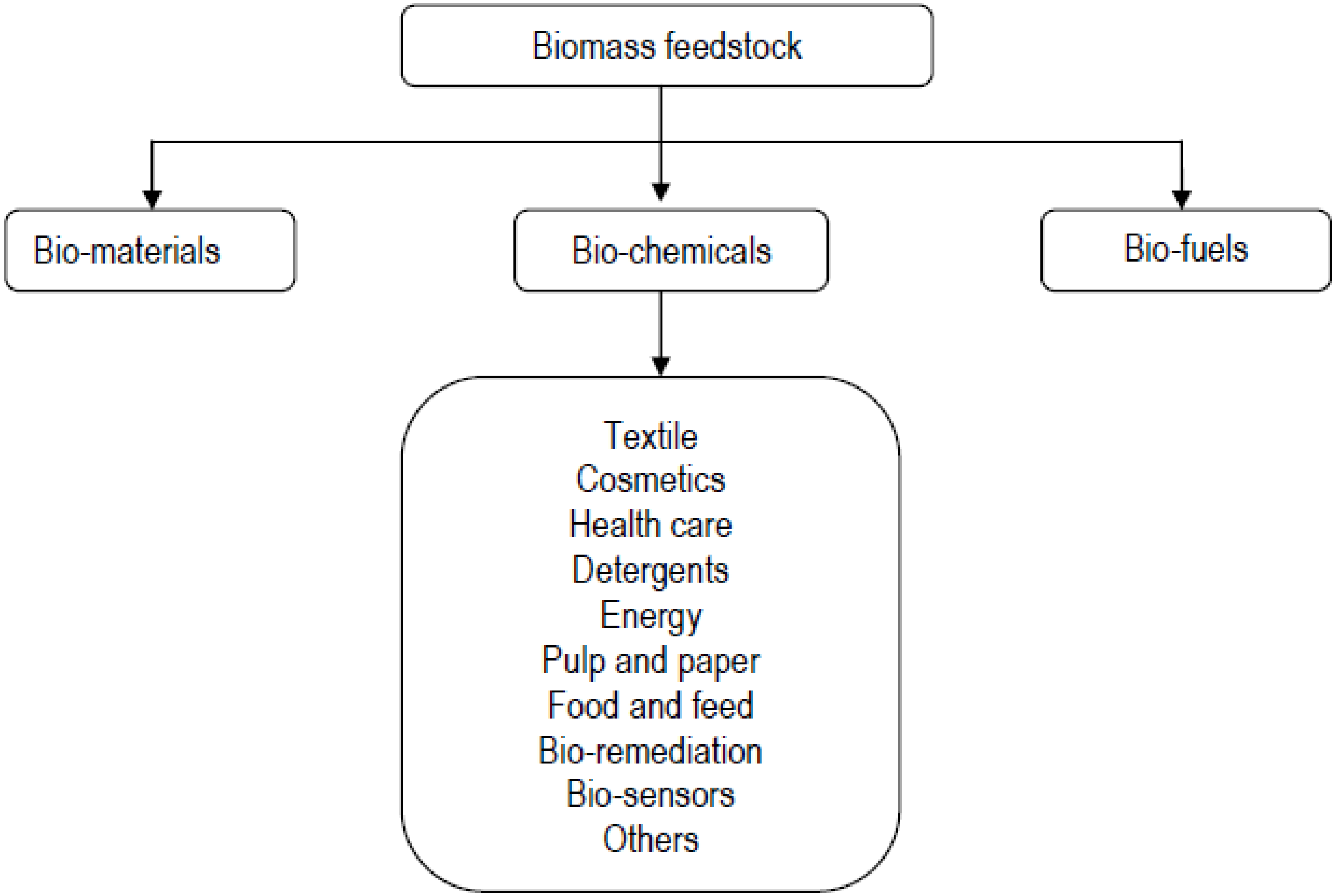

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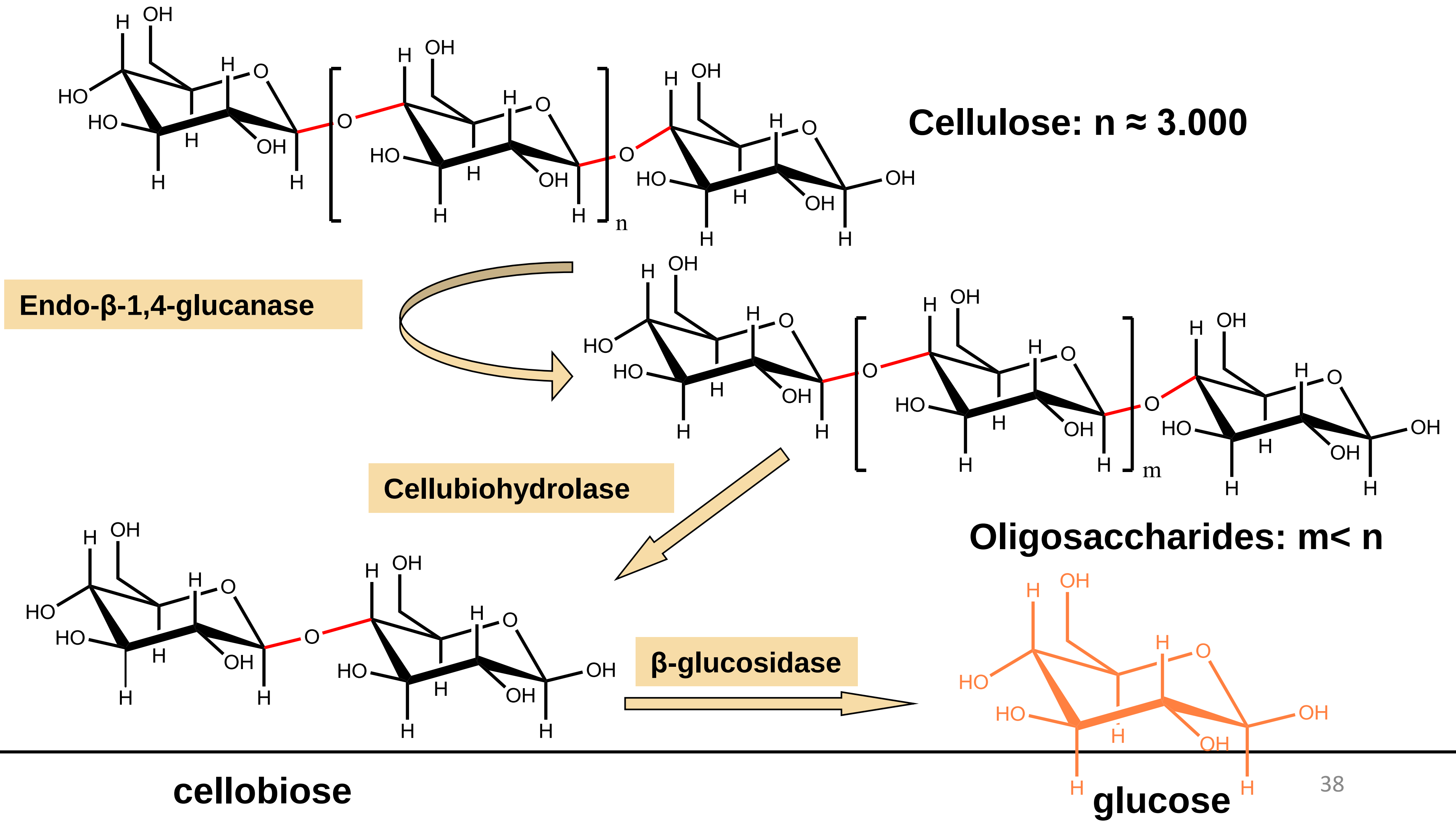
Bioethanol: production of ethanol from fermentation of glucose-based crops such as sugar cane and corn starch using yeast.



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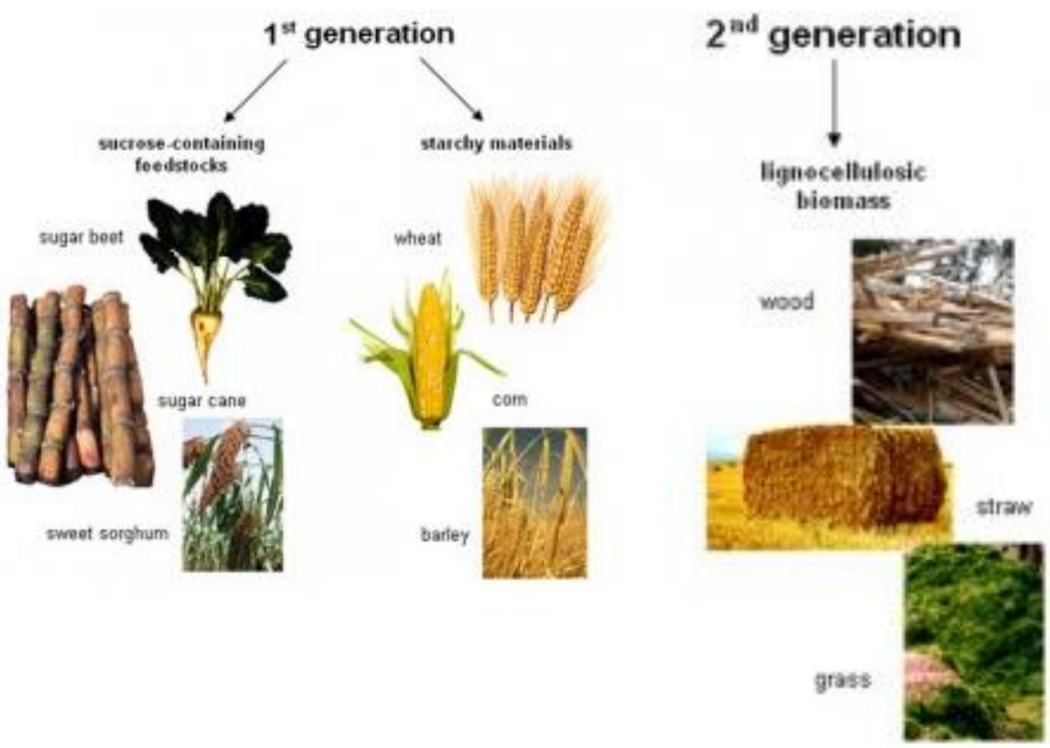


Disadvantages

- ✓ Waste disposal after the manufacturing process of ethanol;
- ✓ fermentation processes typically give a product with an ethanol concentration of between 7% and 15%. Distillation is required to obtain higher concentration

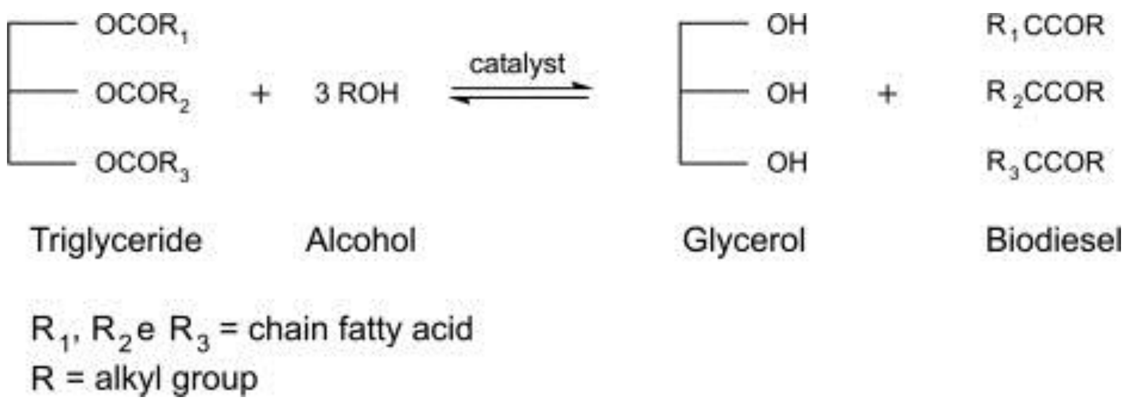
7) A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Biodiesel

"L'uso degli oli vegetali come carburanti per i motori può sembrare insignificante oggi, ma tali oli nel corso del tempo possono diventare altrettanto importanti quanto il petrolio e il carbone; la forza motrice potrà essere ottenuta col calore del Sole anche quando le riserve dei combustibili liquidi e solidi saranno esaurite".

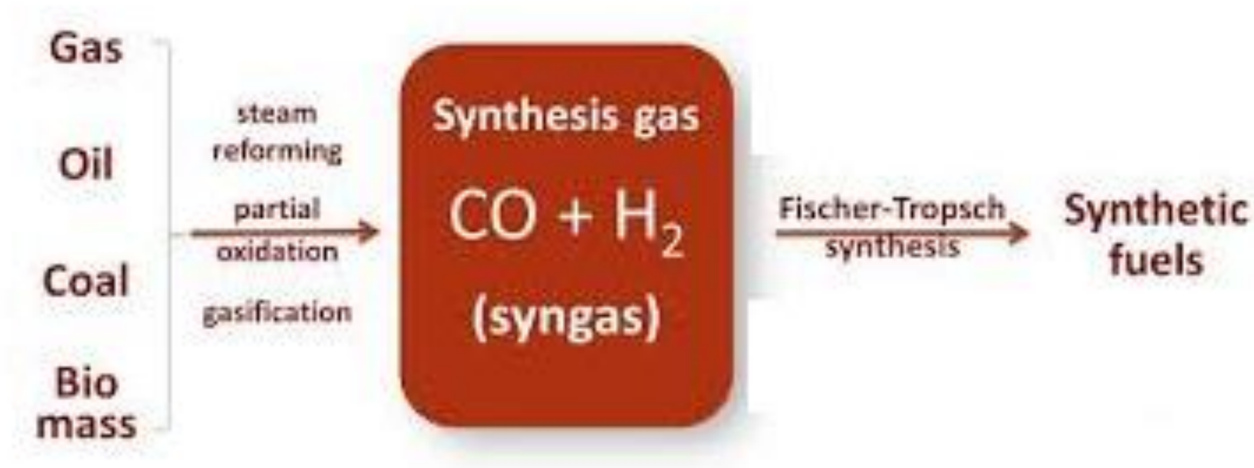
Rudolph Diesel, 1912

Biodiesel from vegetable oils



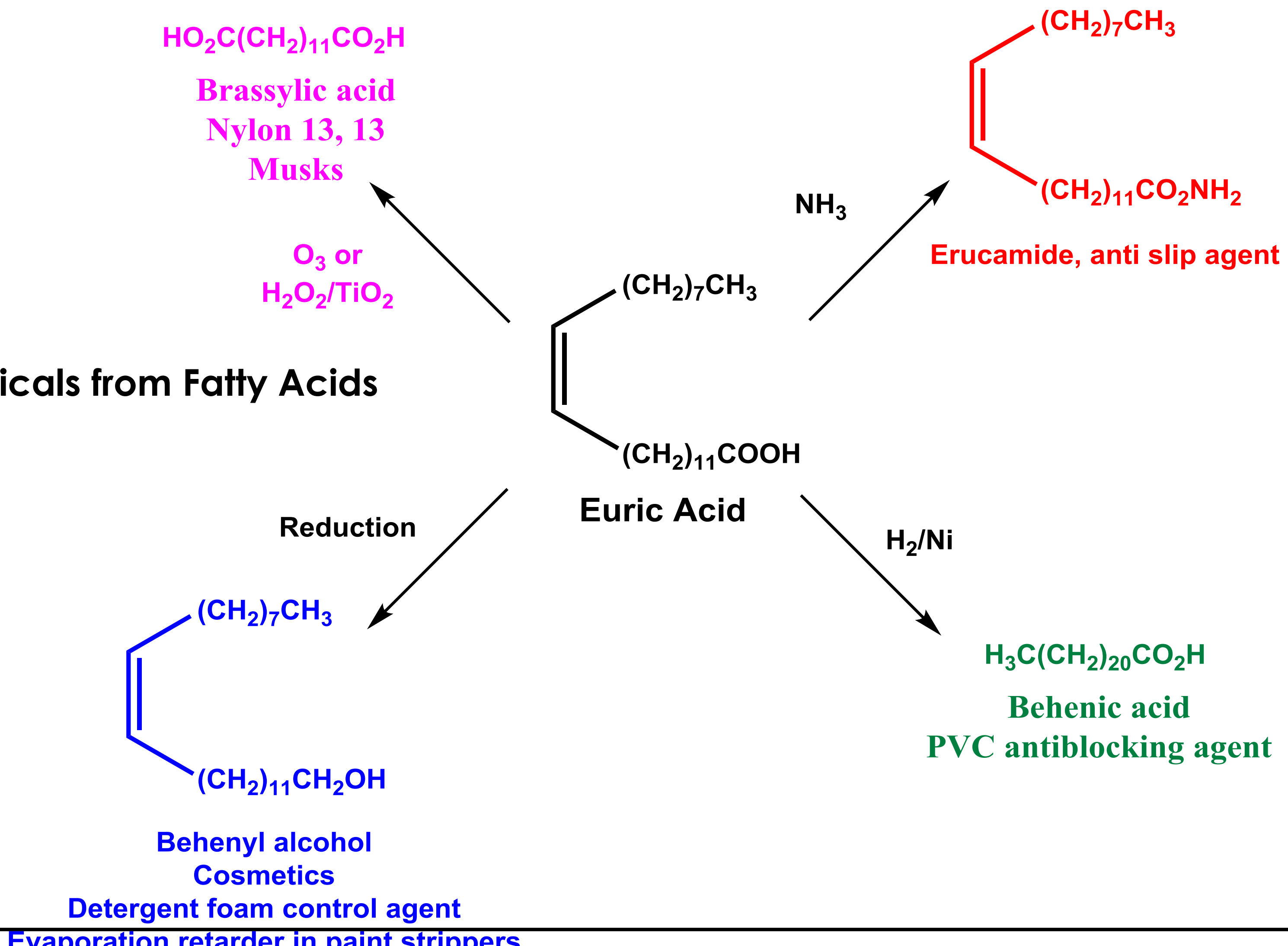
7) A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Syngas

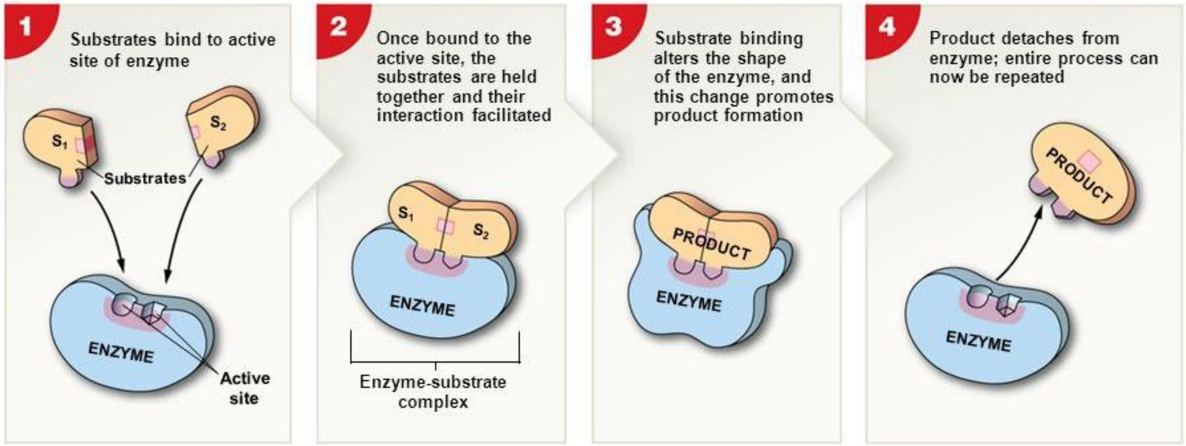


7) A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

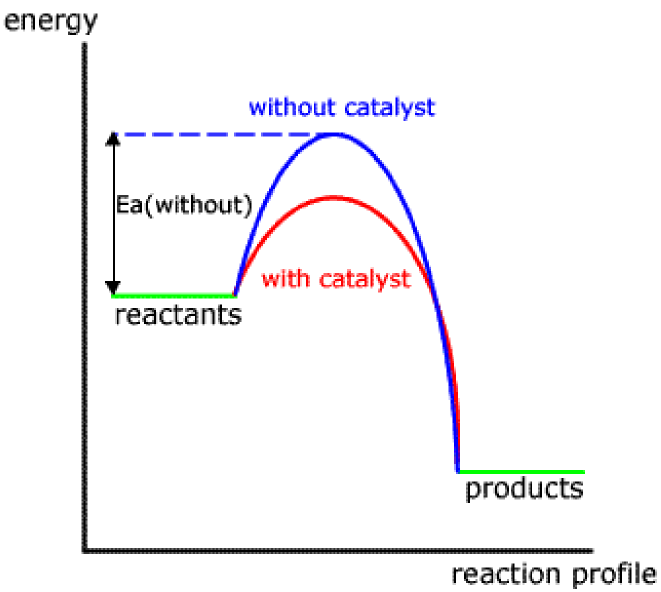
Chemicals from Fatty Acids



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



Catalyst: a material which changes (usually increases) the rate of attainment of chemical equilibrium without itself being changed or consumed in the process.



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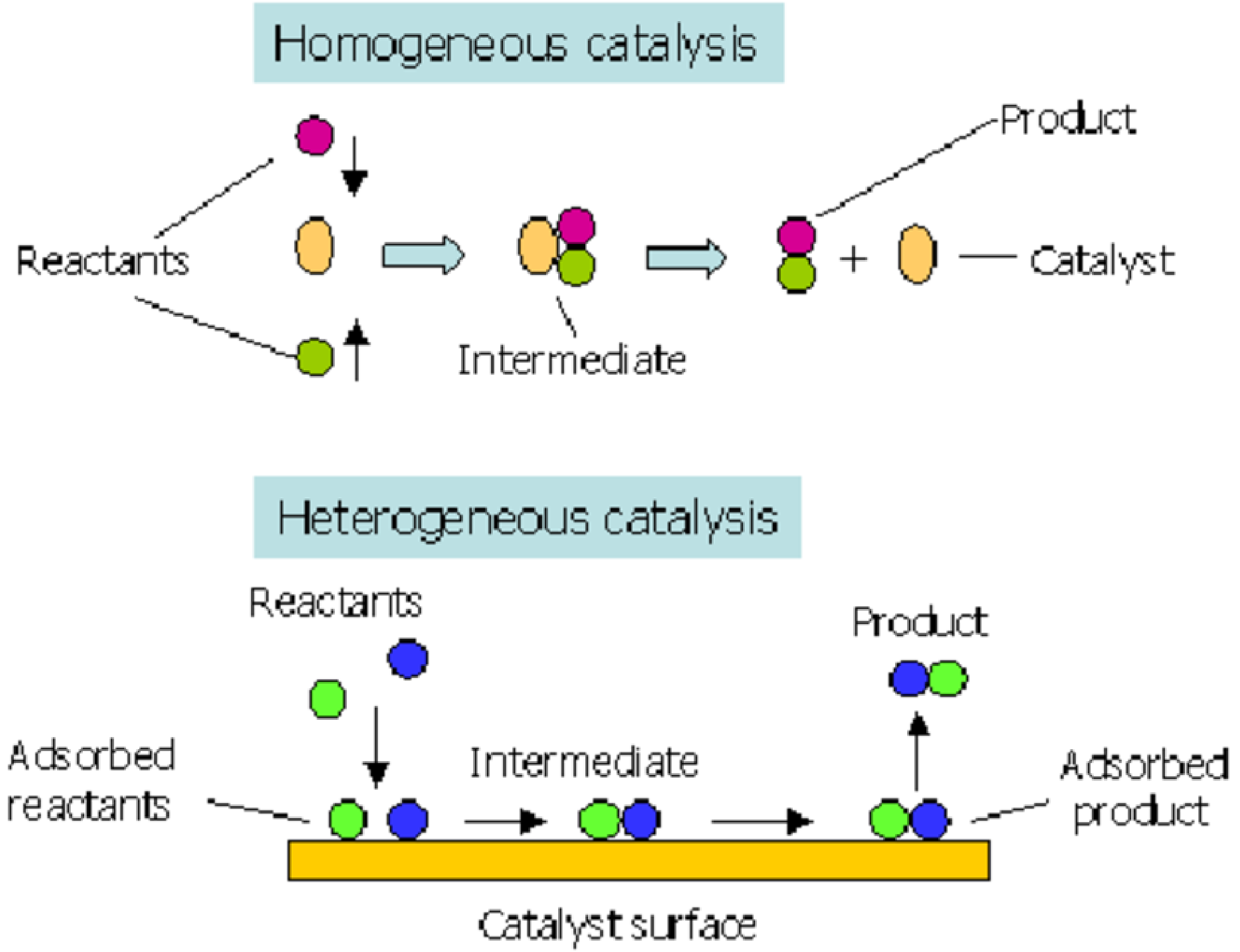
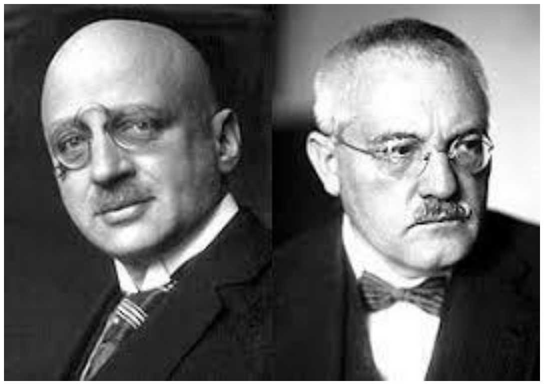


9) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

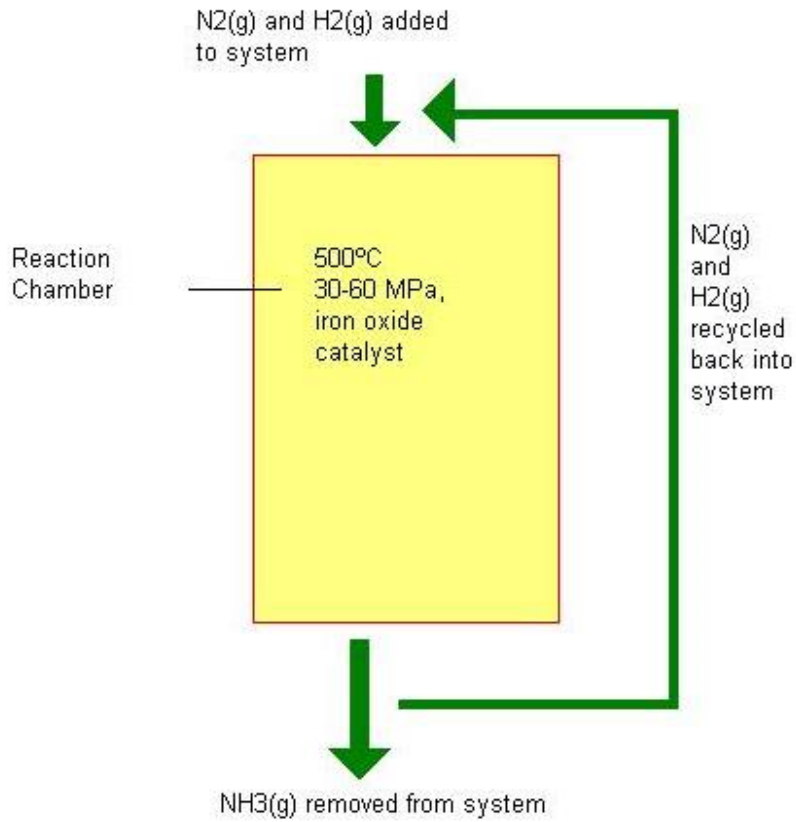
Heterogeneous catalysis	Homogeneous catalysis
Distinct solid phase	Same phase as reaction medium
Readily separated	Often difficult to separate
Readily regenerated and recycled	Expensive/difficult to recycle
Long service life	Short service life
Rates not usually as fast as homogeneous	Often very high rates
Quite sensitive to poisons	Usually robust to poisons
Low selectivity	High selectivity
Often high energy process	Often takes place under mild conditions
Poor mechanistic understanding	Often mechanism well understood

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

Haber Bosch process



$$N_2 + 3H_2 \xrightarrow[\text{[Fe]}]{\text{600°C, 150-200 bar}} 2NH_3$$

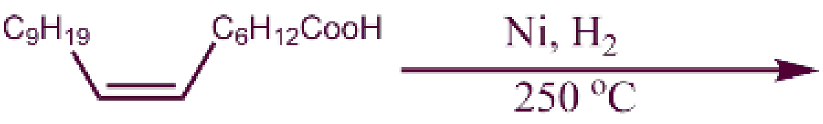


$$NH_3 \xrightarrow{Ox} HNO_3$$

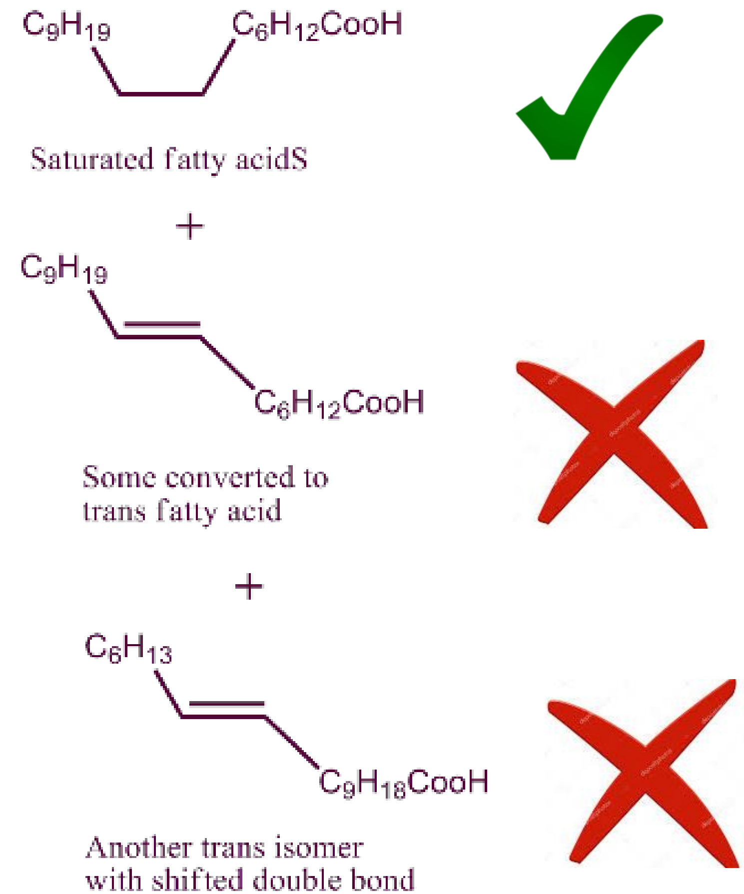
$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

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

Catalytic hydrogenation of Fatty Acids



Cis fatty acid



During partial hydrogenation some molecules get hydrogenated, some get converted to a low energy trans state and in some molecules double bonds get shifted to different carbons

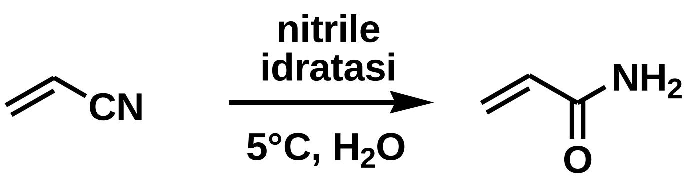
9) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Biocatalysis: use of biological systems (or reagents) to catalyze the conversion of a substrate to the desired product.

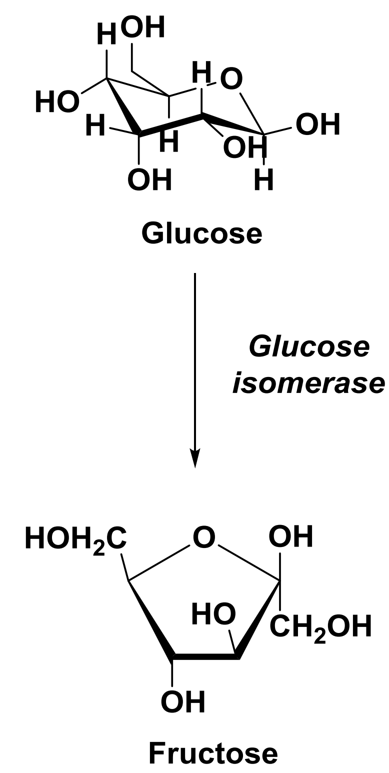
- ✓ Opportunity for aqueous phase reactions;
- ✓ non-toxic, low hazard catalysts;
- ✓ energy efficient reactions under moderate conditions of pH, temperature;
- ✓ high degree of selectivity.

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

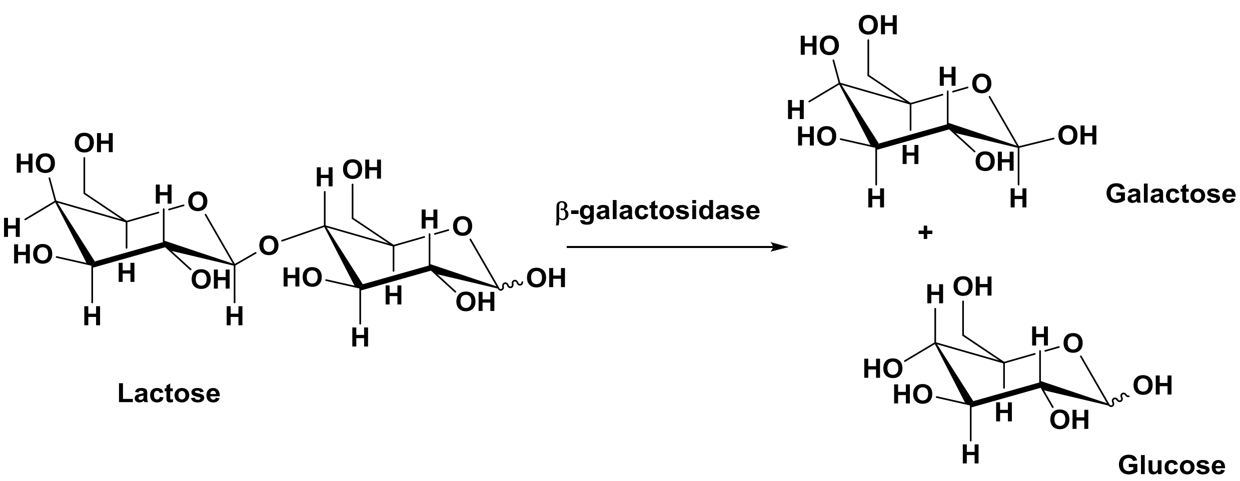
Production of acrylamide



Fructose synthesis

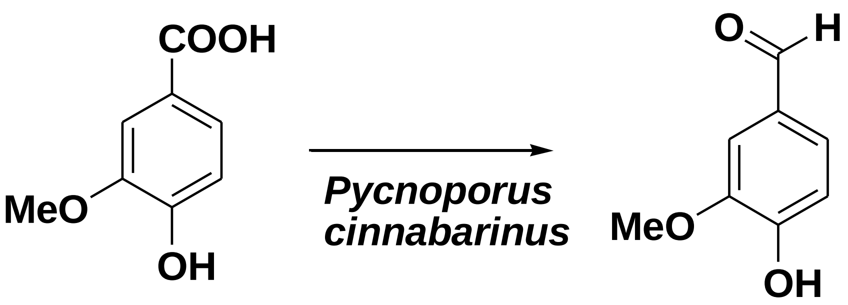


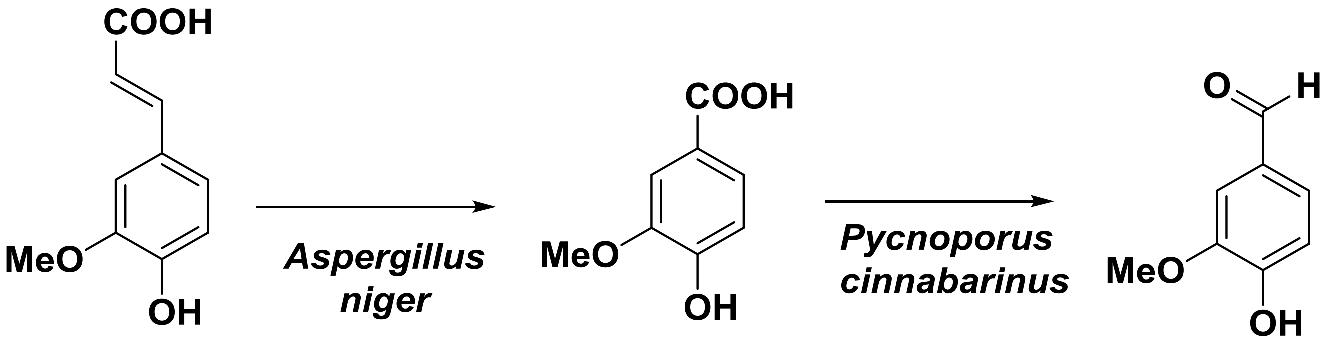
Cleavage of galactose



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

Vanilline synthesis

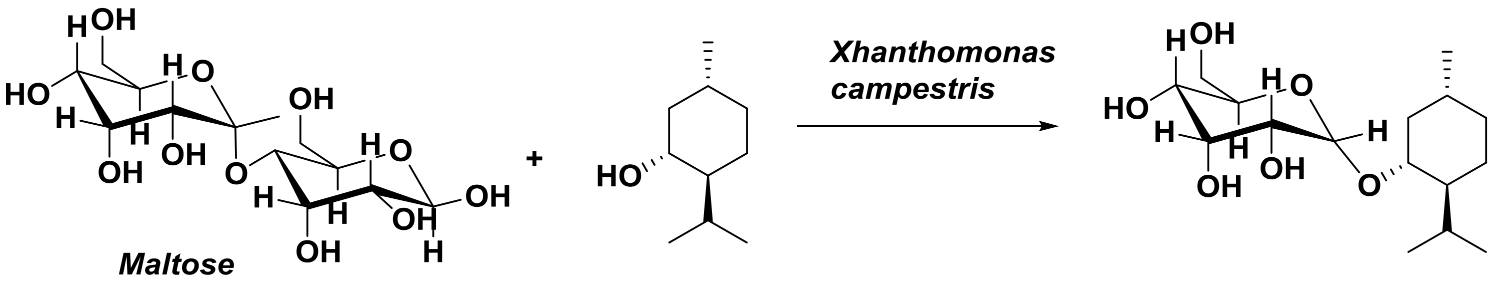




9) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Limitations of biocatalysis

- ✓ Stability of enzymes within a narrow range of pH and T;
- ✓ cost of enzymes and recovery difficulties once the cycle has been completed;
- ✓ isolation of the products obtained;
- ✓ difficulty of using enzymes in solvents other than water.



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

Photocatalysis: change in the **rate of a chemical reaction** or its initiation under the action of **ultraviolet, visble or infrared radiation** in the presence of a substance—the photocatalyst—that absorbs light and is involved in the chemical transformations of the reaction partners.

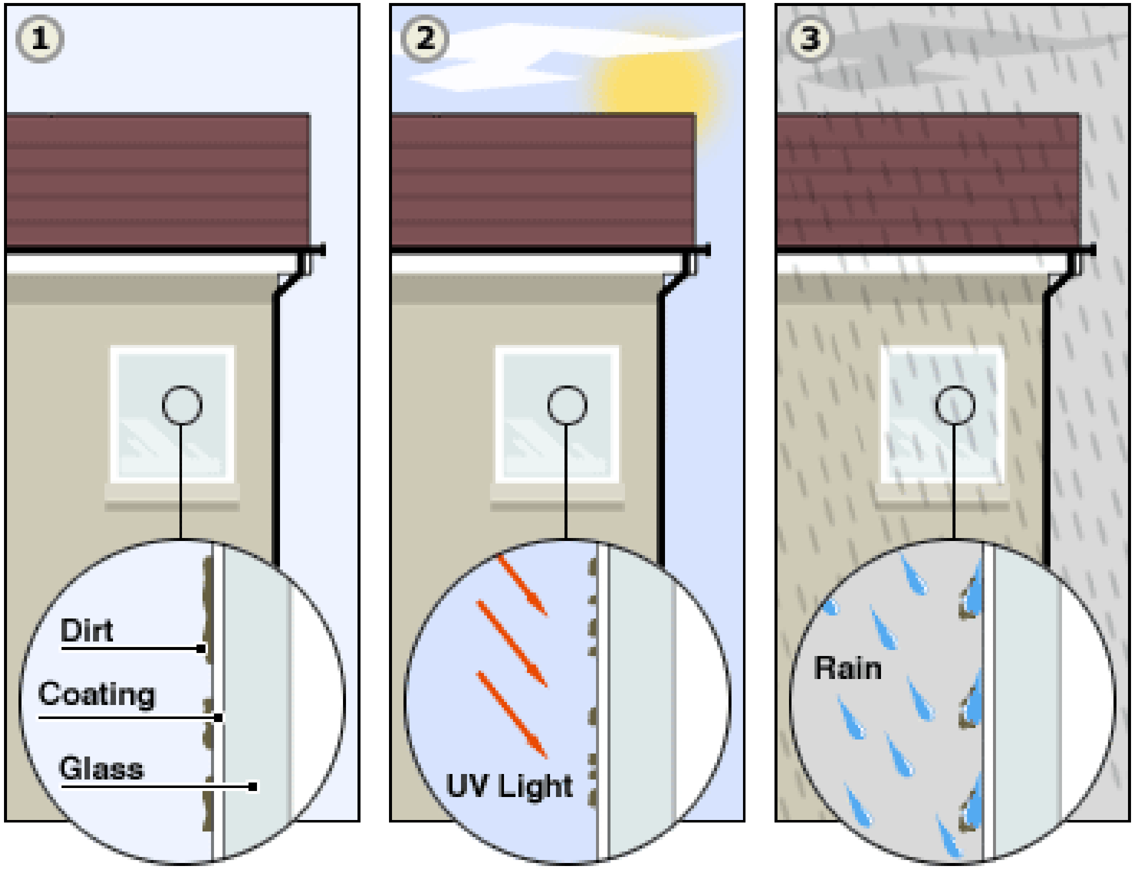
IUPAC GOLD BOOK

Photocatalyst: catalyst able to produce, **upon absorption of light, chemical transformations** of the reaction partners. The excited state of the photocatalyst repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such interactions.

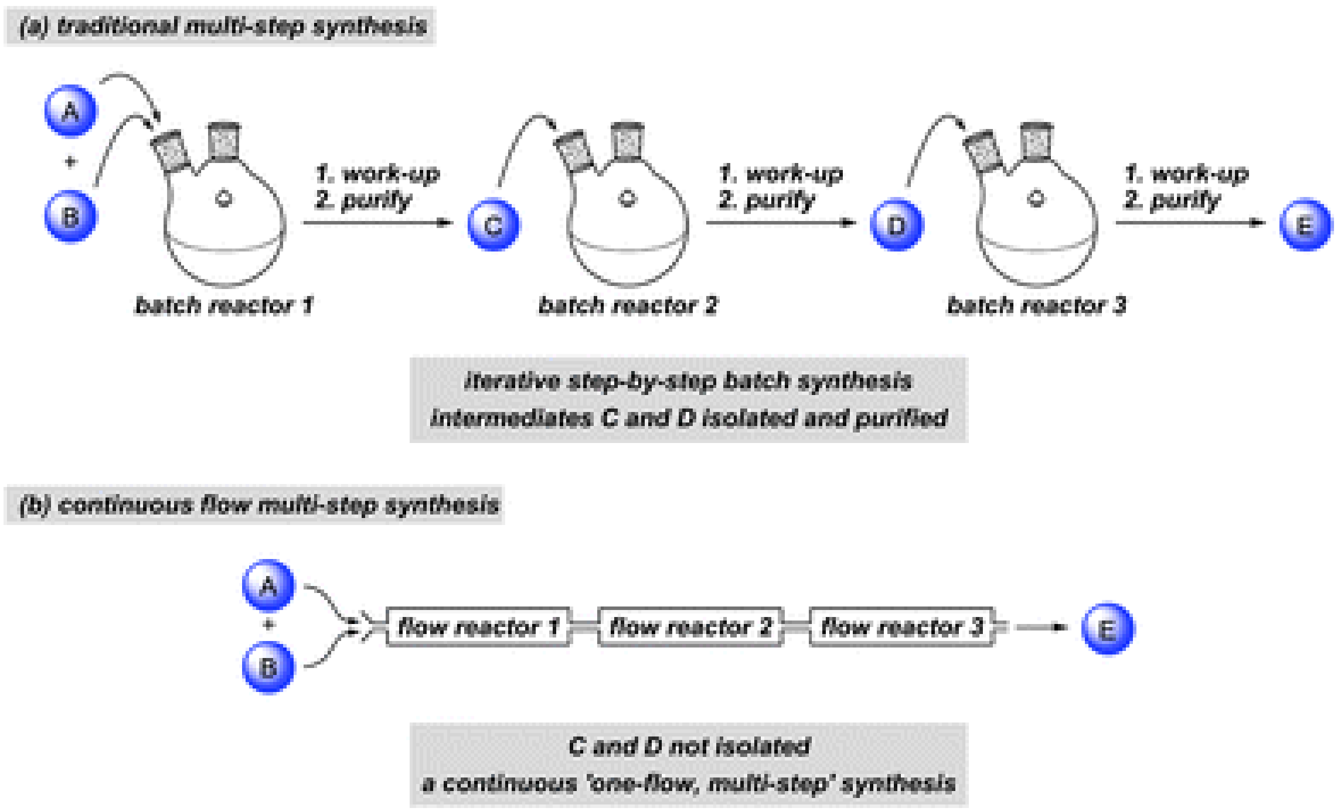
IUPAC GOLD BOOK

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

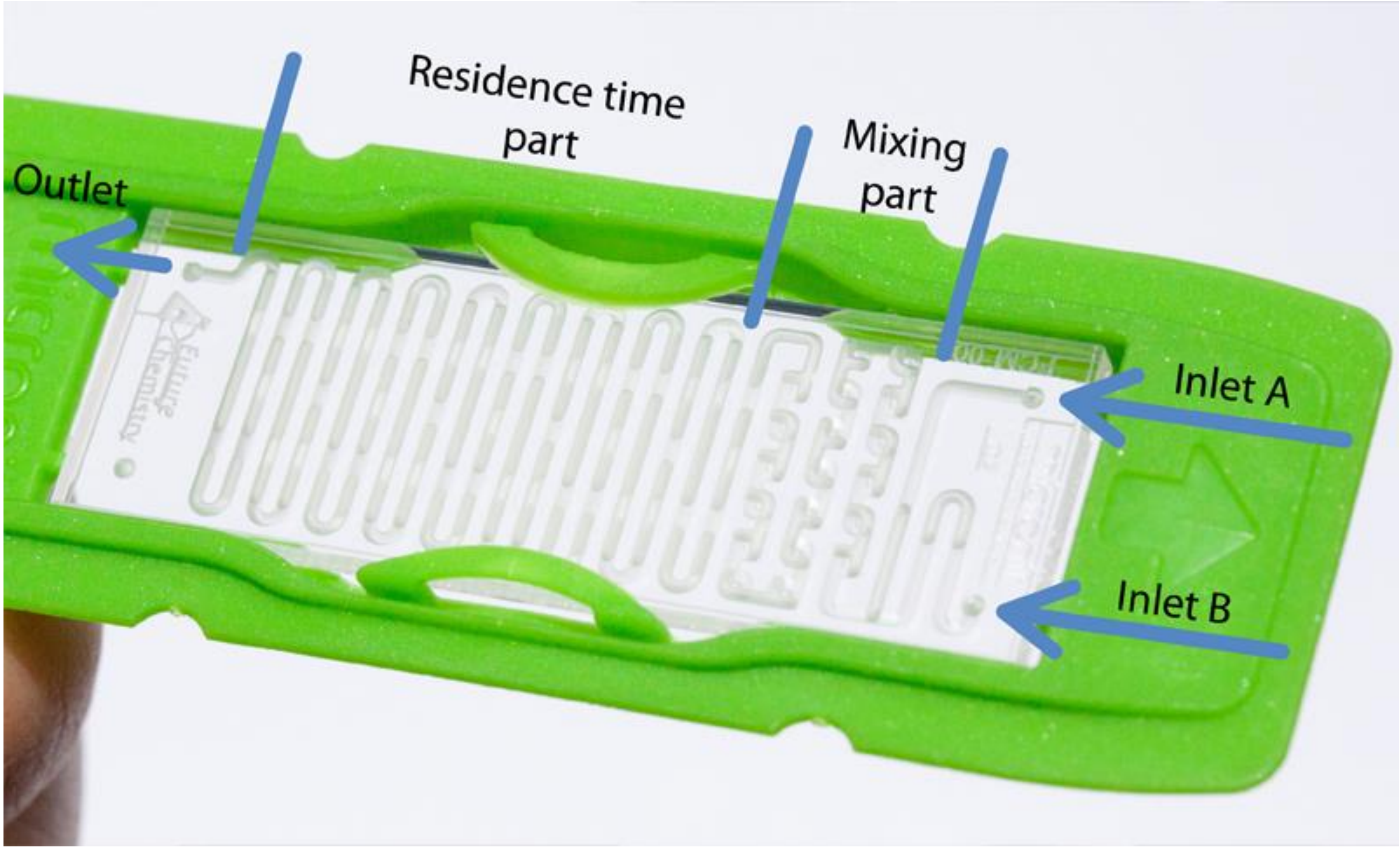
Titanium dioxide-self cleaning window



Designing Greener processes

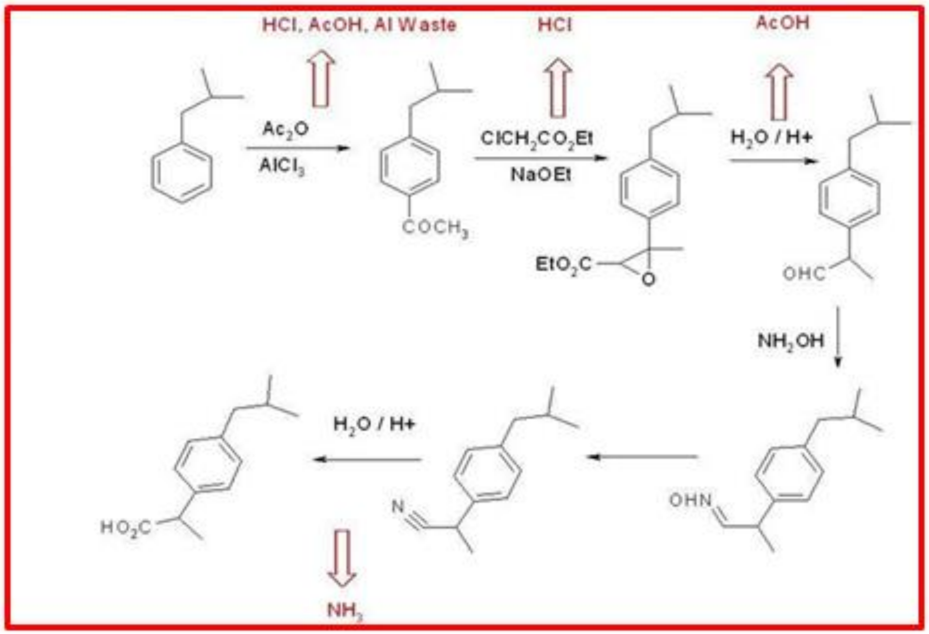


Designing Greener processes-Microreactors



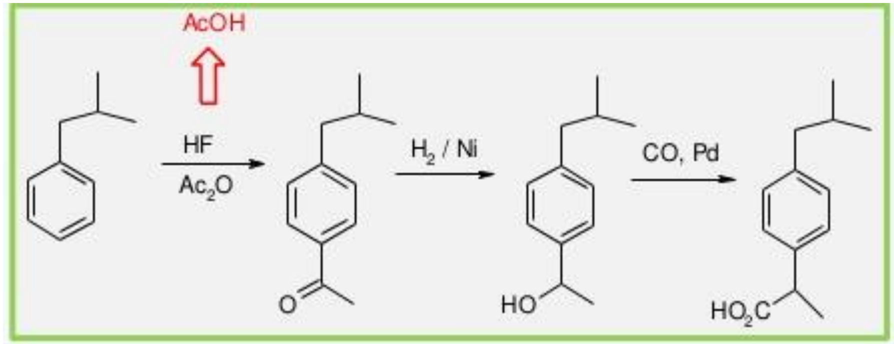
Ibuprofen synthesis

Ibuprofen Synthesis by Boots



- ✓ 6 steps;
- ✓ reagents rather than catalysts;
- ✓ copious amounts of waste.

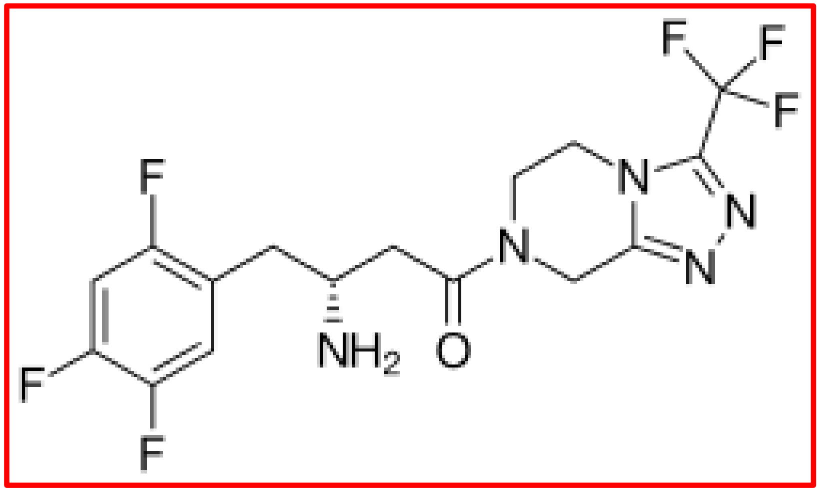
Green Synthesis



- ✓ 3 steps;
- ✓ catalysts rather than reagents;
- ✓ less waste.
- ✓ last two steps 100% A.E. and 100% yields;

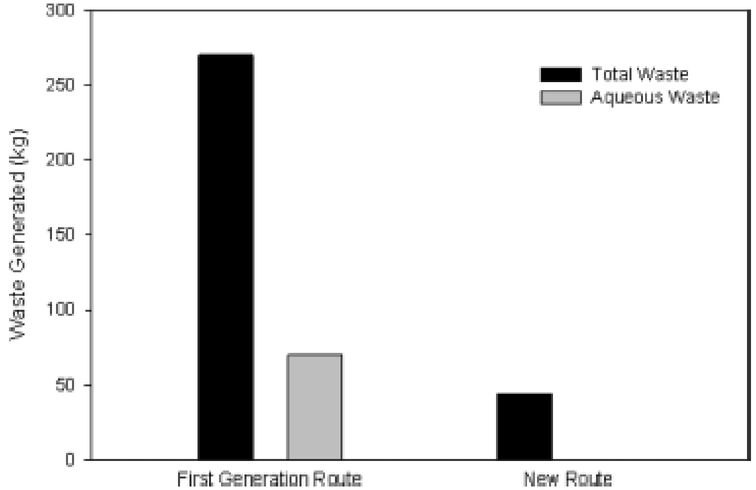
- ✓ CO

Highly efficient synthesis of Sitagliptin

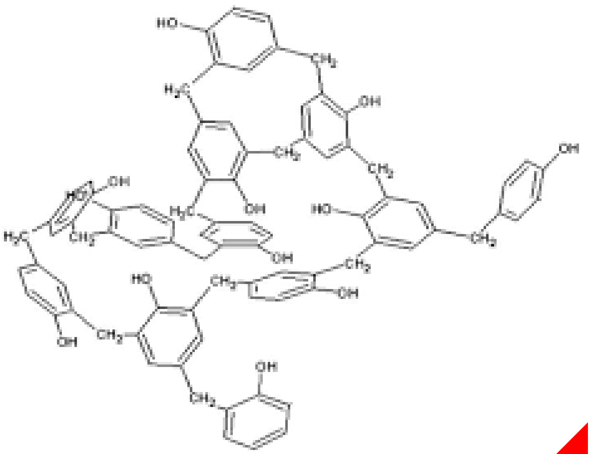


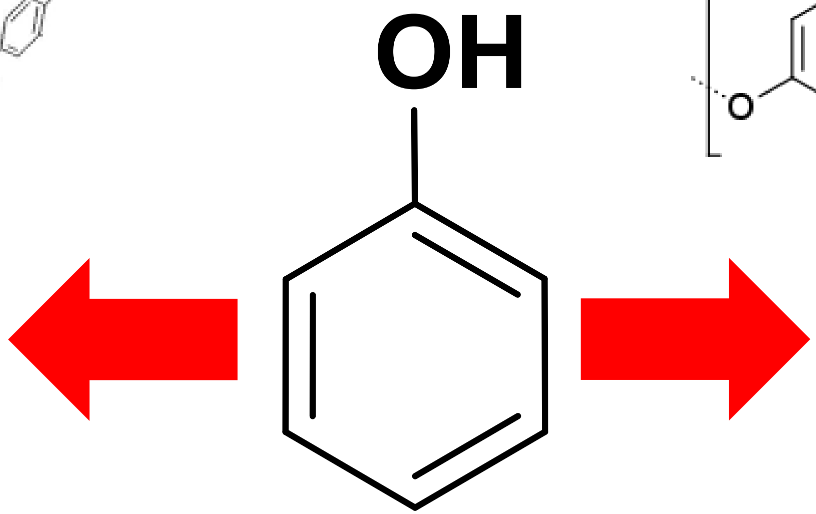
Presidential Green Chemistry Award 2006 and ICHEME AstraZeneca for sustainability award

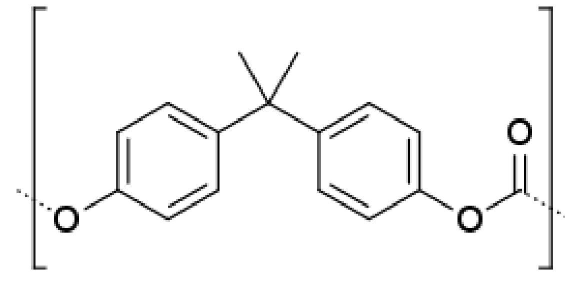
- ✓ 3 steps;
- ✓ 50% increase in yield;
- ✓ less waste.



Phenol Synthesis





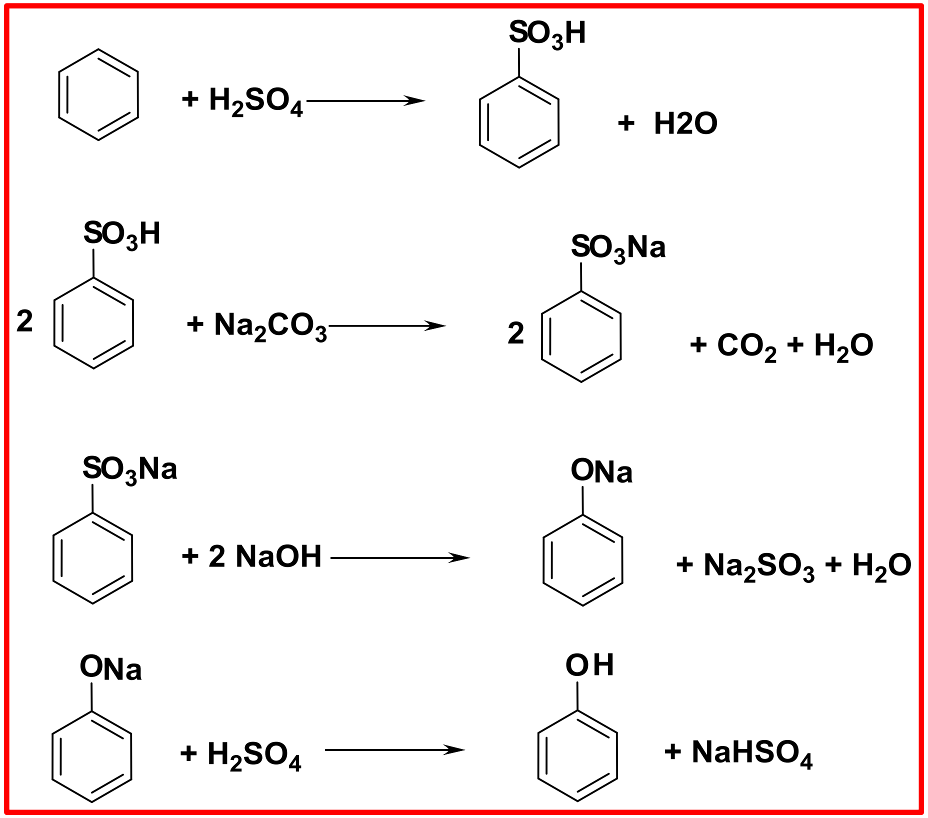


Bakelite

Polycarbonates

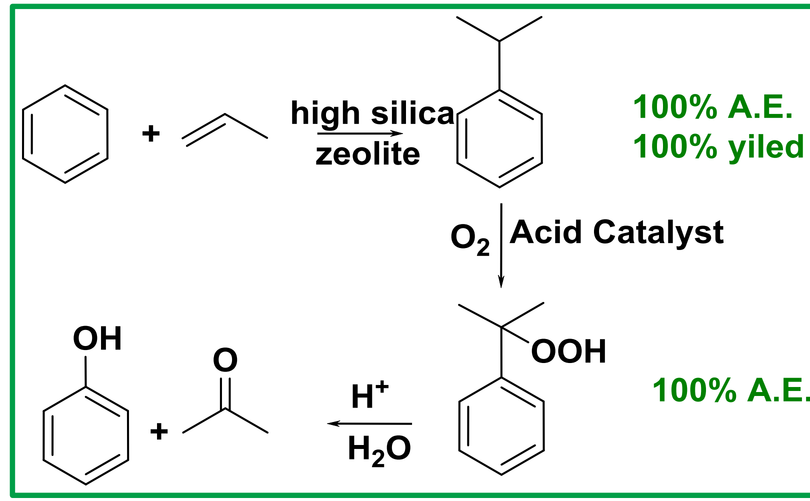
Phenol Synthesis

Old Synthesis



- ✓ 4 steps;
- ✓ copious amounts of waste;
- ✓ low atom economy.

Green Synthesis



- ✓ 3 steps;
- ✓ two steps 100% atom economy.