CH-429: Petroleum and Petrochemicals

Marking and evaluation:

• **Quiz 1:**	**5%**
• **Assignments/presentation:**	**5%**
• **Topics on petrochemicals:**	**A Group of 5 students**
• **Mid-semester examination**	**40%**
• **Attendance (top-up)**	**0.5 mark/class**
• **Class notes**	**0.5 mark/class**

PSU: Public Sector Undertaking

- Coal India Limited
- Bharat Petroleum Corpor...
- Bharat Heavy Electricals ...
- Bharat Electronics Limited
- Engineers India Limited
- Indian Oil Corporation
- Bank of Baroda
- GAIL
- BEML Limited
- NTPC
- Container Corporation of...
- Bharat Dynamics Ltd
- Hindustan Aeronautics Li...
- Balmer Lawrie
- Airports Authority of India
- Bharat Sanchar Nigam Li...
- Hindustan Petroleum
- Bharat Coking Coal
- Steel Authority Of India
- Central Coalfields Limited
- Central Electronics Limited
- Indian Bank
- Canara Bank
- Antrix Corporation


गेल
GAIL
ओएनजीसी
ONGC
बी एच ई एल
BHEL
इंडियनऑयल
IndianOil
सेल SAIL
Empowering India • Enabling Life • Nurturing Nature
Coal India
एनटीपीसी
NTPC
Bharat Petroleum
भारत की
महारत्न, नवरत्न और
मिनीरत्न कम्पनियाँ

List Of Maharatna Companies In India

GREEN CHEMISTRY

Bhisma K. Patel. ***FASc, FNASc***

Department of Chemistry
IIT Guwahati

The Purpose of this lecture is to introduce the concept of Green Chemistry followed by circular economy through circular chemistry. The first lecture is about green chemistry. During 1990's to control environmental pollution a concept called "Green Chemistry" evolved based on 12 principles. Many of you can be future "Environmental Entrepreneur" if you know the current status of the production of chemicals from renewable raw materials via "biorefinaries Processes". The list is vast, I have given selected a few to stimulate your thinking for "Startup India". However, there are lots of challenges associated with these processes and are often economically not viable.

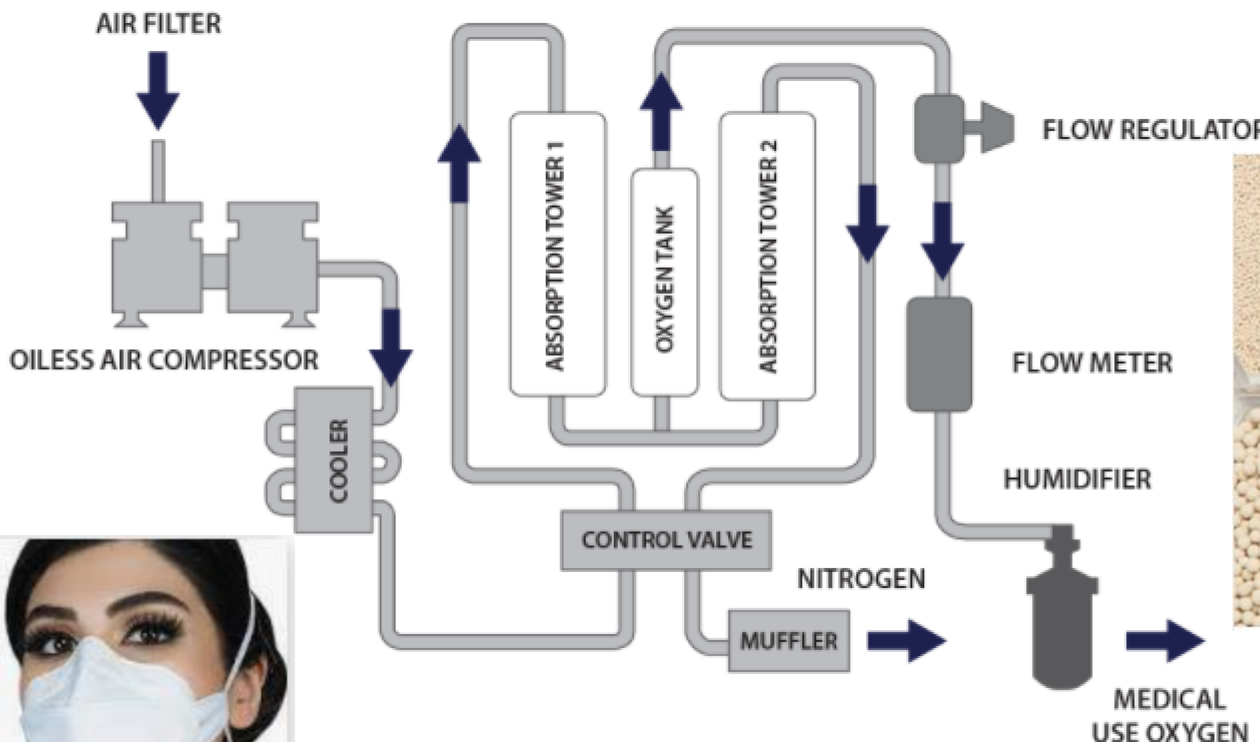
The "platform molecules" obtained can be transformed into numerous other industrially useful molecules.

If you are having "an entrepreneurship" ship in mind these topics are very much relevant.

Chemistry is both a central science and an enabling science.

Chemistry plays a key role in

- **Conquering diseases**
- **Solving energy problems**
- **Solving environmental problems**
- **Providing the discoveries that lead to new industries**
- **Developing new materials and new technologies.**


AIR FILTER
OILESS AIR COMPRESSOR
COOLER
ABSORPTION TOWER 1
OXYGEN TANK
ABSORPTION TOWER 2
CONTROL VALVE
MUFFLER
NITROGEN
FLOW REGULATOR
FLOW METER
HUMIDIFIER
MEDICAL USE OXYGEN


HAND SANITIZER


Dr.Reddy's
2-Deoxy-D-Glucose Oral Powder 2.34 g
O2DG
For Use in hospital/ institutional set up only
2.34 g
2-Deoxy-D-Glucose Oral Powder 2.34 g
O2DG
For Use in hospital/ institutional set up only
2.34 g

Oxygen concentrator developed by IIT Guwahati.

The Major Challenges to Sustainability in the 21st Century

Population:

Energy:

Global change:

Human health:

Resource depletion:

Food supply:

Toxics in the environment:

Chemistry has the privilege of being singularly responsible for the tremendous advancements that humankind has made in “different areas”. Almost all fields have used chemistry in some form or the other for its betterment

However, industrial chemistry is not always benign, and it is also criticized for being responsible for a number of environmental problems. Thus there is need for sustainable development and practice of Green chemistry.

Green Chemistry

- Life style have been enhanced by chemistry, something chemists and students need to celebrate.

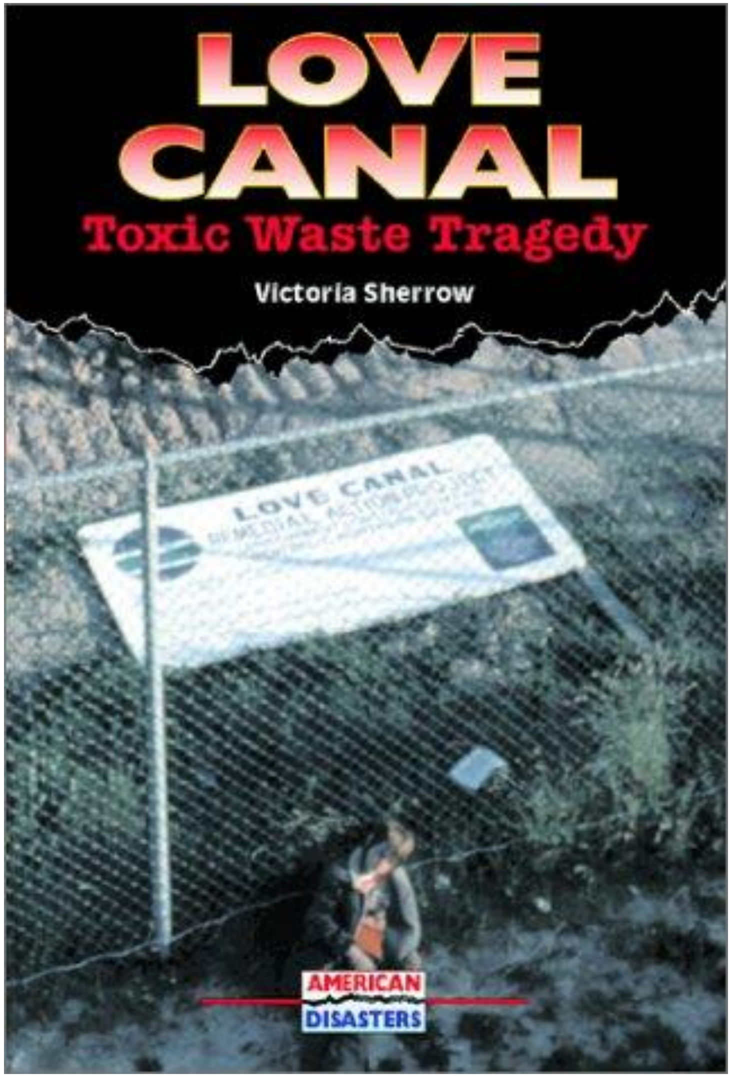
- Estimates from the United Nations put the world population as high as 10.7 billion people by 2050 (current 8.1) – this population population will create a huge demand for chemical goods and services shortly.

- Much of the growth of the chemical industry is likely to take place in the developing world, coincident with the rising population.

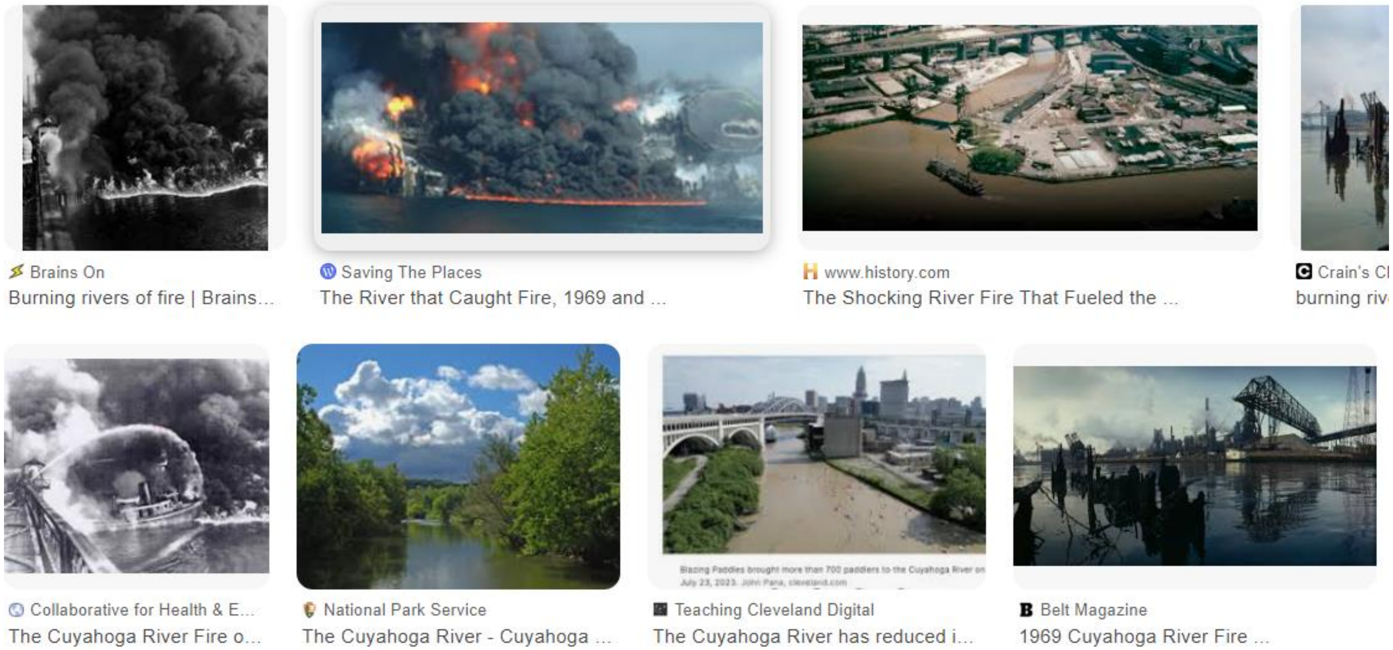
- Environmental problems such as ozone depletion, the Love Canal, Bhopal, Cuyahoga River, Changing Climate, Sea Level Change and the Loss of Biological Species are all too familiar examples of chemistry gone wrong.

- (140 birth/minutes)

The Love Canal Tragedy



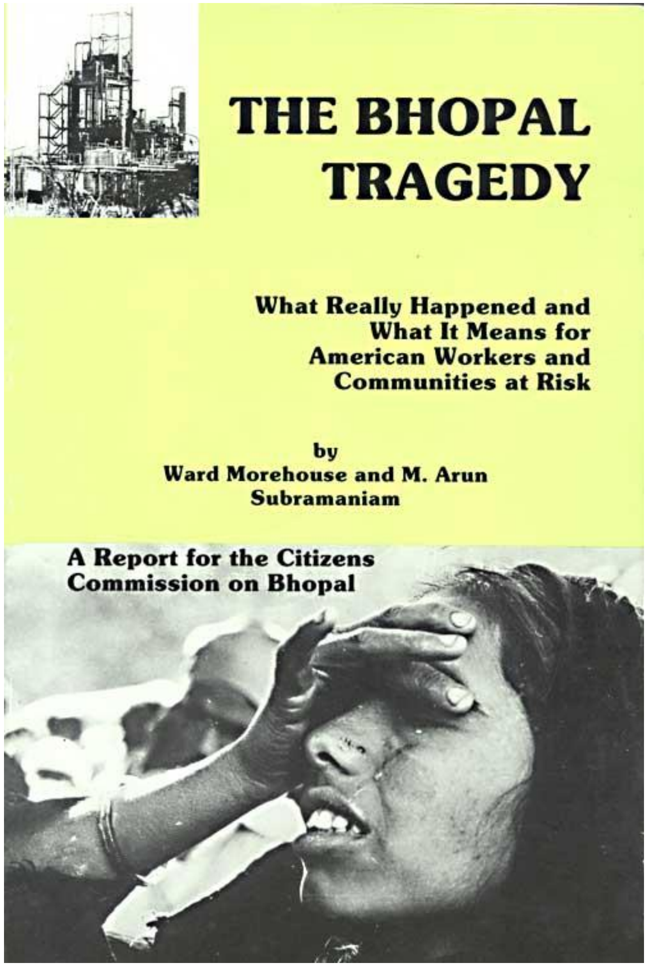
Love Canal, in Niagara Falls, New York was used as the site for chemical waste. Hundreds of suspected carcinogens were dumped. The site was eventually closed, but a school and several apartment homes were built. Heavy rains led to leaching and puddles of chemical wastes formed in the neighborhood. Higher than normal rates of miscarriage and birth defects were reported.



Cuyahoga River

The river was one of the most polluted waterways in the country. A hundred years of dumping unregulated factory waste had smothered the river in a foot of oil. In fact, the Cuyahoga had burned at least 13 times since the 1860s.

The Bhopal Tragedy



The accidental release of methyl isocyanate in Bhopal, India, in 1984 killed 3,800 people and disabled another 2700.

Green Chemistry

- **In recent years, the chemistry community has been mobilized to develop new chemistries that are less hazardous to human health and the environment.**

- **One of the foremost challenges currently facing synthetic organic chemistry is the demand for alternative methods that are simple, environmentally friendly, highly chemo- and regio-selective, and also more convenient for industrial applications.**

- **It is necessary to develop new chemical methods that are more economical and less hazardous to human health and the environment.**

- **The key to waste minimization in fine chemical synthesis is the widespread substitution of classical organic reactions employing stoichiometric amounts of reagents with cleaner and catalytic alternatives.**

Global Warming & Climate Change

The **boiling frog** story is a widespread anecdote describing a frog slowly being boiled alive.
The premise is that if a frog is placed in boiling water, it will jump out, but if it is placed in cold water that is slowly heated, it will not perceive the danger and will be cooked to death.
As a metaphor for the inability of people to react to significant changes that occur gradually.

Environmental Science and Green Chemistry

Both areas of study seek to make the world a better place

These two are complementary to each other.

Environmental Science identifies sources, elucidates mechanisms and quantifies problems in the earth's environment

Green Chemistry seeks to solve these problems by creating alternative, safe technologies

Green Chemistry is NOT Environmental Chemistry

Green Chemistry targets pollution; prevents at the source during the design stage of a chemical process and thus prevents pollution before it begins

DEFINITION OF CHOICE

Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. It also refers to the ***discovery of new chemistry*** and/or technology leading to prevention and/or reduction of environmental, health and safety impact at source.

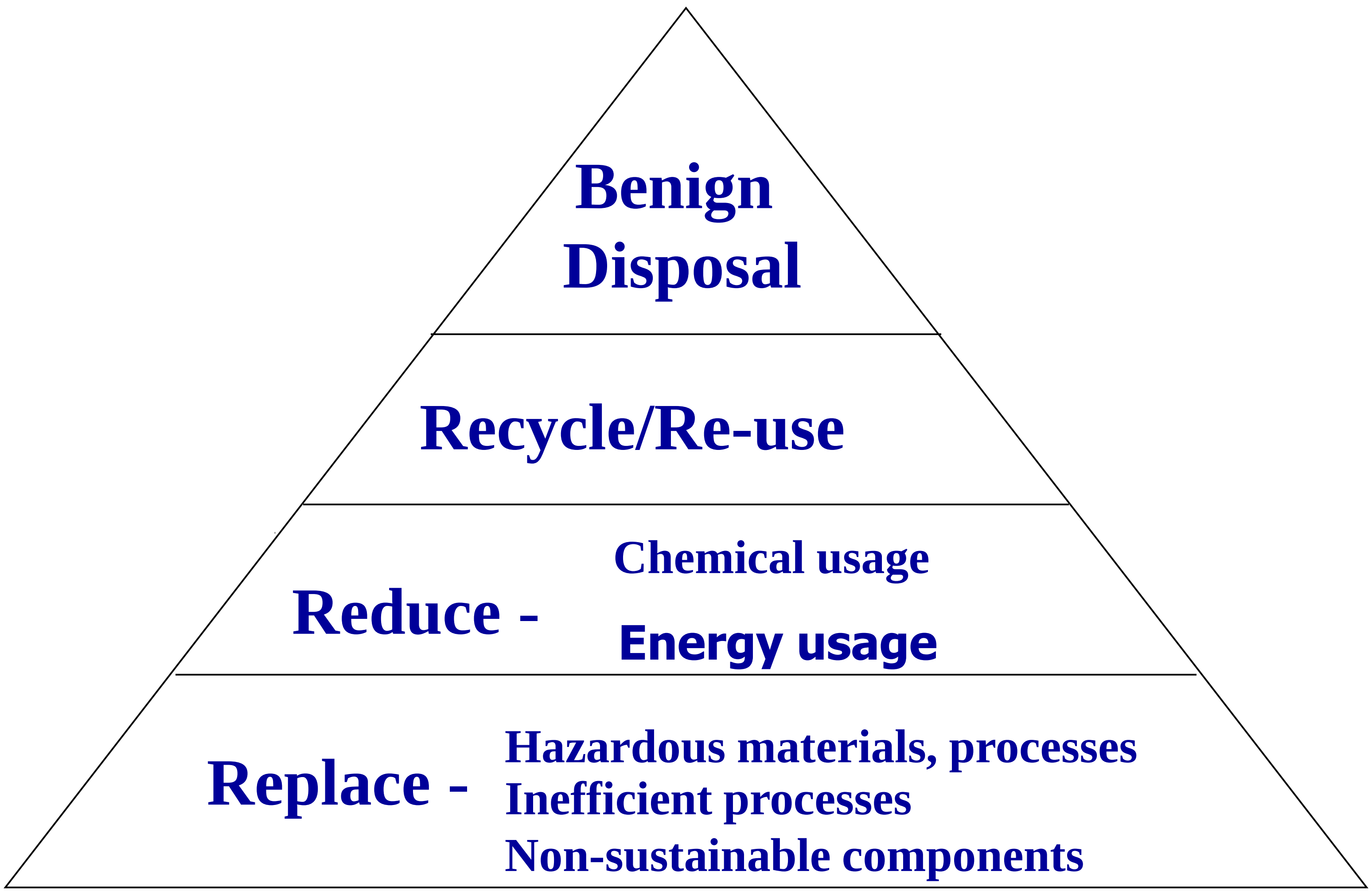
– JH Clark, University of York, UK

An out and out interdisciplinary field of chemistry where chemical engineers also can contribute meaningfully.

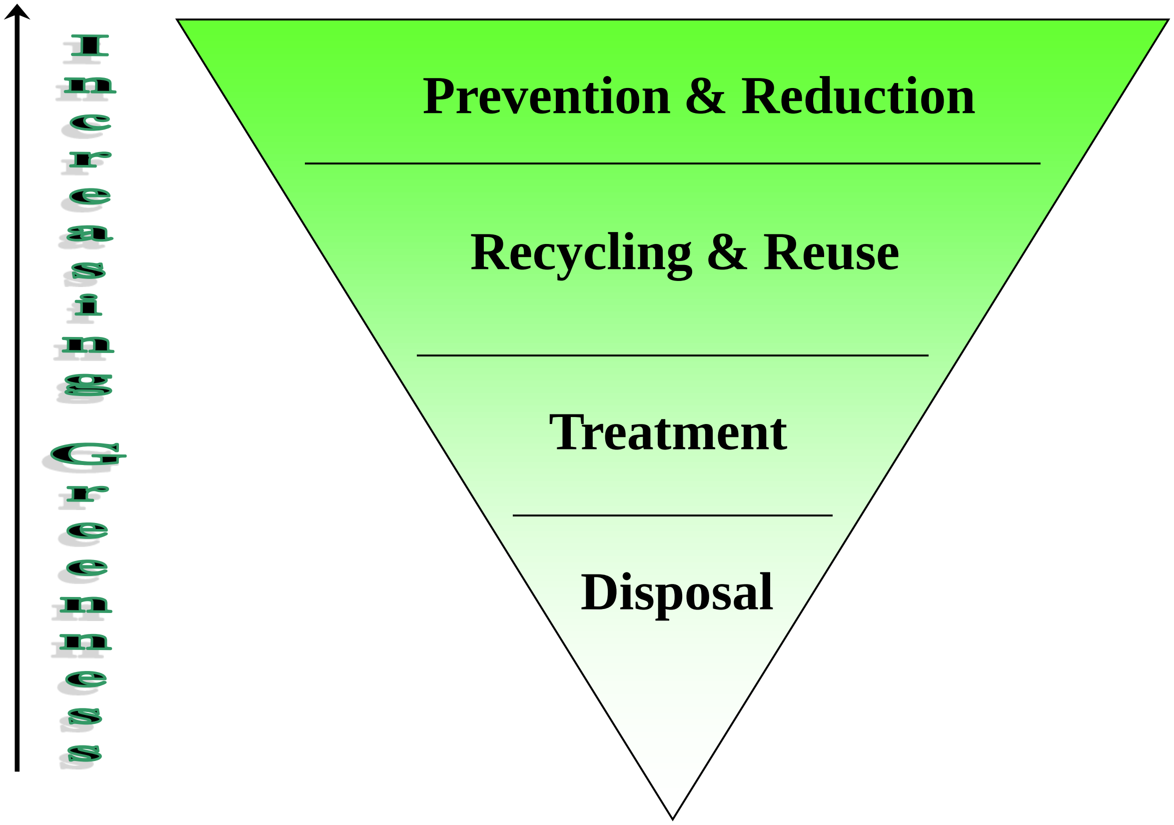
Fundamentals of Green Chemistry

- It is better to prevent waste than to treat or clean up waste after it is formed
- Atom economy
- Benign by design
- The raw material feedstocks should be renewable
- Performing reactions at ambient temperature and pressure
- Use of catalytic reagents (as selective as possible)
- Use of substances, which minimizing the chemical accidents
- Environmentally friendly and economically sound medium
- Design chemical products to break down into innocuous degradation products
- Unnecessary derivatization should be avoided whenever possible

What is Green Chemistry?



Pollution Prevention Hierarchy



Green Chemistry Is About...

Reducing

- **Waste**
- **Materials**
- **Hazard**
- **Risk**
- **Energy**
- **Environmental Impact**
- **COST**

PRODUCTIVE IMPROVEMENTS

The 24 Principles of Green Chemistry and Green Engineering

PRINCIPLES OF GREEN CHEMISTRY		PRINCIPLES OF GREEN ENGINEERING	
P	**P**revent wastes	I	**I**nherently non-hazardous and safe
R	**R**enewable materials	M	**M**inimize material diversity
O	**O**mit derivatization steps	P	**P**revention instead of treatment
D	**D**egradable chemical products	R	**R**enewable materials and energy inputs
U	**U**se safe synthetic methods	O	**O**utput-led design
C	**C**atalytic reagents	V	**V**ery simple
T	**T**emperature, Pressure ambient	E	**E**fficient use of mass,energy, space & time
I	**I**n-Process Monitoring	M	**M**eet the need
V	**V**ery few auxiliary substances	E	**E**asy to separate by design
E	**E**-factor, maximize feed in product	N	**N**etworks for exchange of local mass & energy
L	**L**ow toxicity of chemical products	T	**T**est the life cycle of the design
Y	**Y**es it's safe	S	**S**ustainability throughout product life cycle

Poliakoff et al., *Green Chem.*, 2008, 10, 268

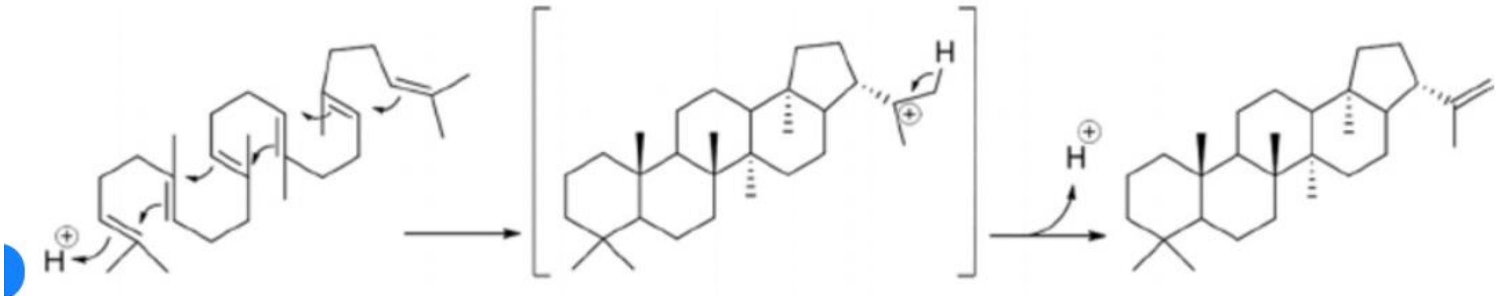
Principle 1:

Prevent waste: **Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.**

Many strategies exist in chemical synthesis that go beyond converting reactant A to reaction product B.

In CASCADE reactions multiple chemical transformations take place within a single reactant, in multi-component reactions up to 11 different reactants form a single reaction product

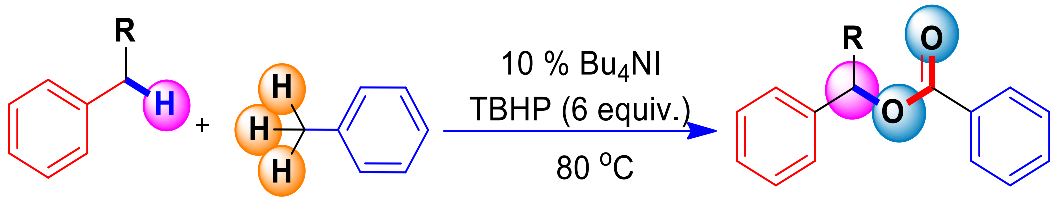
A cascade reaction or tandem reaction or domino reaction is a consecutive series of intramolecular organic reactions which often proceed via highly reactive intermediates.



Assignment no 1:

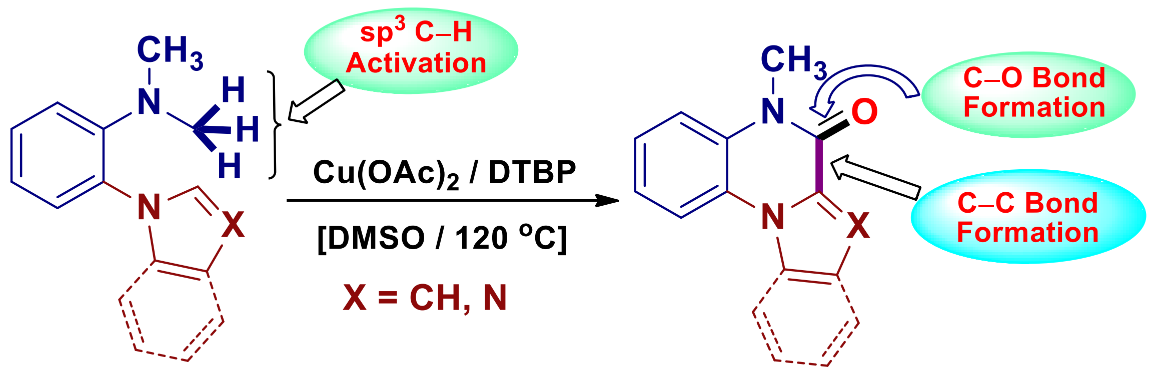
Give two examples of cascade reaction and multicomponent reaction. One example may be from my (BKP) research work

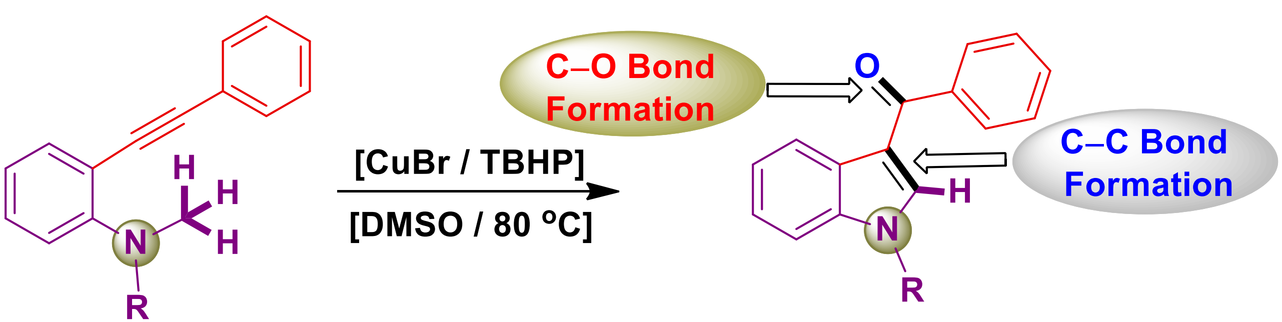
A Typical Reaction

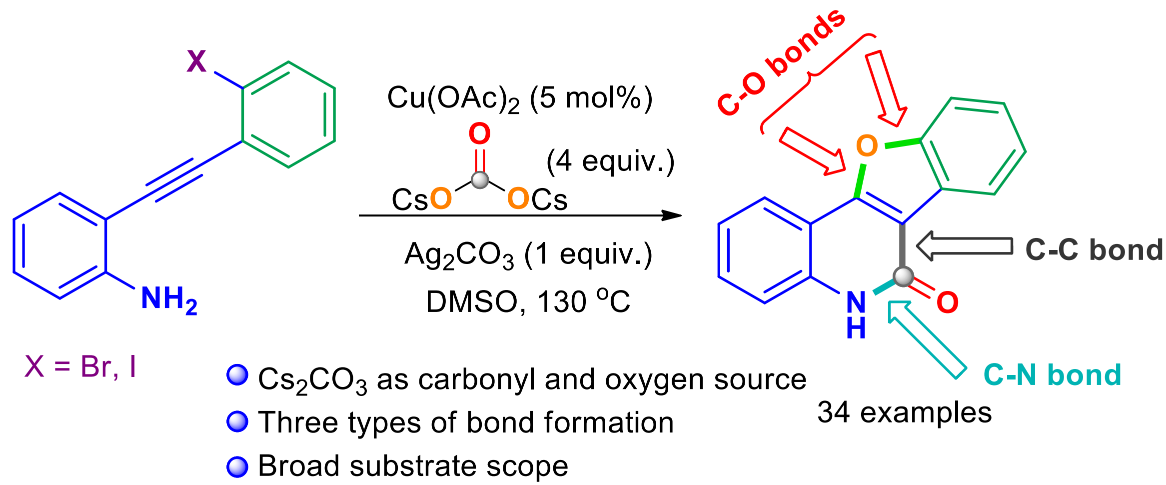


***Chem Commun.* 2013, *49*, 3031**

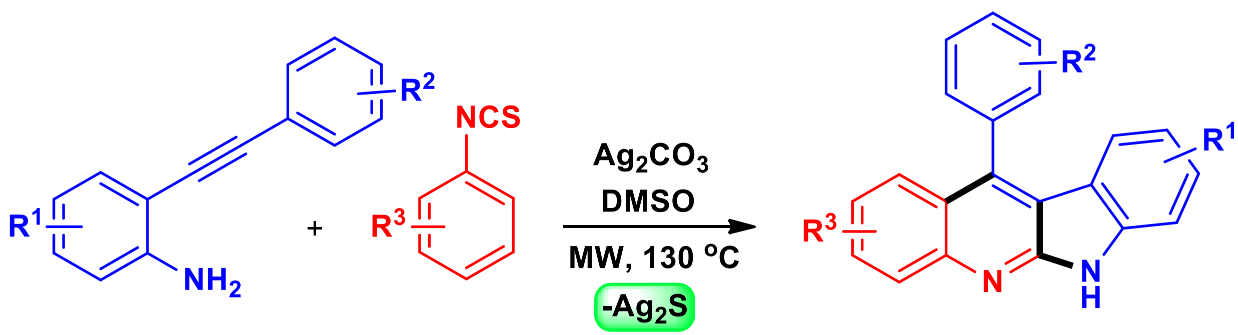
Examples of Cascade Reactions



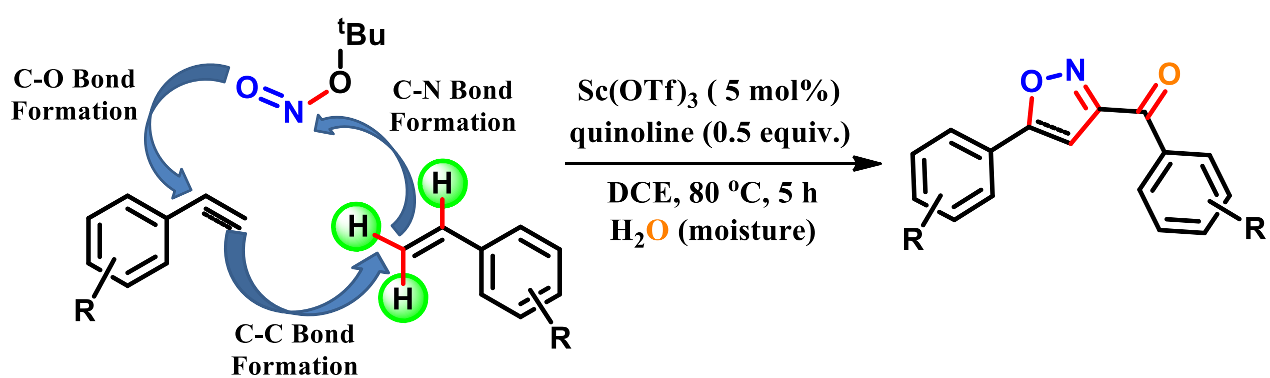




X
NH2
X = Br, I
Cu(OAc)2 (5 mol%)
(4 equiv.)
CsO OCs
Ag2CO3 (1 equiv.)
DMSO, 130 °C
C-O bonds
C-C bond
C-N bond
34 examples
Cs2CO3 as carbonyl and oxygen source
Three types of bond formation
Broad substrate scope



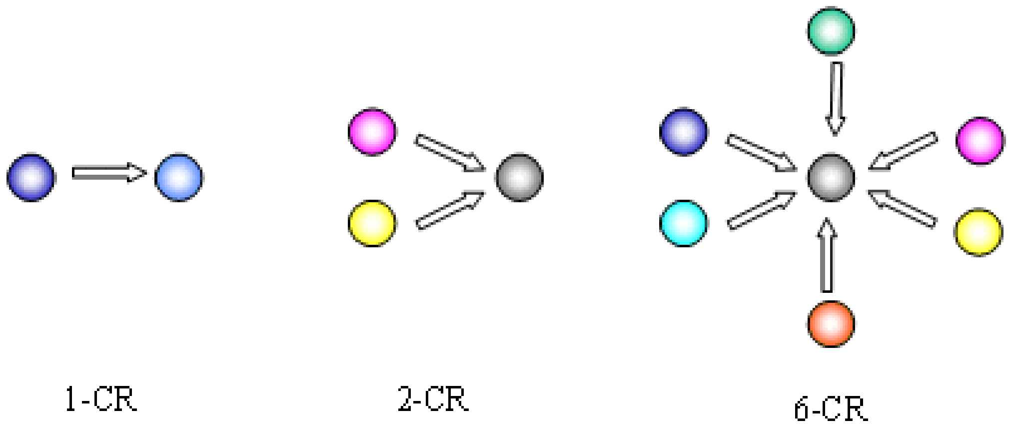
R1
R2
NH2
+
NCS
R3
Ag2CO3
DMSO
MW, 130 °C
-Ag2S



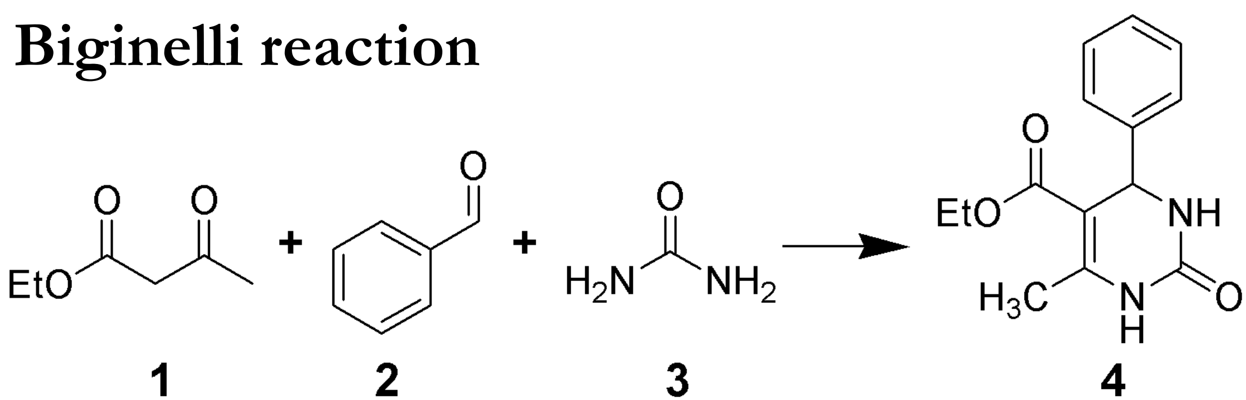
tBu
C-O Bond Formation
C-N Bond Formation
C-C Bond Formation
Sc(OTf)3 (5 mol%)
quinoline (0.5 equiv.)
DCE, 80 °C, 5 h
H2O (moisture)
R

Multicomponent reaction

In chemistry, a **multi-component reaction** (or **MCR**) is a chemical reaction where three or more compounds react to form a single product.

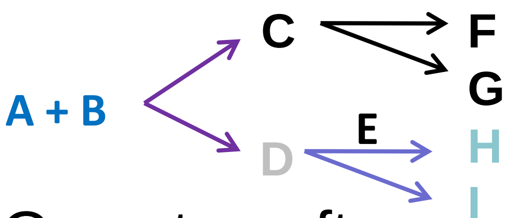


Biginelli reaction

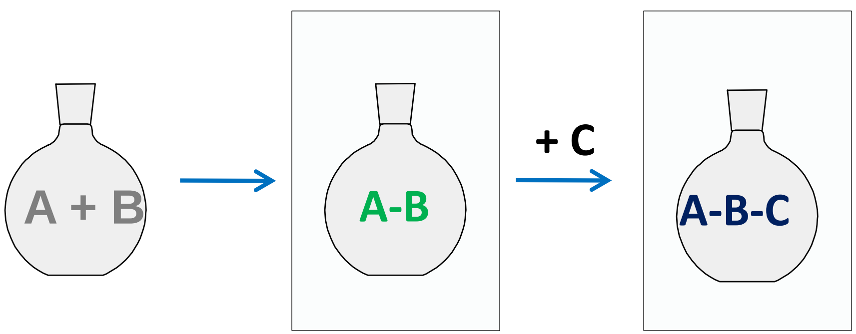


MULTICOMPONENT V/S MULTISTEP REACTIONS

- Multistep Reactions
  - Divergent Reactions

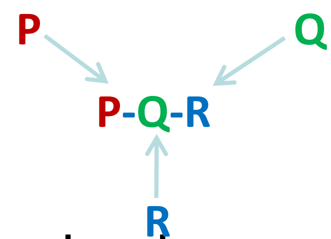


  - One step after another

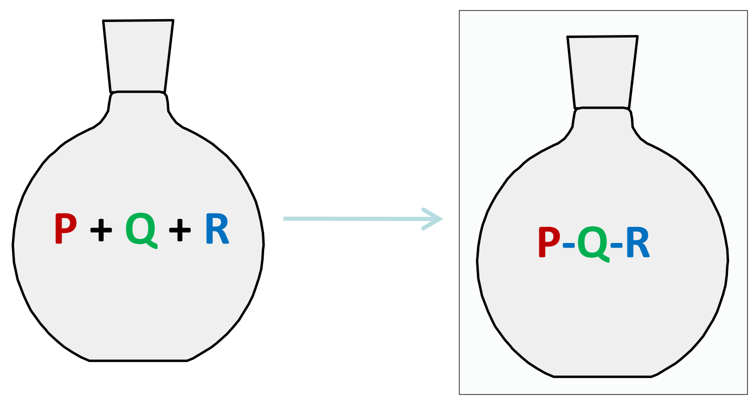


  - Low Efficiency
  - Low Diversity per Step

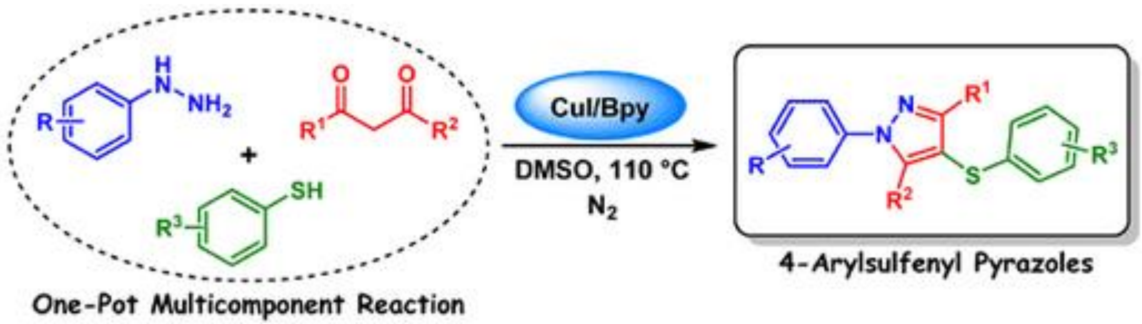
- Multicomponent Reactions
  - Convergent Reactions



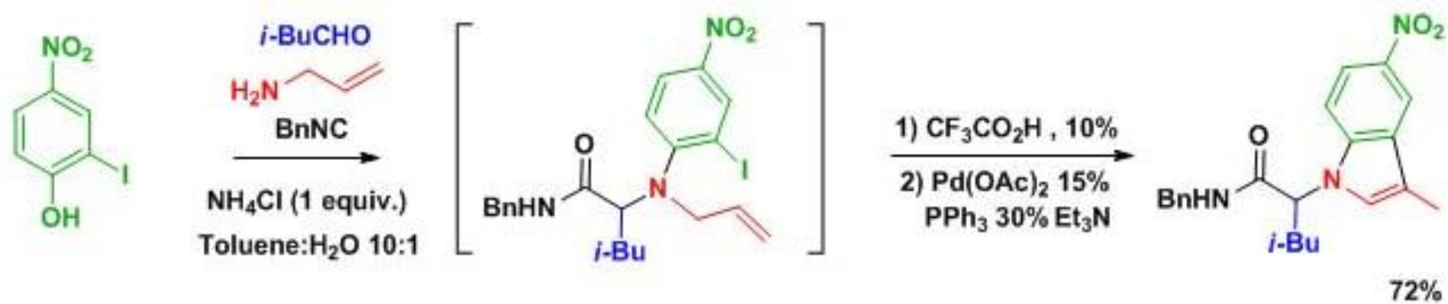
  - Reaction in one pot



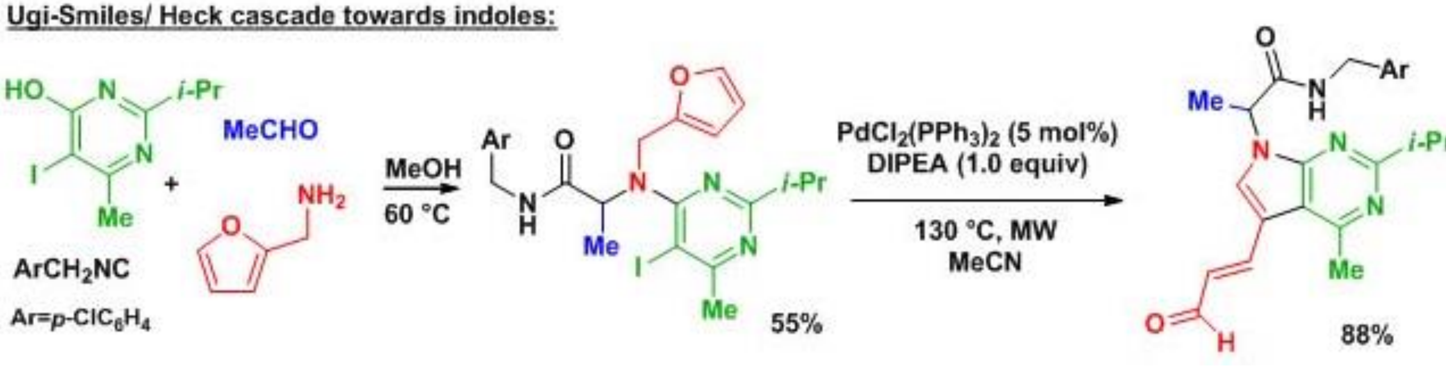
  - Higher Efficiency
  - High Diversity per Step

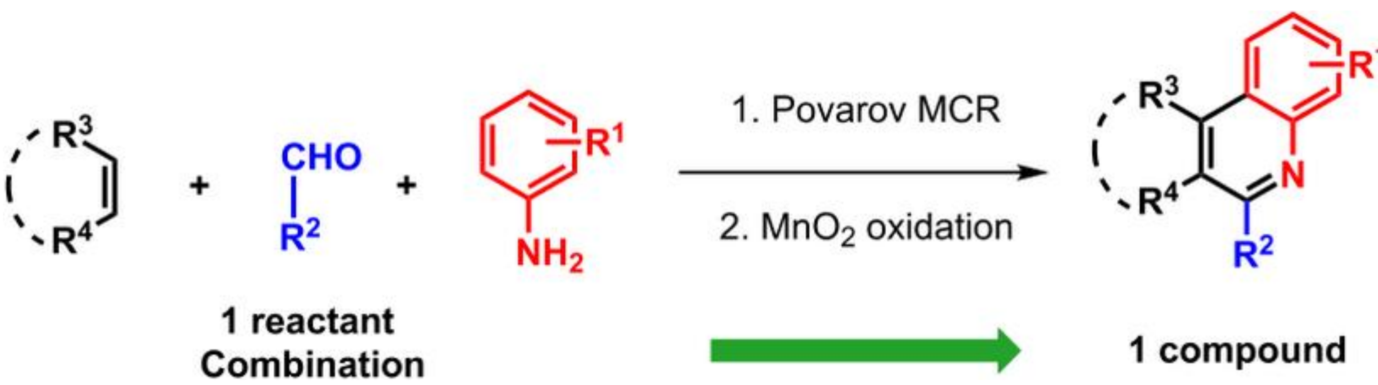


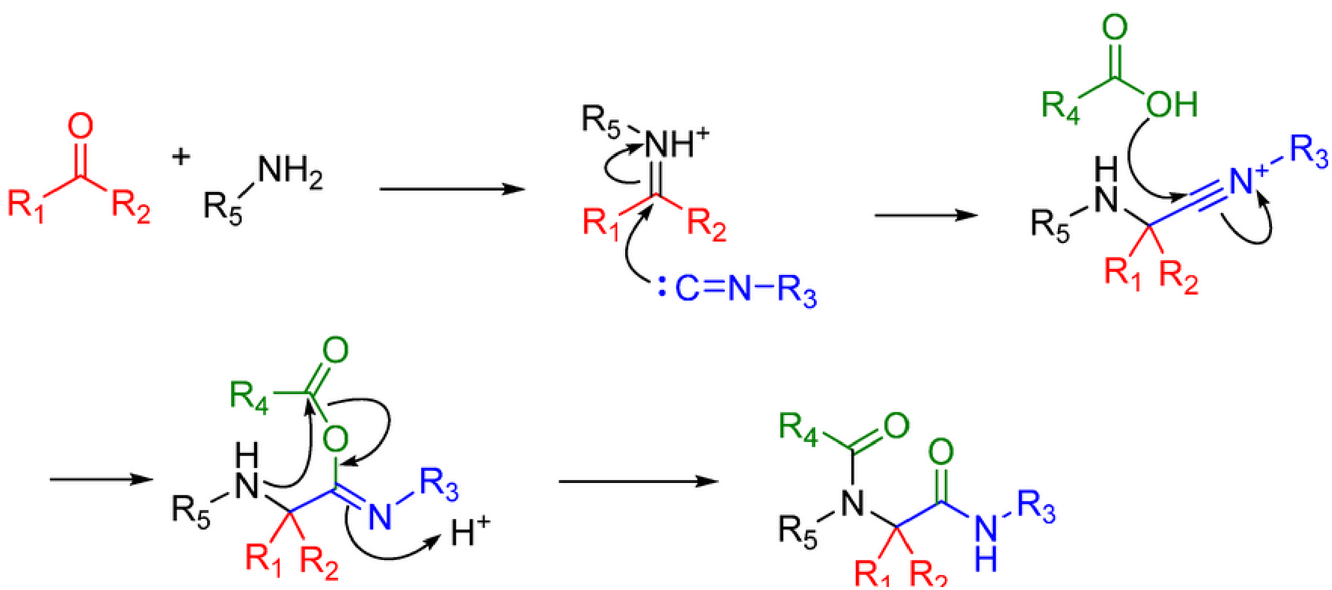
Ugi-Smiles/ Heck cascade towards indoles:



Ugi-Smiles/ Heck cascade towards indoles:




1. Povarov MCR
2. MnO2 oxidation
1 reactant
Combination
1 compound



Principle 2:

Design safer chemicals and products: **Design chemical products to be fully effective, yet have little or no toxicity.**

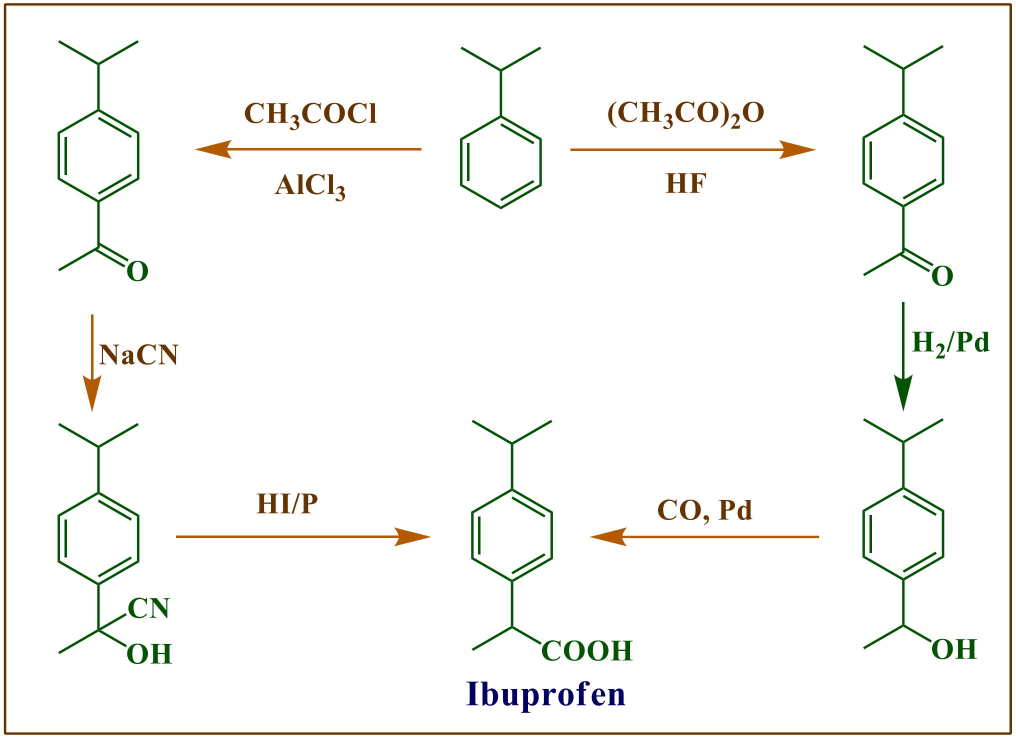
Chemicals include inorganic substances such as lead, mercury, asbestos, hydrofluoric acid, and chlorine gas, organic compounds such as methyl alcohol, most medications, and poisons from living things.

Principle 3:

Design less hazardous chemical syntheses: **Design syntheses to use and generate substances with little or no toxicity to humans and the environment.**

Green Chemistry - Heterogeneous Catalysis

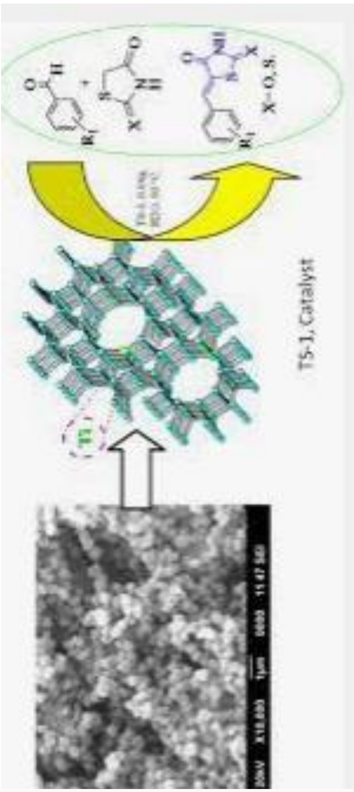
Synthesis of Ibuprofen

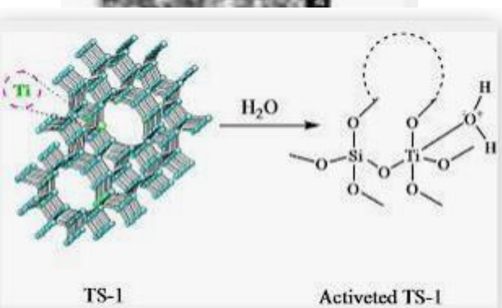


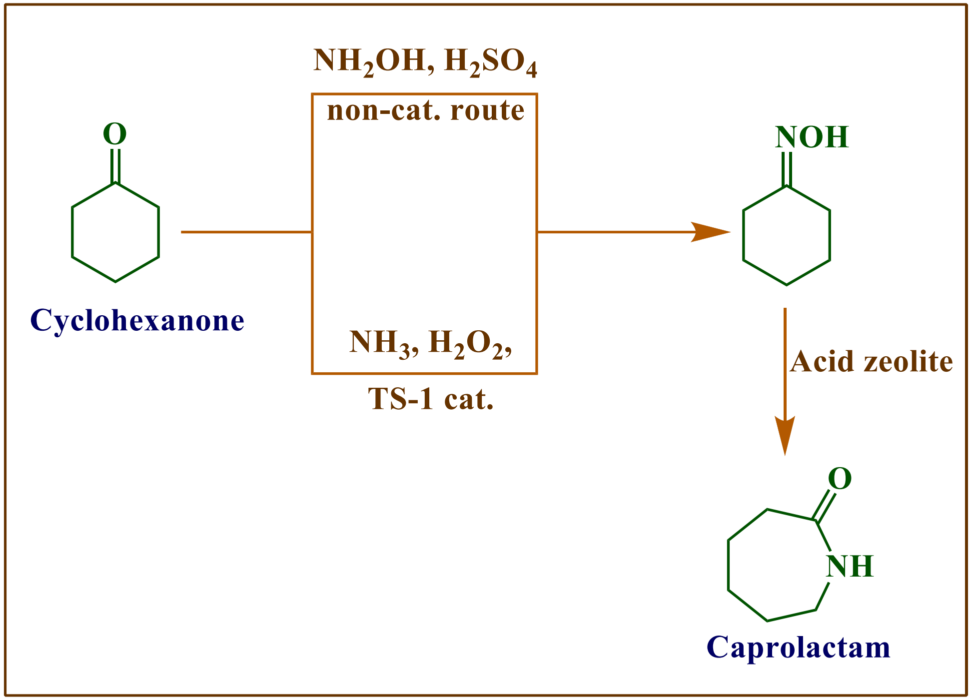
Traditional synthesis of ibuprofen is based on Friedel-Craft acylation. BHC (Boots Hoechst-Celanese, UK) developed a new cleaner process based on the use of HF as the Friedel-Craft catalyst. HF is being recovered and recycled

Green Chemistry - Heterogeneous Catalysis

Synthesis of Caprolactam, Starting material for the preparation of Nylon-6







Precursor of Nylon-6
4.5 billion KG required annually

In conventional synthesis, substantial amounts of ammonium sulphate is produced as a salt waste in both the oximation and rearrangement stages.

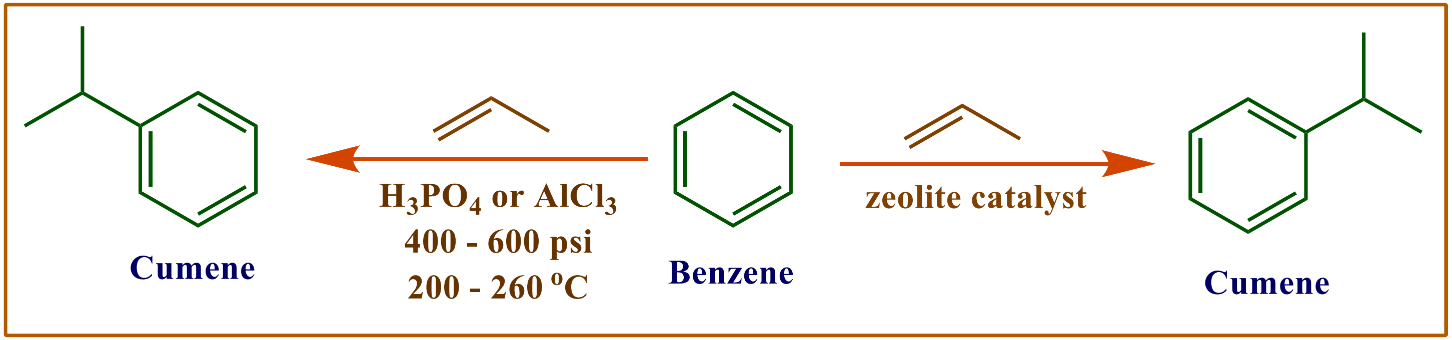
The liquid-phase ammoximation of cyclohexanone with a mixture of ammonia and aqueous hydrogen peroxide eliminates the co-production of ammonium sulphate. The heterogeneous catalyst employed is titanium silicalite TS-1 (redox molecular sieves).

Green Chemistry

Design a safer chemical process

It is better to adopt reactions that utilize non-toxic reagents and yield non-toxic product from the environmental and often economic perspectives.

Approximately 7 million metric tons of cumene are produced annually on a global scale. The traditional cumene synthesis employs alkylation of benzene with propene over a phosphoric acid or aluminium chloride catalyst. Both catalysts are corrosive and are categorized as hazardous wastes.



Mobil/Badger for production of cumene involves an environmentally benign catalyst, zeolite. The new process is carried out at atmospheric pressure, generates less waste and employs a non-corrosive catalyst.

Example 1 of green chemistry

Production of **allyl alcohol** $CH_2=CHCH_2OH$

Traditional route: Alkaline hydrolysis of allyl chloride, which generates the product and hydrochloric acid as a by-product

$$CH_2=CHCH_2Cl + H_2O \rightarrow CH_2=CHCH_2OH + HCl$$

problem

product

Greener route, to avoid chlorine: Two-step using propylene ($CH_2=CHCH_3$), acetic acid (CH_3COOH) and oxygen (O_2)

$$CH_2=CHCH_3 + CH_3COOH + \tfrac{1}{2}\,O_2 \rightarrow CH_2=CHCH_2OCOCH_3 + H_2O$$

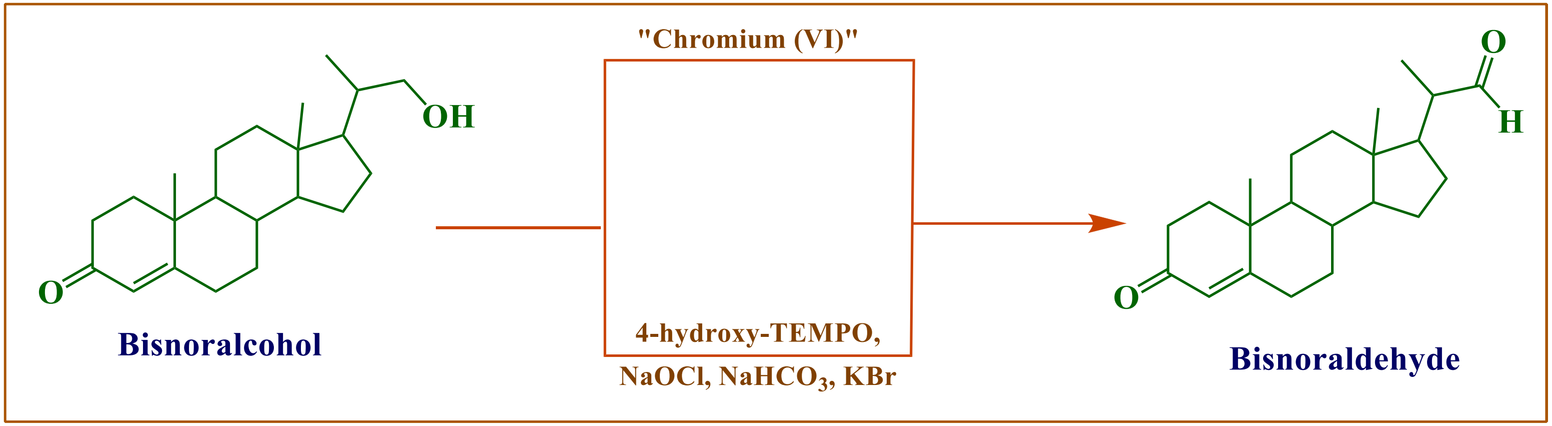
$$CH_2=CHCH_2OCOCH_3 + H_2O \rightarrow CH_2=CHCH_2OH + CH_3COOH$$

Added benefit: The acetic acid produced in the 2nd reaction can be recovered and used again for the 1st reaction, leaving no unwanted by-product.

Green Chemistry

Waste prevention

Waste prevention brings both environmental and economic benefits. A reaction needs to be designed in a way so as to minimize the generation of waste and other hazardous substances.



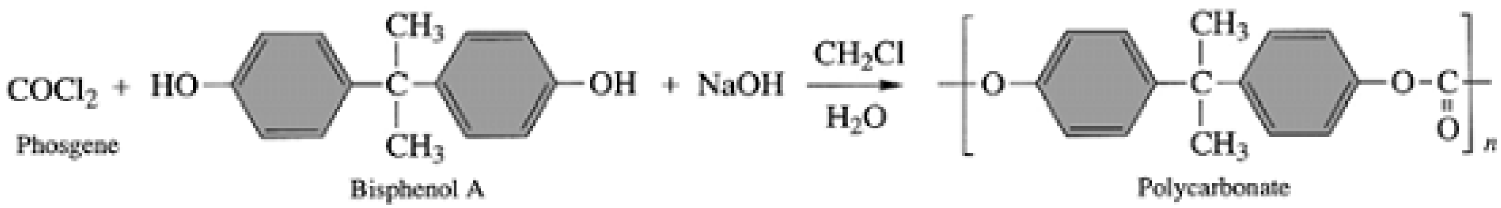
Pharmacia and Upjohn improved the manufacturing process of bisnoraldehyde, a key intermediate in the synthesis of progesterone and corticosteroids, by replacing heavy metal oxidant chromium (VI) by a bleach (NaOCl) and environmental benign 4-hydoxy-TEMPO catalyst system.

Example 2 of green chemistry

Production of **polycarbonate** (polymers)

Traditional route: Start with phosgene ($COCl_2$), which is extremely toxic, and end with methyl chloride (CH_2Cl), which is harmful, as a by-product.

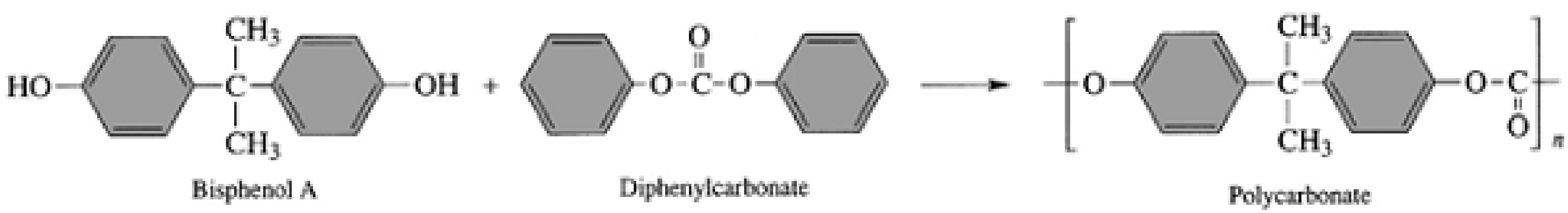
$$COCl_2 + \text{Biphenol A} + NaOH \rightarrow \text{Polycarbonate} + H_2O + CH_2Cl$$



Greener route, to avoid phosgene:

$$\text{Biphenol A} + \text{Diphenylcarbonate} \rightarrow \text{Polycarbonate}$$

(This process was developed by Ashai Chemicals Co. in Japan.)



Principle 4:

Use renewable feedstock: Use raw materials and feedstock that are renewable rather than depleting.

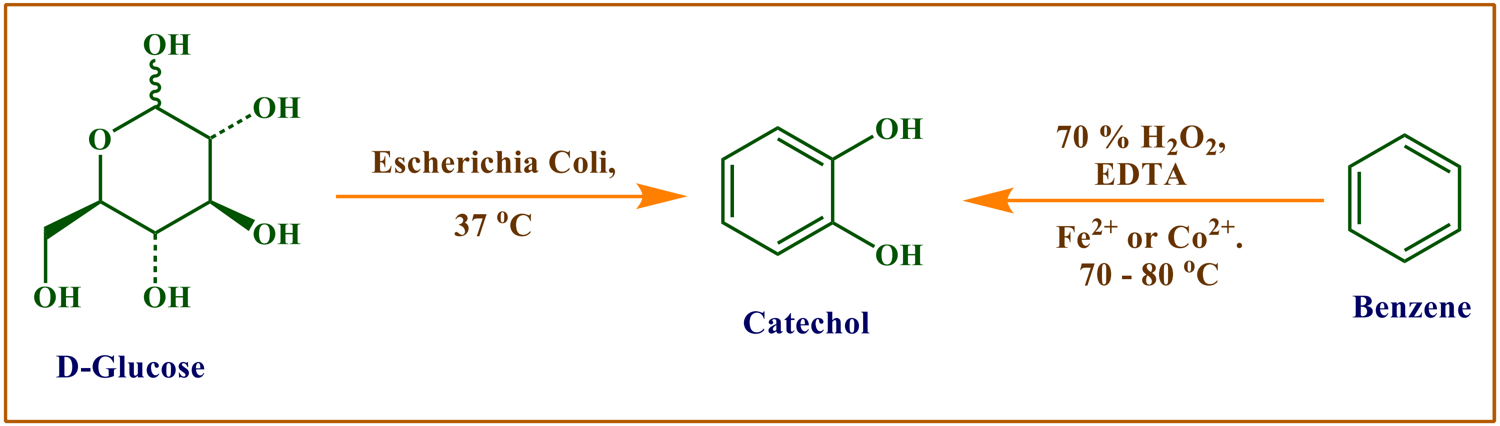
Renewable feedstock are often made from agricultural products or are the wastes of other processes;

CO_2 is renewable feed stock, oils (plant) and fats, glycerine are also renewable.

depleting feedstock are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

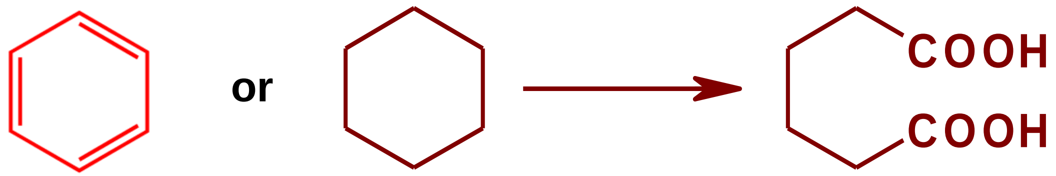
Renewable feedstocks

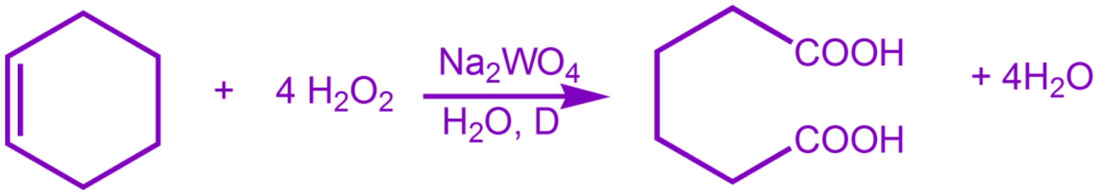
The utilization of benign, renewable feedstocks is a need component for addressing the global depletion of resources.



Using genetically-engineered *E.Coli*, catechol was obtained in a single step from D-glucose. The biocatalytic pathway eliminates the use of hazardous substances present in the synthesis of catechol and decreases the energy demands of the reaction.

Adipic Acid Synthesis

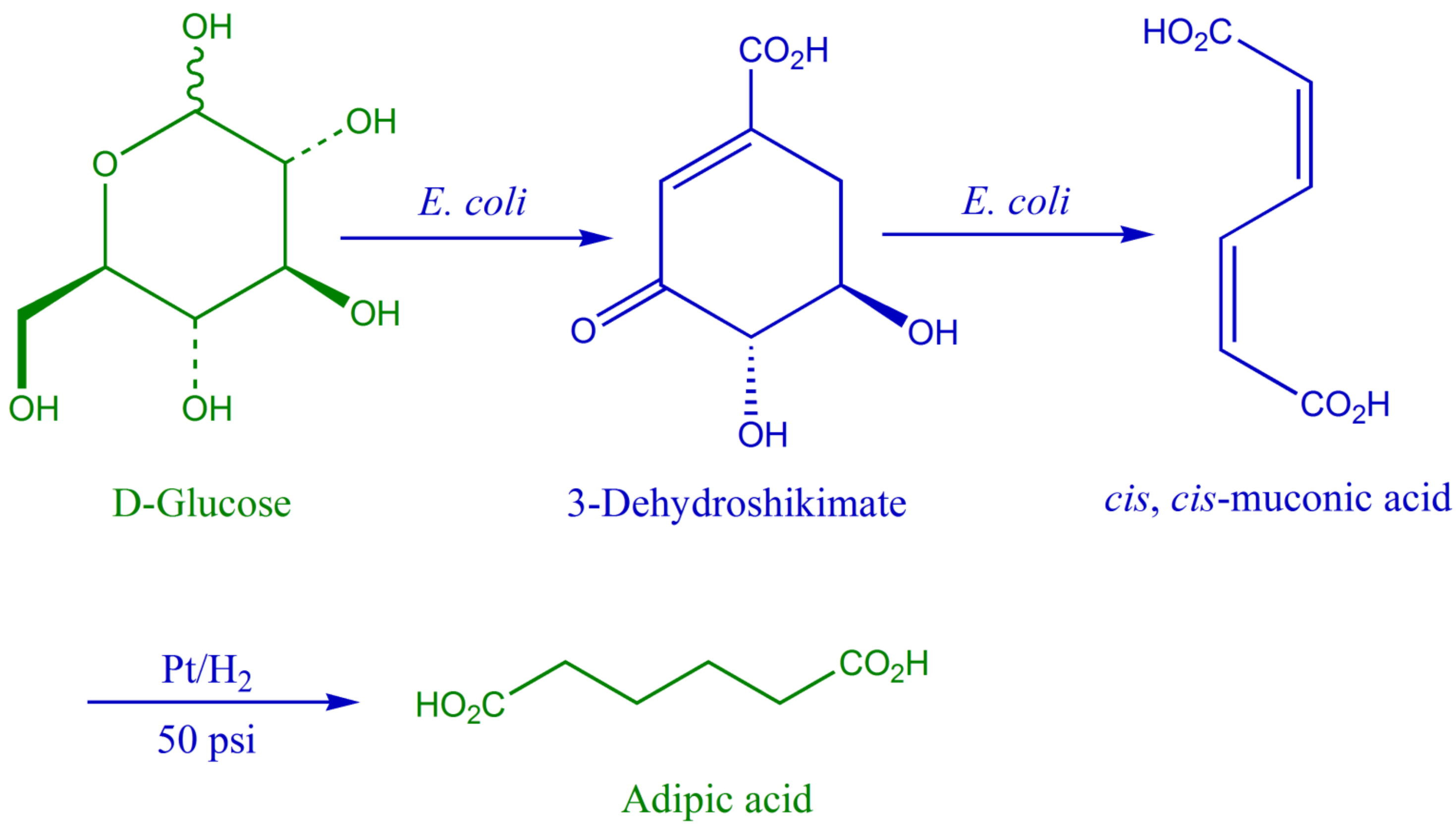




HNO_3 oxidation needed for conversion of ol/one mixture

Not environmentally friendly

Biocatalysed production of adipic acid



(Draths-Frost synthesis)

GC Advantages of D-F Synthesis

1. Highly choosy genetically engineered microbe used
2. Avoids using carcinogenic benzene
3. Eliminates N_2O formation
4. Uses glucose as a renewable source

An outstanding instance of *biocatalysis*. Although transition metal based catalysts also may be effective, the above is an attractive reaction. Commercially?

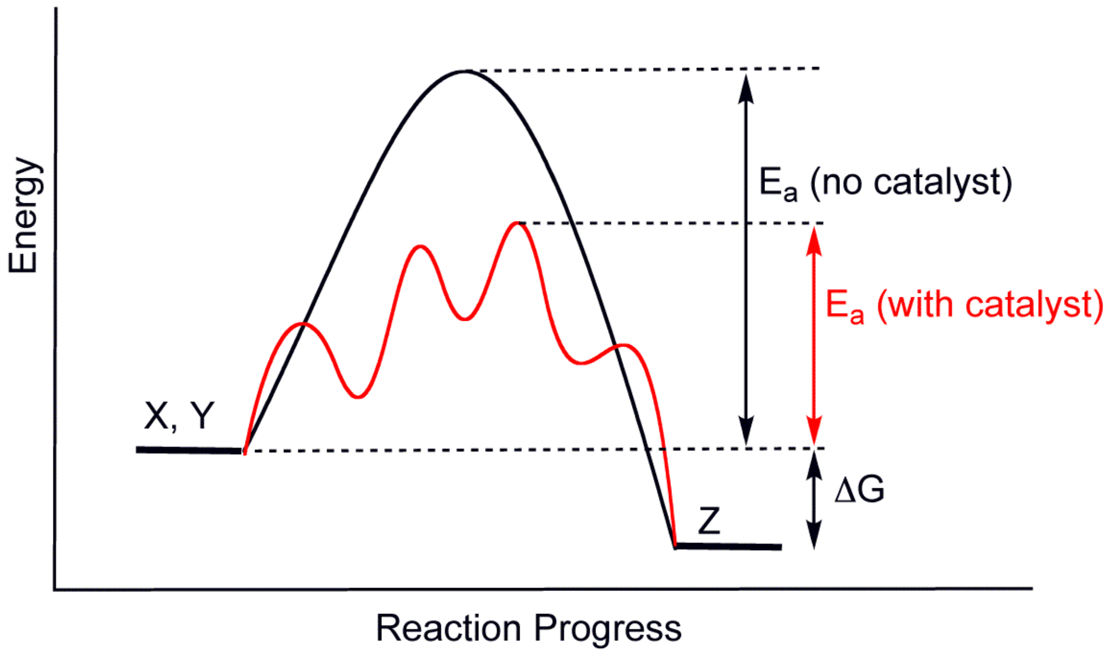
BIO-DEGRADABLE: IS IT GOOD?

- Non-Biodegradable
  None-Compostable
  Collection, Recycling
  Cleaning, Blendable
  Better Properties
  Thermal
  Hydrolytic Resist
  Anti-Microbial

- Bio-degradable
  Compostable
  Difficult to Collect, Recycle, Clean.
  Poorer Properties
  Thermal
  Hydrolysable
  Microbial Attack

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*

Catalytic Turnover number

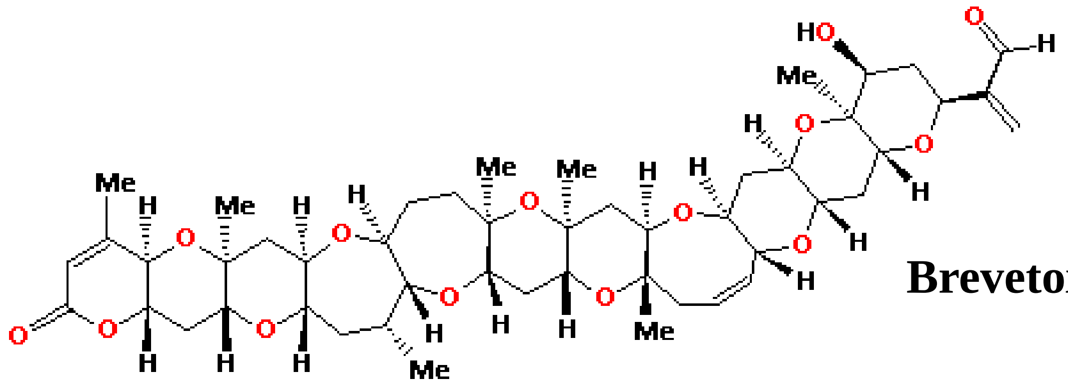
In enzymology, turnover number (also termed kcat) is defined as the maximum number of molecules of substrate that an enzyme can convert to product per catalytic site per unit of time.
For example, carbonic anhydrase has a turnover number of 400,000 to 600,000 s^{-1}, which means that each carbonic anhydrase molecule can produce up to 600,000 molecules of product (CO_2) per second.

In other chemical fields, such as organometallic catalysis, turnover number (abbreviated *TON*) is used with a slightly different meaning: the number of moles of substrate that a mole of catalyst can convert before becoming inactivated.

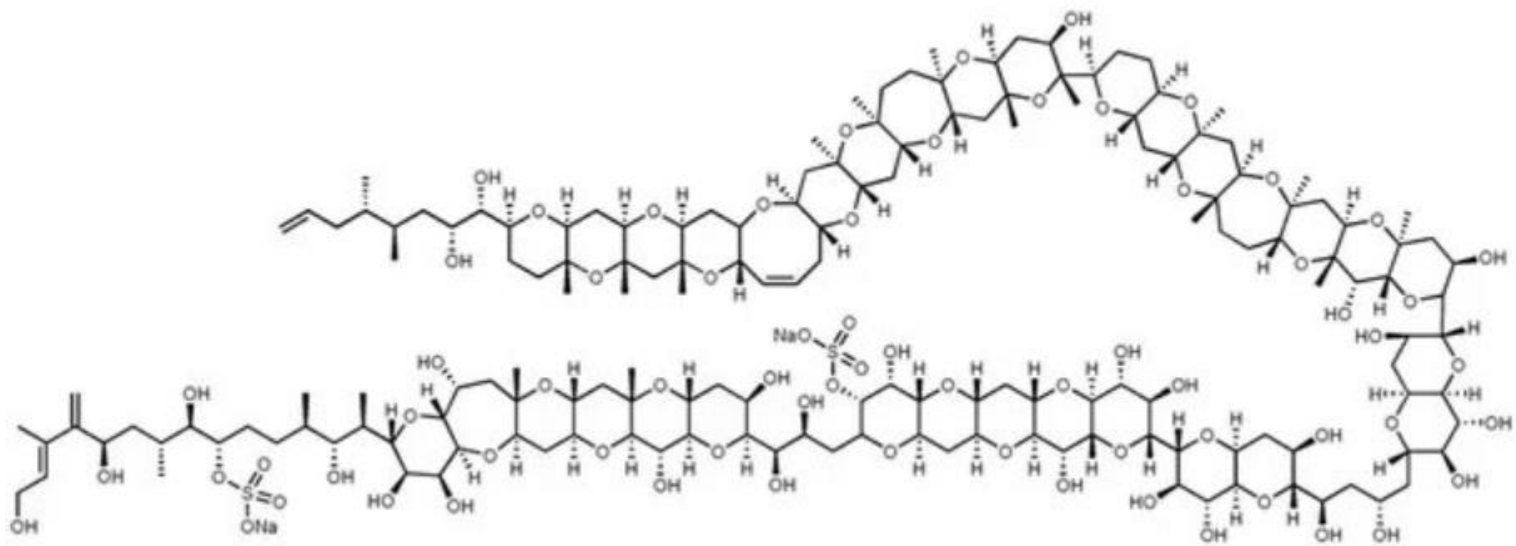
An ideal catalyst would have an infinite turnover number in this sense, because it wouldn't ever be consumed, but in actual practice one often sees turnover numbers which go from 100 to a million or more.
The term turnover frequency (abbreviated *TOF*) is used to refer to the turnover per unit time, as in enzymology.

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



Calicheamicin - An antibiotics produced by bacteria *Micromonospora echinospora*. Note the highly unusual triple sulfur chain (yellow), "enediyne" motif with 2 carbon triple bonds (grey chains) and the iodine (purple).

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.**

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

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 B. M 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

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

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

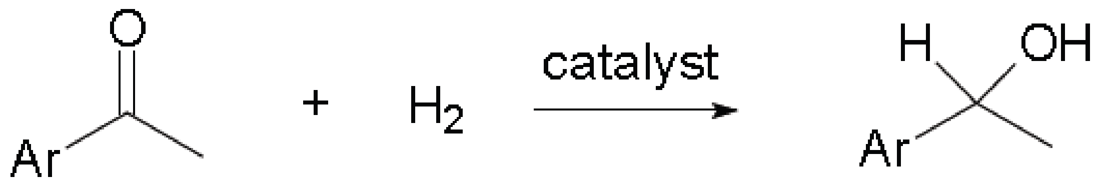
Inherent Atom Economy

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:

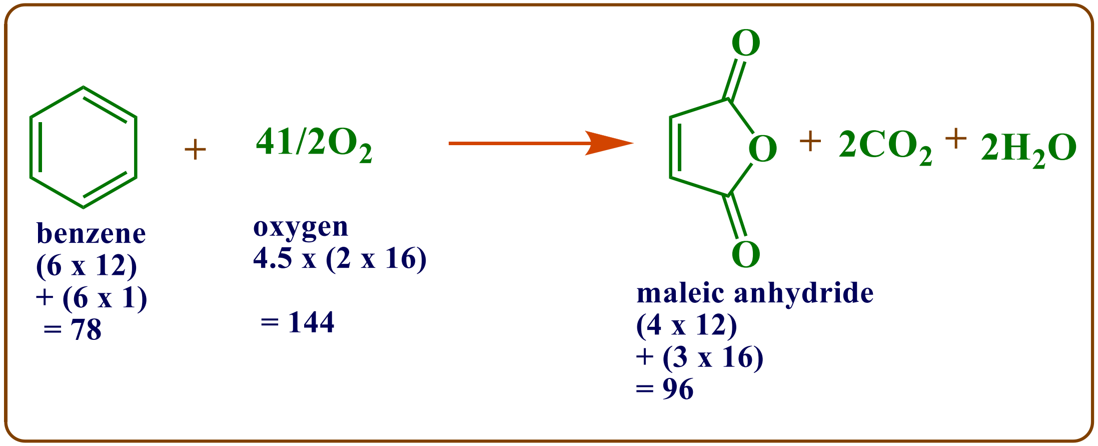
100% atom efficient

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

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.**

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

A2P Energy Solution Of Sukmit Singh

Jovita Aranha July 18, 2019

Solution to Stubble Burning: Punjab Man Uses Straw to Make Fuel, Eco-Products!

Meet Sukhmeet Singh, the man who is solving the nation's paddy straw burning problem with this national award-winning startup, A2P (Agri2Power) Energy Solution.

Meet Sukhmeet Singh, the man who is solving the nation's paddy straw burning problem with his national award-winning startup, A2P (Agri2Power) Energy Solution.

- The economic and health costs to tackle this are estimated to be $30 billion in a single season. This amount is 1.5 times the Indian budget for health and education.

Sukmit Singh quit his job at the Indian School of Business to establish A2P Energy Solution

sukhmeet.singh@gmail.com

Singh’s vision was to create a model that would:

1) Educate and convince farmers to not burn straw

2) Give them additional income by buying it off them

3) And use the paddy straw to produce high-value products for the energy industry.

Animal feed

Fuel for boiler

Bu-coal as fuel

From waste to wealth: IIT Delhi incubated startup aims to reduce pollution by converting rice straw into biodegradable cutlery

By Roshni Balaji | April 5, 2019

Kriya Labs, a **startup incubated at the Indian Institute of Technology-Delhi** (IIT-D) has come up with a solution to this alarming problem. It has developed a technology that can convert agro-waste like **rice straw into pulp,** and further process it to make **biodegradable cutlery.**

Founder: Ankur Kumar, Kanika Prajapat and Pracheer Dutta

info@kriyalabs.co.in
+91 9599790998

ATOM EFFICIENCY: STOICHIOMETRIC VS CATALYTIC OXIDATION

Stoichiometric: The Jones Reagent (Sir Ewart Jones)

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

Atom efficiency = 360 / 860 = 42%

Catalytic:

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

Atom efficiency = 120/138 = 87%

Byproduct: H_2O

ATOM ECONOMY

$$H_3C-CH_2-CH_2-CH_2-OH + Na-Br + H_2SO_4 \longrightarrow H_3C-CH_2-CH_2-CH_2-Br + NaHSO_4 + H_2O$$

1 2 3 4 5 6

Atom Economy Table

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 C_4H_9OH	74	4C,9H	57	HO	17
2 NaBr	103	Br	80	Na	23
3 H_2SO_4	98	—	0	2H,4O,S	98
Total 4C,12H,5O,BrNaS	275	4C,9H,Br	137	3H,5O,Na,S	138

% Atom Economy = (FW of atoms utilized/FW of all reactants)

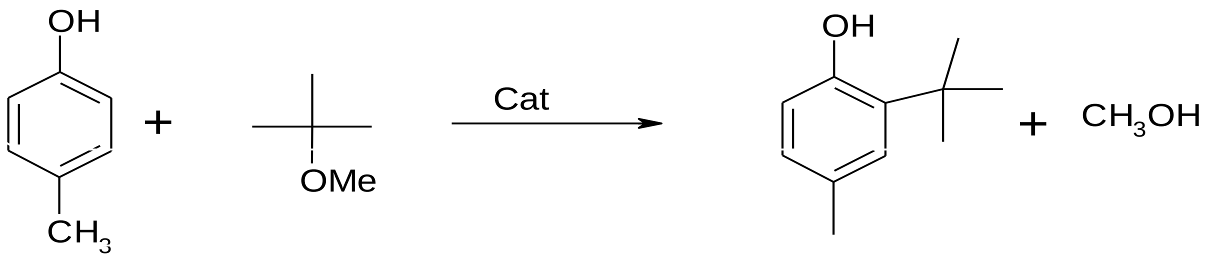
X 100 = (137/275) X 100 = 50%

Alkylation of p-cresol using heterogeneous acid catalyst.

Conditions: p-cresol (19.61g, 0.22 mol), MTBE (24.31g, 0.22mol) and silica / zirconia catalyst (3.5 wt %) were heated at 100^{o}C for 3 hr. After cooling the products were identified by gc. The main product was 2-t-butyl-p-cresol (13.0g), 10.78g of p-cresol remained unreacted.

Calculate the yield, and atom efficiency

Example of Yield v Selectivity v Atom Economy

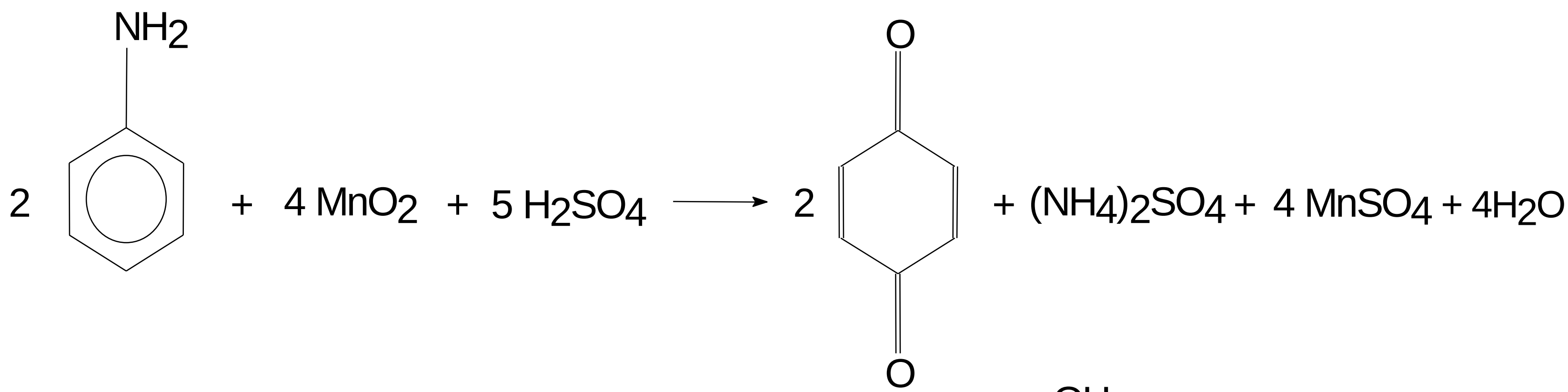


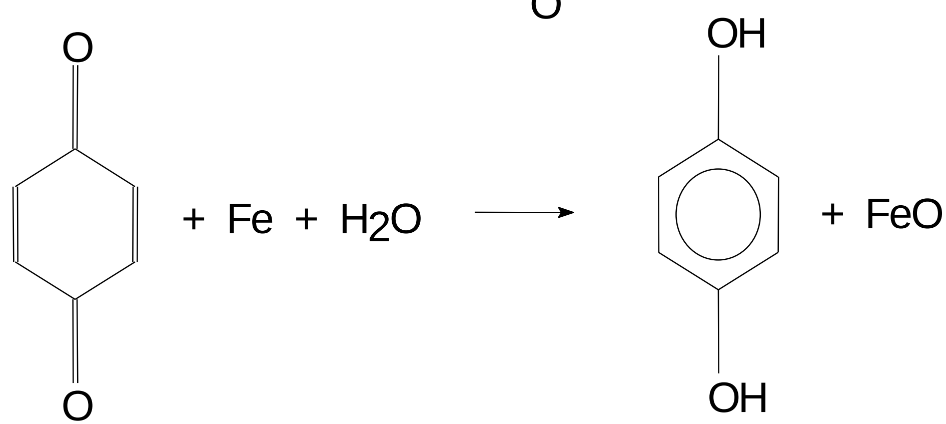
Theoretical yield = 19.61x164/108 = 29.77

% Yield = 100x13/29.77 = 43.7%

%AE = 100x164/(164+32) = 83.6%

Reactions May Give 100% Yield But Low AE : Classic Route to Hydroquinone





Hydroquinone AE Calculation

%AE = 100 (MWt desired product / MWt all products)

= 110 / [110 + 72 + 0.5(132) + 2(151) + 2(18)]

= 110 / 586

=**18.8%**

i.e - may have 100% yield but we make less than 20% useful product!

"Enviropreneurs" – A Possible Bridge

Academia:

1. Limitations to Customize, Scale-up & Commercialize
2. Limitations to Market their Innovations

Enviropreneurs

Great Career Opportunity

Industry:

1. Limitations of In-house R&D
2. Limitation to approach & define their problems

CIRCULAR CHEMISTRY TO CIRCULAR ECONOMY

Bhisma K. Patel. *FASc, FNASc*

Department of Chemistry
IIT Guwahati

Expanding the sustainability to the entire lifecycle of all chemical products. What is practice today: 'Take–Make–Dispose'/'T–M–D'

Circular Chemistry aims to replace 'T–M–D' approach with "Circular Processes".

Benefit: optimize resource, enable a closed-loop, waste-free chemical industry. (Collecting garbages and recycling is circular process)

A Dentist was conducting a survey: "How long do you use your Toothbrush...?"

Chinese:
"3 months...!!!"

American:
"1 month...!!!"

Indian:
"There is no fixed time limit doctor, may be years...!!! Initially we use it for brushing our teeth; then we use it for dying our hair, cleaning comb, cleaning ornaments, cleaning machine parts of our vehicles, cleaning the dirt in between two tiles in bathroom etc... etc... Then when there are no bristles left on the brush, we do not throw it doctor. we start using it for pushing 'Naada' in our Chaddis, Pajamas & Petticoats...!!!"

Credit: European Parliament

It is obvious that the linear route of production, in which scarce resources are consumed (Lithium for example) and their value added products are degraded to waste. This cause several global crises such as climate change, diminished biodiversity, as well as food, water and energy shortages.

Lithium ions are getting exhausted during batteries manufacturing processes

A circular economy is defined as "restorative and regenerative by design, and aims to keep products, components and materials at their highest utility and value at all times"

Chemistry is crucial:

(i) designing and developing indispensable materials and technologies

(ii) recognize the potentially detrimental effects

(iii) aware of the designed or reassessed with sustainability in mind.

No doubt Green chemistry has provided a framework for teaching and performing sustainable chemistry, and has delivered an impetus for developing cleaner products and processes but the methods is linear 'T–M–D'.

downtoearth.org.in

SUBSCRIBE TO COMMON SENSE

ReCircle | Get ready to recycle your old clothes responsibly ...

Instagram · recircle.in
18 Apr 2024

Upcycling textile waste to high fashion through traditional ...

YouTube · Down To Earth
22 Jul 2021

How Old Clothes Can Become New Clothes | Textile ...

YouTube · My Green Closet
19 Apr 2018

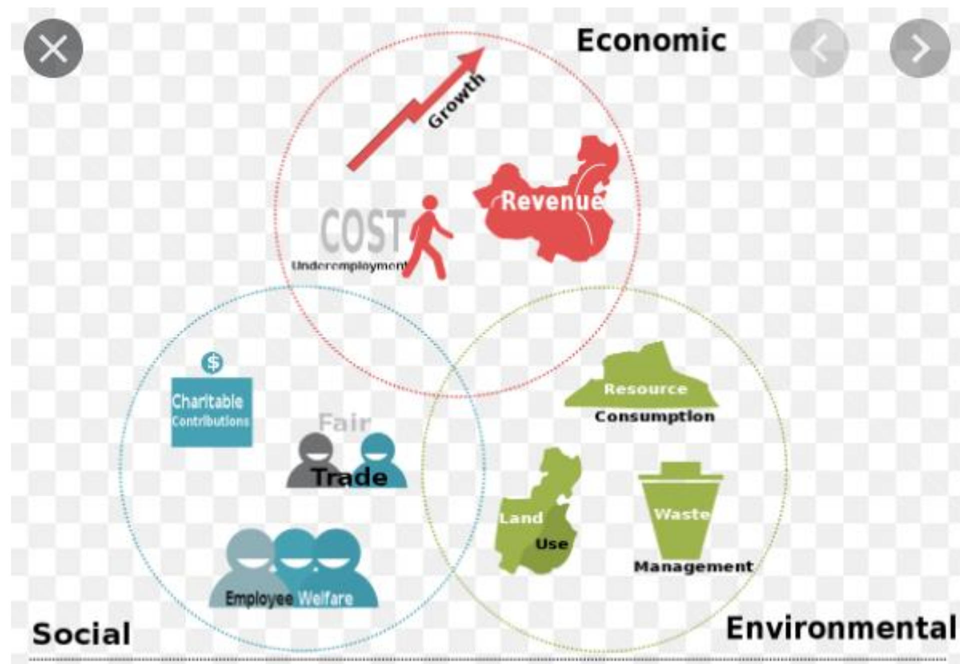
How To Recycle Old Clothes | One Small Step

YouTube · NowThis Earth
25 May 2019

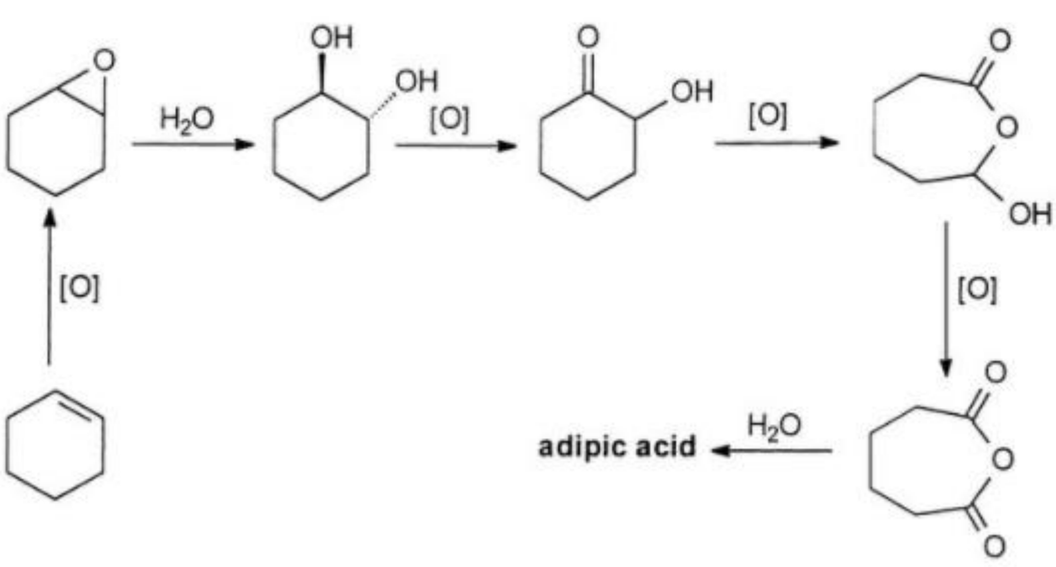
Innovative chemistry designed with sustainability in mind is only effective when translated into economically viable applications.

The **triple bottom line** is an accounting framework having: social, environmental (or ecological) and financial.

Some organizations have adopted the TBL framework to evaluate their performance in a broader perspective to create greater business value.



Adipic acid precursors for Nylon 66



Following many Green Chemistry principles:

(i) Solvent-free conditions are applied (GC 2),

(ii) Avoiding the use of the corrosive nitric acid (GC 3)

(iii) N_2O — a waste product of the current industrial synthesis (GC 4).

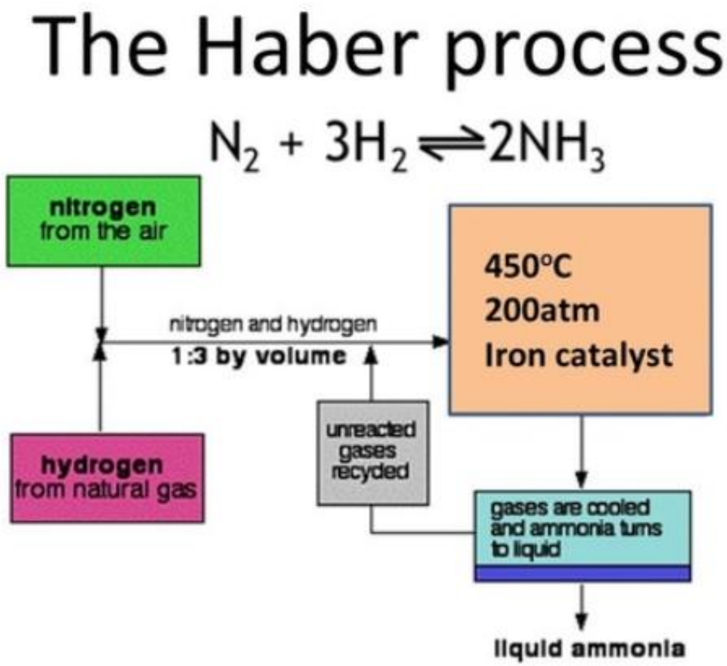
Why no industries has adopts this!!!!????

Cost: 100 mL 30% H_2O_2 Rs. 5000/-

Cost: 100 gm Adipic acid Rs. 2100/-

Violates the value chain so not contributed to Sustainability i.e economically viable

Other chemical processes may satisfy the green chemistry principles while being economically viable, **yet remain unsustainable**.



GC principles:

(i) use of catalysts (GC 9)

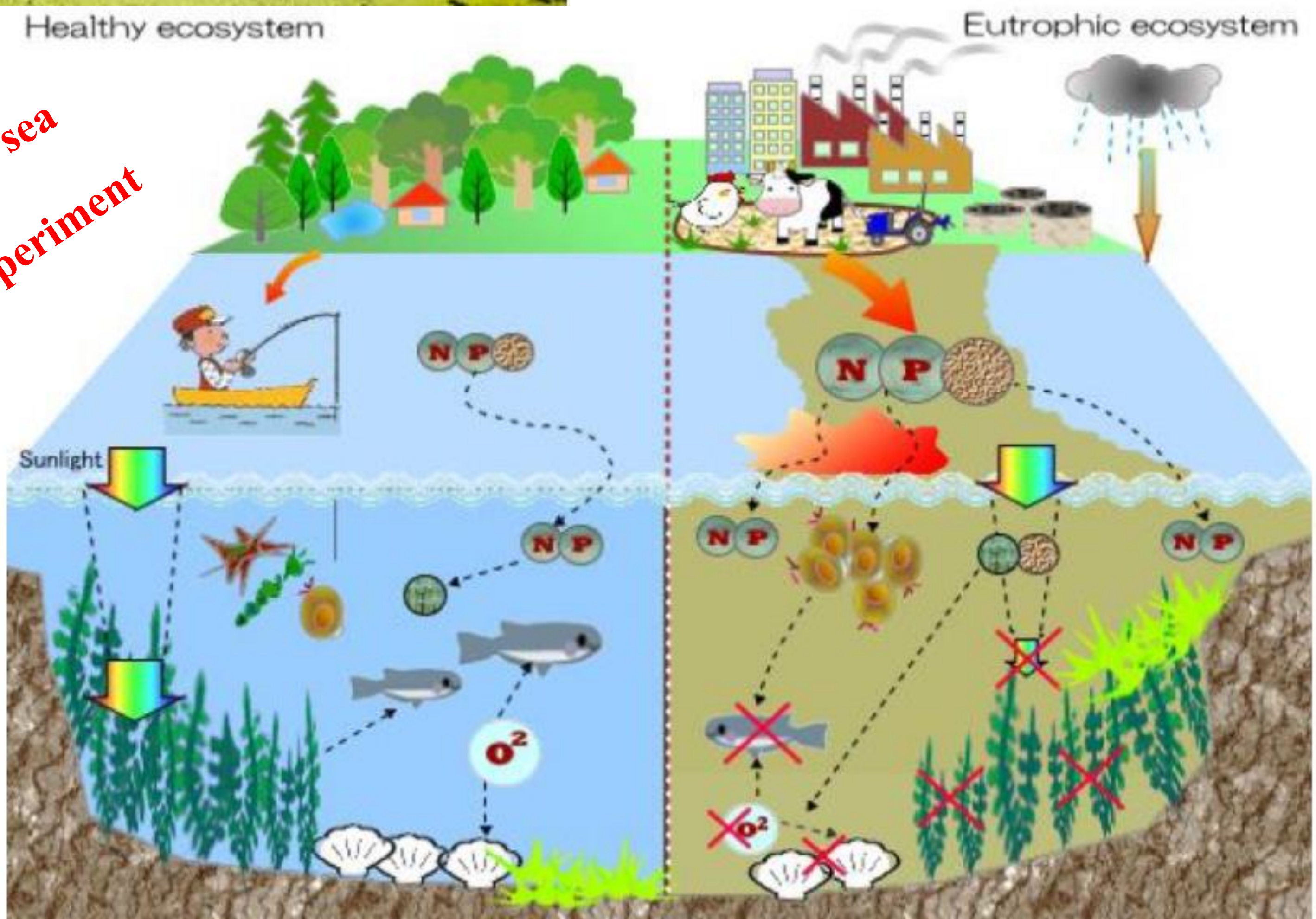
(ii) increasing energy efficiency (GC 6).

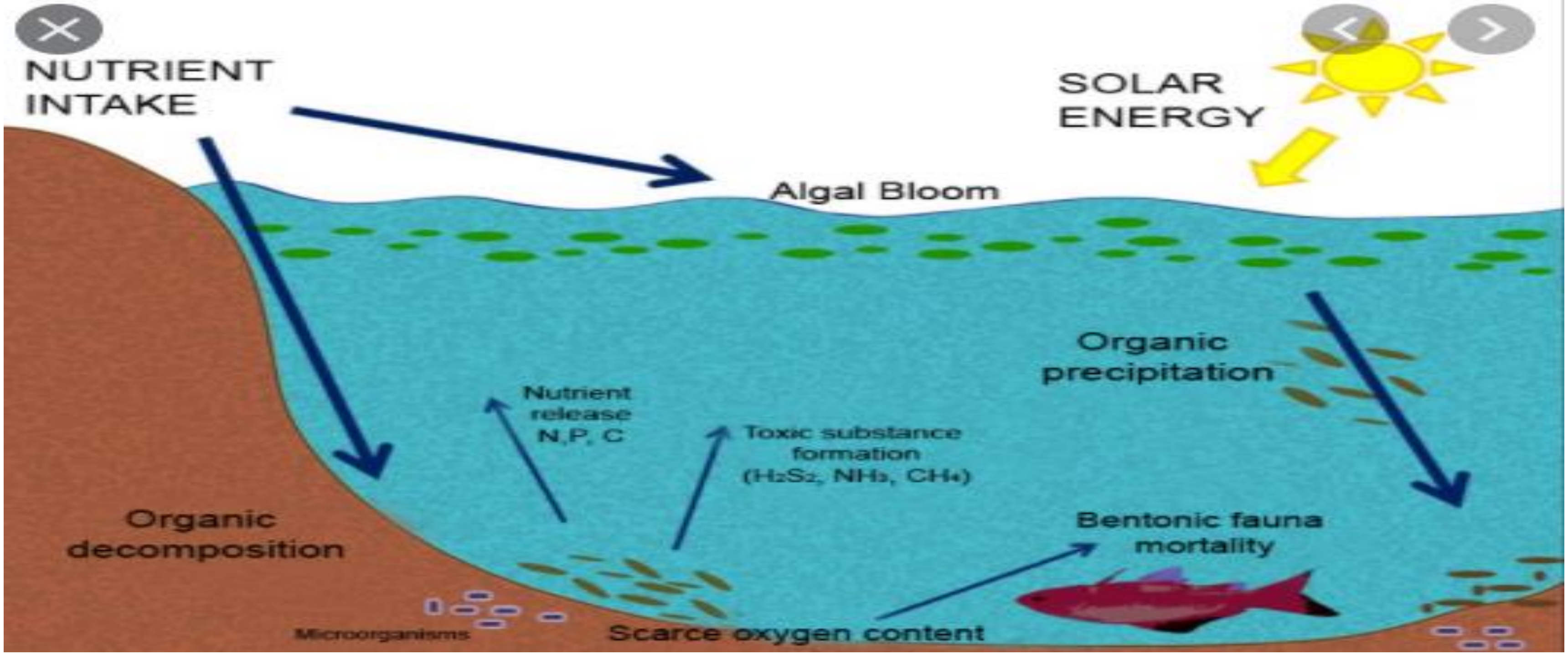
But requires high temperatures and pressures

After its use as fertilizer, large portions of the fixated nitrogen are lost to the environment, causing **eutrophication**, a global environmental concern, the importance of which should not be underestimated[1]

Oxygen from sea

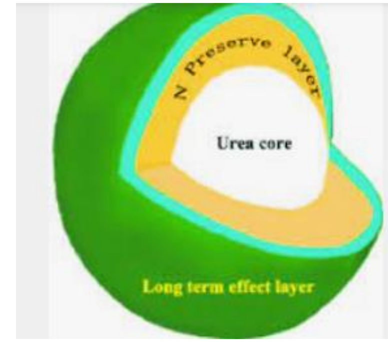
The jar experiment



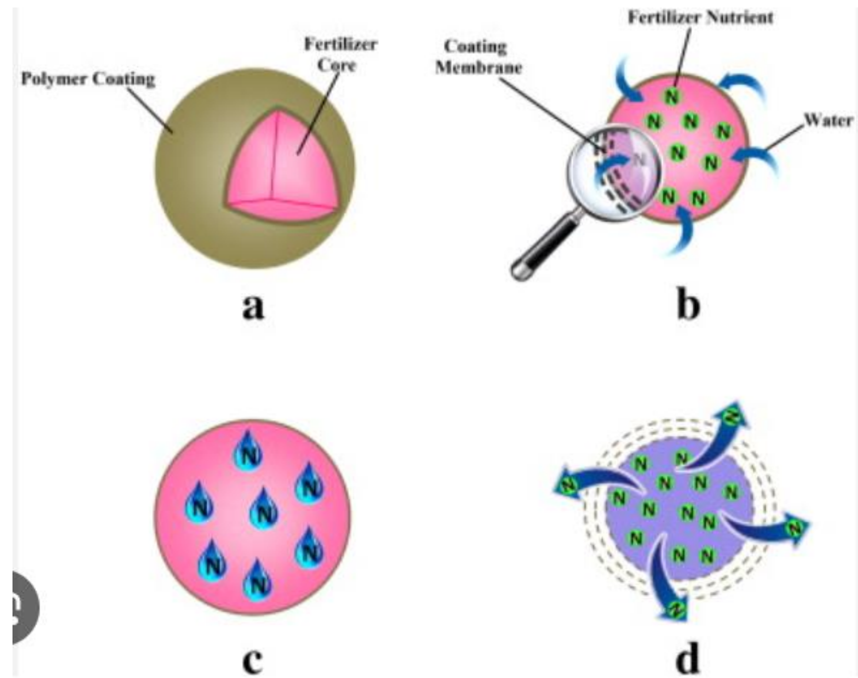


This results in increase in water and air pollution, both of which threaten to destabilize the Earth's system beyond the proposed 'planetary boundaries' or "safe operating space" for anthropogenic activities.

This highlights the importance of looking beyond the scientific discovery and analysing the global impact of chemistry. Role of chemist to develop better fertilizers……



The application of controlled release urea (CRU) is an abatement strategy for avoiding this economic loss and preventing water eutrophication (via urea leaching) and hazardous nitrous emissions into the stratosphere



Iffco Nano Urea Liquid 500ml

₹ 400/ Litre [Get Latest Price]

Product Name	Nano Urea
Packaging Size	500 ml
Country of Origin	Made in India
Minimum Order Quantity	1 Litre

IFFCO Nano Urea is a nanotechnology based revolutionary Agri-input which provides nitrogen to plants. Nano Urea is a sustainable option for farmers towards smart agriculture and combat climate change. These fulfil the plant nutrient requirement as a fertilizer since Nano urea is bio...

View Complete Details

Get Latest Price
Request a quote

The MRP of urea is statutorily fixed by the Government of India and at present it is Rs. 268 for a 50 Kg bag of urea/ Rs. 242 for a 45 kg bag of urea which includes Rs. 354/MT as dealer margin for private traders/PSUs/Cooperatives and Rs.

Department of Fertilizers
https://www.fert.nic.in › urea-pricing-policy-section

Urea Pricing Policy Section - Department of Fertilizers

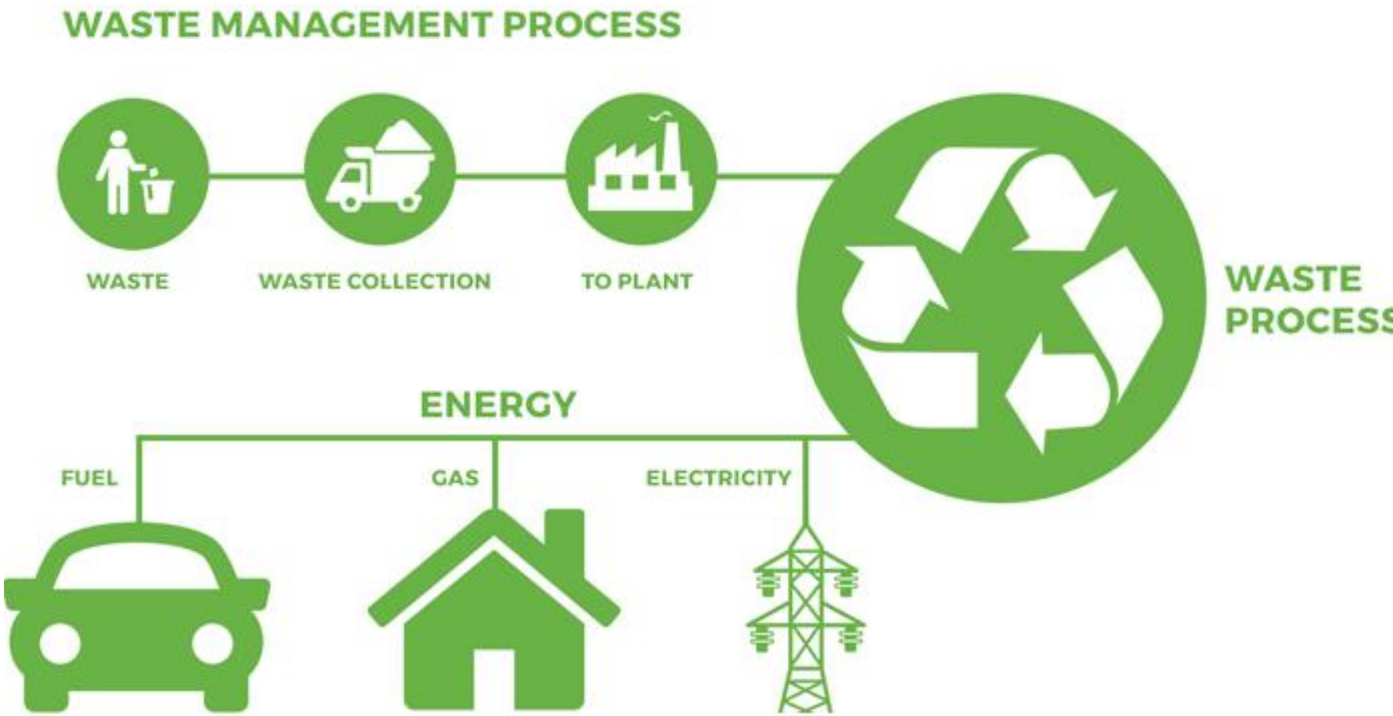
Circular chemistry for sustainability:

This approach aims to make chemical processes truly circular by expanding the scope of sustainability from process optimization to the entire lifecycle of chemical products.

The twelve principles of circular chemistry (CC)

1. Collect and use waste. Waste is a valuable resource that should be transformed into marketable products.

Waste is a resource: Regarding **waste as a resource** is a prerequisite for circularity.



to Energy

Energy produced by waste can be used to heat buildings or **generate electricity.**

However, the major advantage of burning waste is that it **reduces** the amount of material that is deposited in landfills.

Problem: The excess of carbon dioxide, nitrous oxide, ammonia and phosphate waste lost to air, water and land perturbs the carbon, nitrogen and phosphorus cycles, creating a host of adverse environmental impacts.

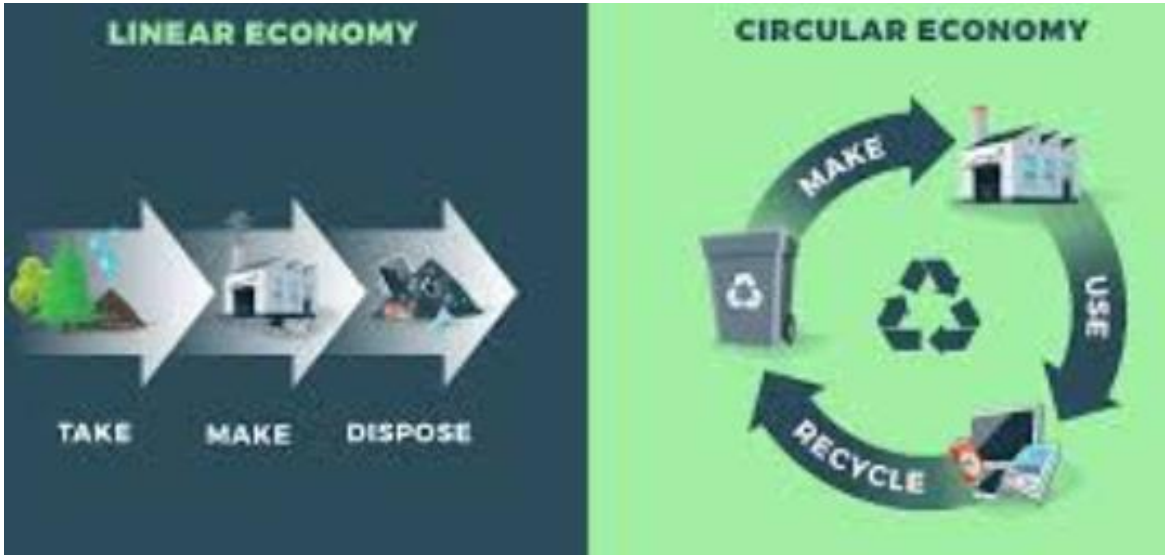
Solution: novel chemical and biochemical conversions are urgently needed that allow for their efficient recovery and recycling.

2. Maximize atom circulation. Circular processes should aim to maximize the utility of all atoms in existing molecules. (Similar to atom economy of Green Chemistry)

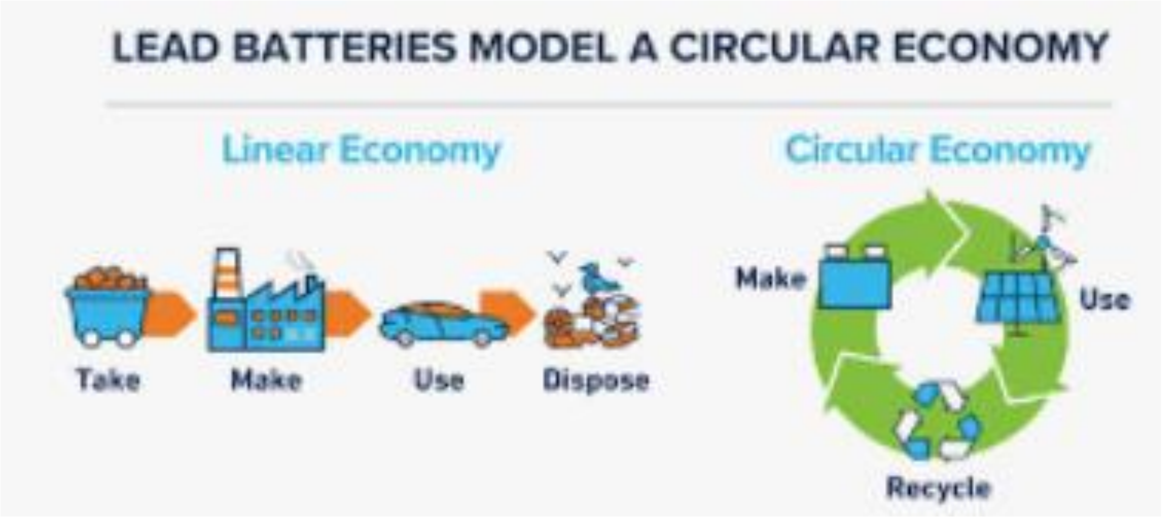
At the process level, circular chemistry targets maximizing atom circulation in chemical products along their **entire life cycles**, regardless of whether chemical bonds are modified or not

Securing renewability:

3. Optimize resource efficiency. Resource conservation should be targeted, promoting reuse and preserving finite feedstocks.



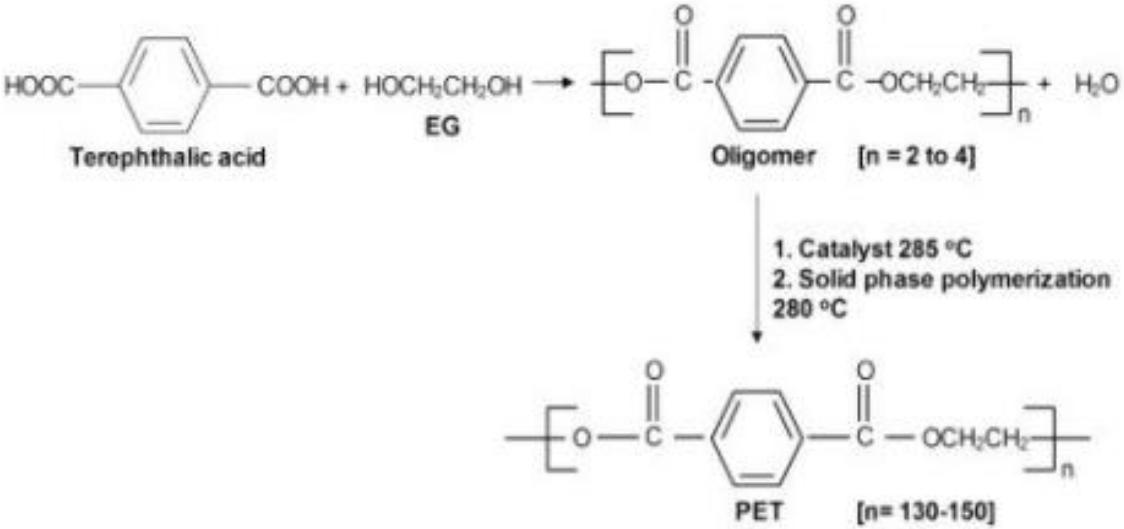
Materials are continuously cycled back through the value chain for reuse, thereby optimizing resource efficiency



Renewable resources offer the chemical industry an opportunity to diversify its raw materials base

Bio-based materials are typically classified as being sustainable, simply because of renewability of the resource, yet these resources are often created in a linear production process without sustainable end-of-life options.

Resource renewability alone is not a measure of sustainability



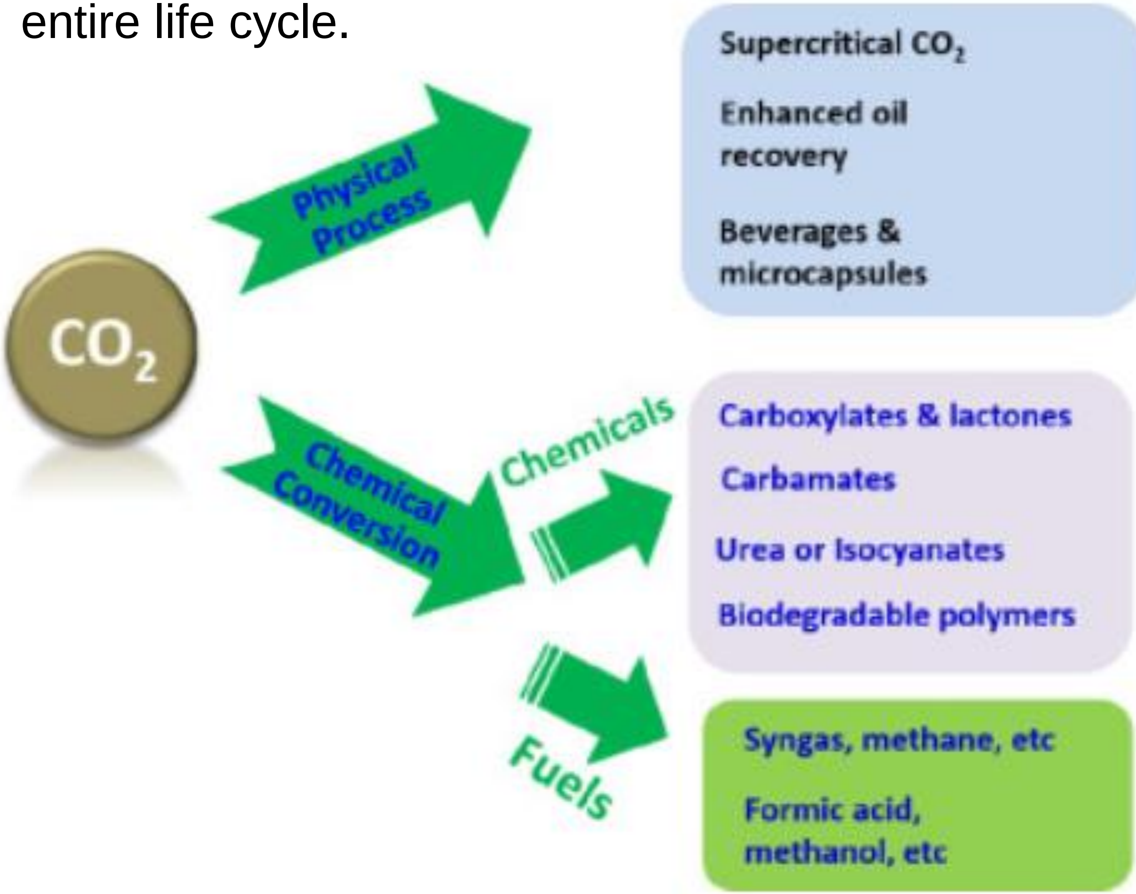
Q. Which one is preferred: Oil-based plastics or bio-based plastics?

A. As far as raw material is concerned oil based is cheaper and more profitable to companies.

Energy input is an investment:

4. Strive for energy persistence. Energy efficiency should be maximized.

Using waste (example CO_2) as a resource can also contribute considerably to the energy efficiency of a chemical product over its entire life cycle.



But the conversion process "shouldn't necessitate more energy" than that offered by the product obtained

Q. What is striving for energy persistence in circular chemistry, justify with suitable examples

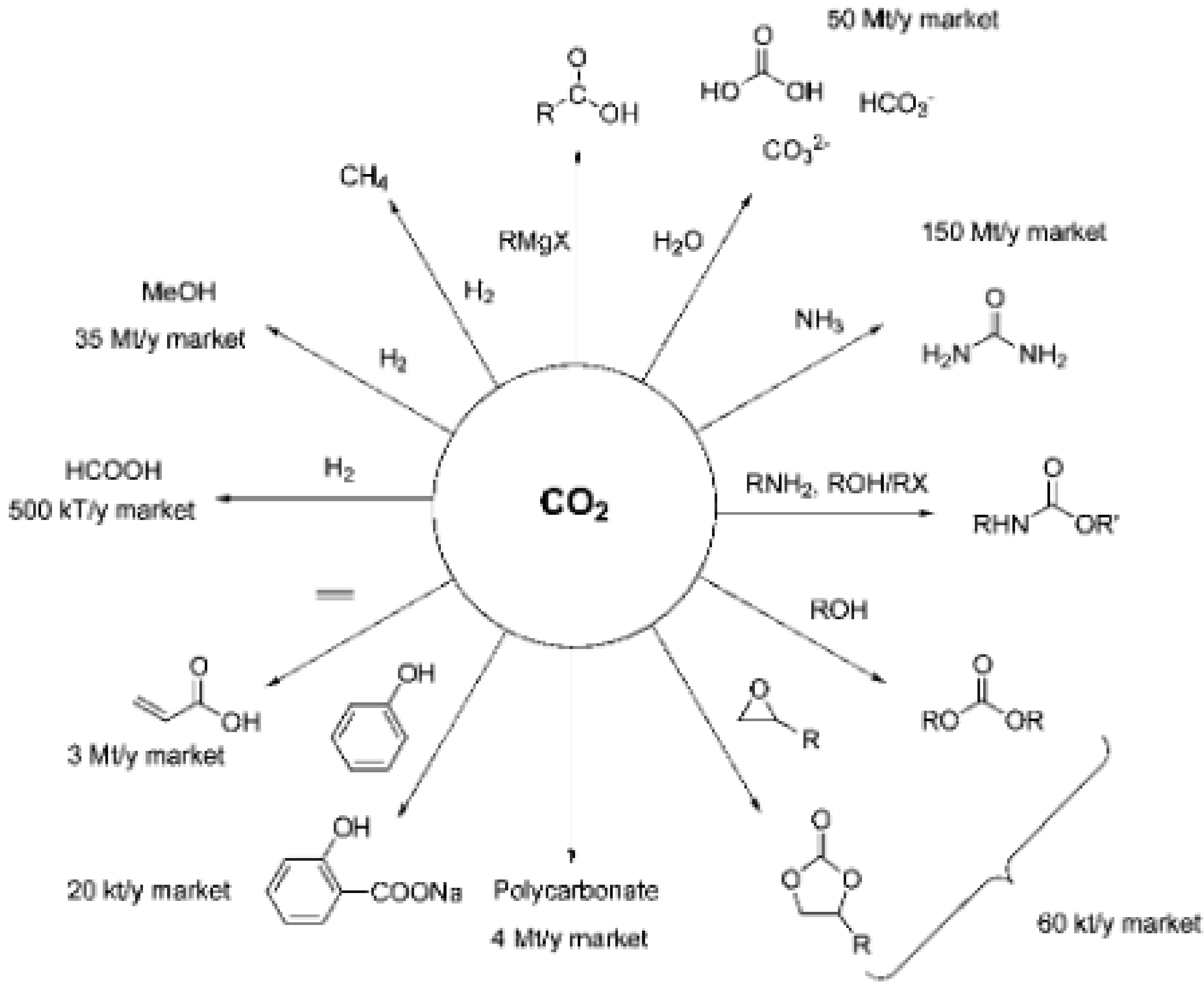


Fig. 11 Chemical transformation of CO_2 into commodity chemicals and market volumes.

5. Enhance process efficiency. Innovations should continuously improve in- and post-process reuse and recycling, preferably on-site.

Difference between Efficiency and **Effectiveness**

Efficiency is the ability to produce an intended result in the way that results in the least waste of time, effort, and resources.

Effectiveness is the ability to produce a better result, one that delivers more value or achieves a better outcome.

These ‘in-process’ developments are followed by ‘post-process’ developments, as the “repurposing” of the consumed products through chemical or biochemical methods is required to reduce primary feedstock use, optimize resource yields and increase the renewability, durability, and multi-functionality of chemicals and products.

Efficacy, efficiency and effectiveness

Can it work?	*Efficacy*
Does it work in reality?	*Effectiveness*
Is it worth doing compared to other things we could do with the same money?	*Cost-effectiveness = Efficiency*

Controlled environment

6. No out-of-plant toxicity. Chemical processes should not release any toxic compounds into the environment.

Although the use of substances of concern may be unavoidable at some facilities, these should not be released to the environment.

7. Target optimal design. Design should be based on the highest end-of-life options, accounting for separation, purification and degradation.

Optimal product design should target the most favourable end-of-life state, avoiding persistence in the environment and breakdown into harmful products.

Biodegradable materials are often seen as sustainable, but promote littering

Therefore, rather than aiming for product degradation, it is preferable to collect waste streams and instead convert them in dedicated plants into value-added materials. ……(Plastic…. Vrs paper…..).

Q.Why target optimal design in important circular chemistry

2

1

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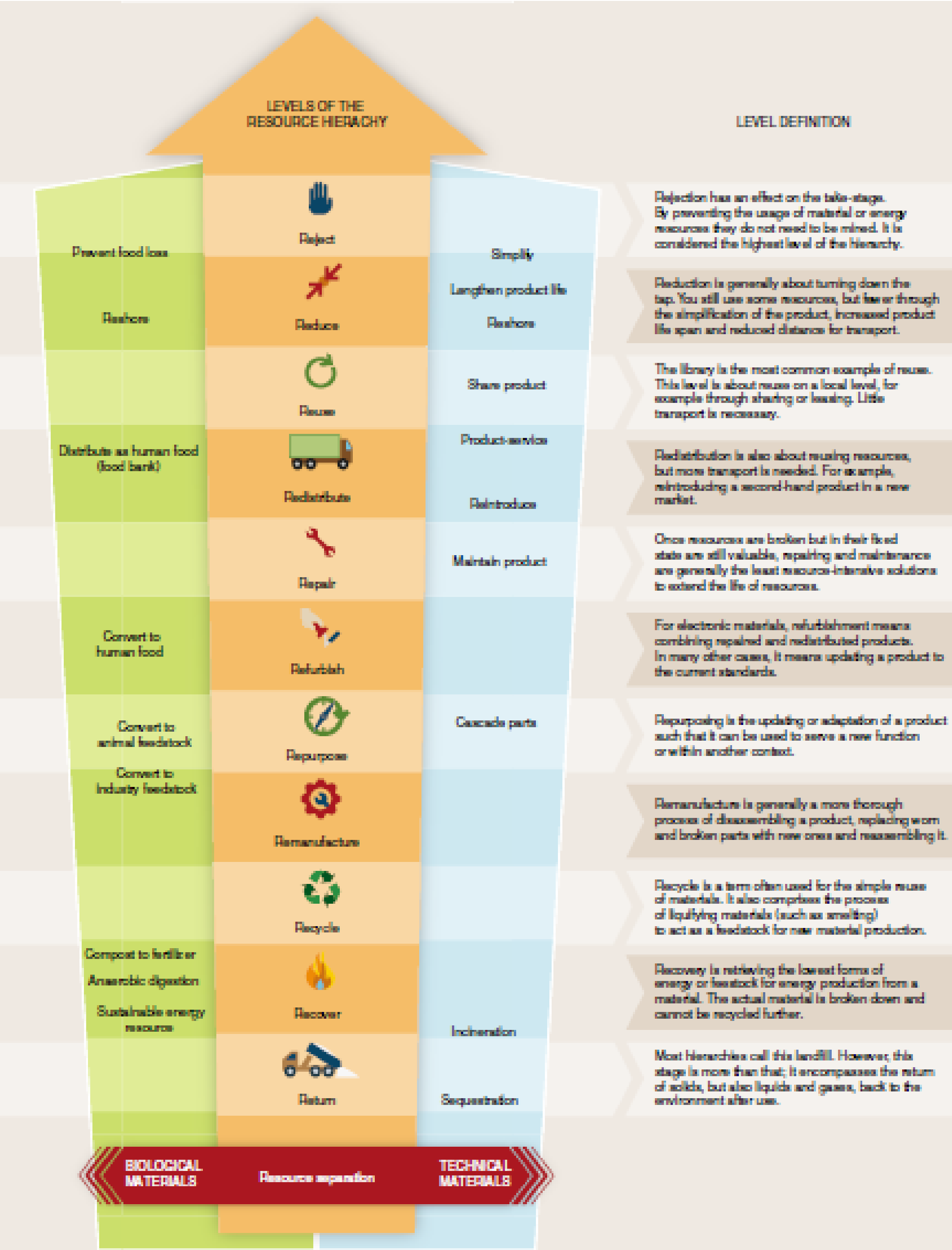
The life cycle assessment (LCA) and the ladder of circularity

8. Assess sustainability. Environmental assessments (typified by the LCA) should become prevalent to identify inefficiencies in chemical processes.

Such metrics, which provide information on the environmental impact of a chemical from its design to its disposal can help to identify opportunities for innovation in a process and can also pinpoint which feedstock is most sustainable to use as resource.

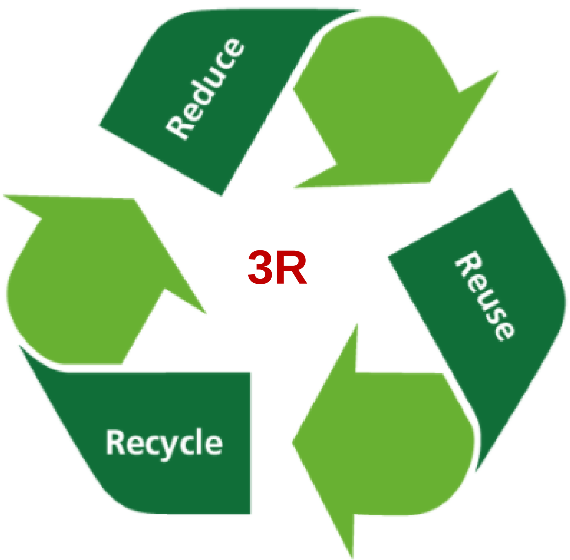


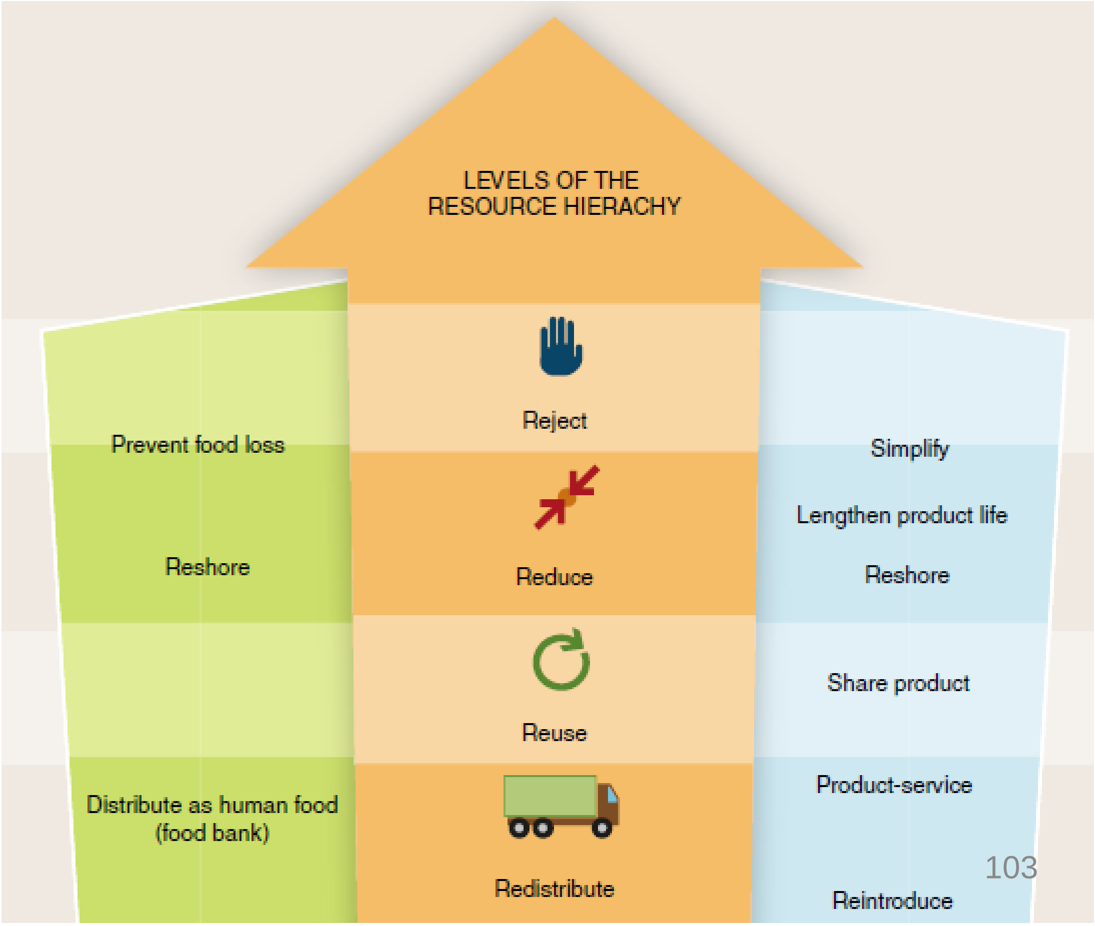
Resource hierarchy: How the necessity of material use is examined by asking the following questions:

- Do we need this material to achieve our goal?
- Do we need to make something new or can available material be reused or repaired?
- Does the used product really need to be disposed of?

9. Apply ladder of circularity. The end-of life options for a product should strive for the highest possibilities on the ladder of circularity.

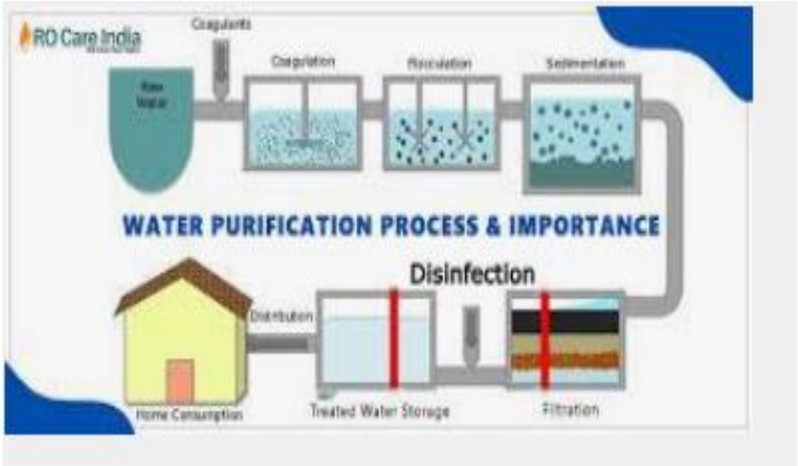
The action associated with ladder of circularity is: **R**eject, **R**educe, **R**euse, **R**edistribute, **R**epair, **R**efurbish, **R**epurpose, **R**emanufacture, **R**ecycle, **R**ecover, **R**eturn, which can be referred to as the "**11 Rs**")





10. **Sell service, not product**. Producers should employ service-based business models such as chemical leasing, promoting efficiency over production rate.

Product stewardship is an approach to managing the environmental impacts of different products and materials and at different stages in their production, use and disposal. It acknowledges that those involved in producing, selling, using and disposing of products have a shared responsibility to ensure that those products or materials are managed in a way that reduces their impact, throughout their lifecycle, on the environment and on human health and safety.

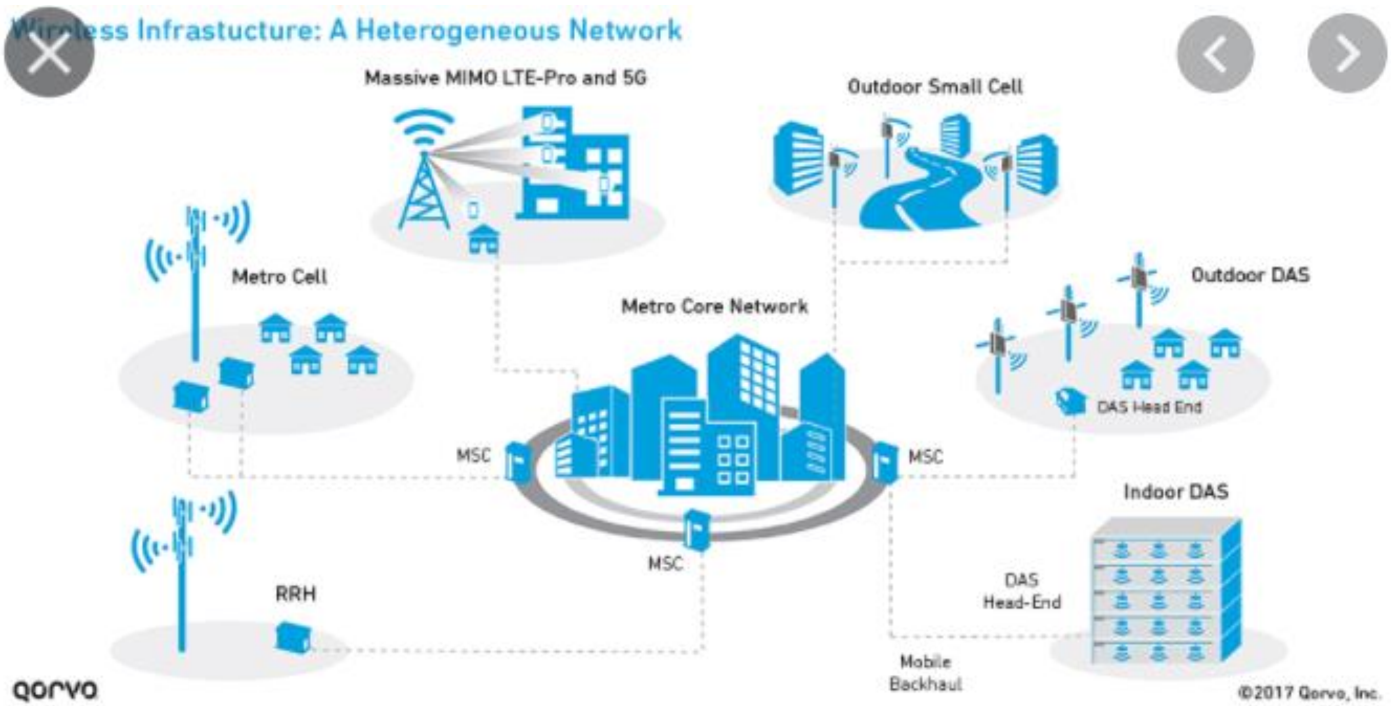

RO Care India
Coagulants
Coagulation
Flocculation
Sedimentation
WATER PURIFICATION PROCESS & IMPORTANCE
Disinfection
Distribution
Home Consumption
Treated Water Storage
Filtration

Abandoned Cycles at IIT Guwahati ...

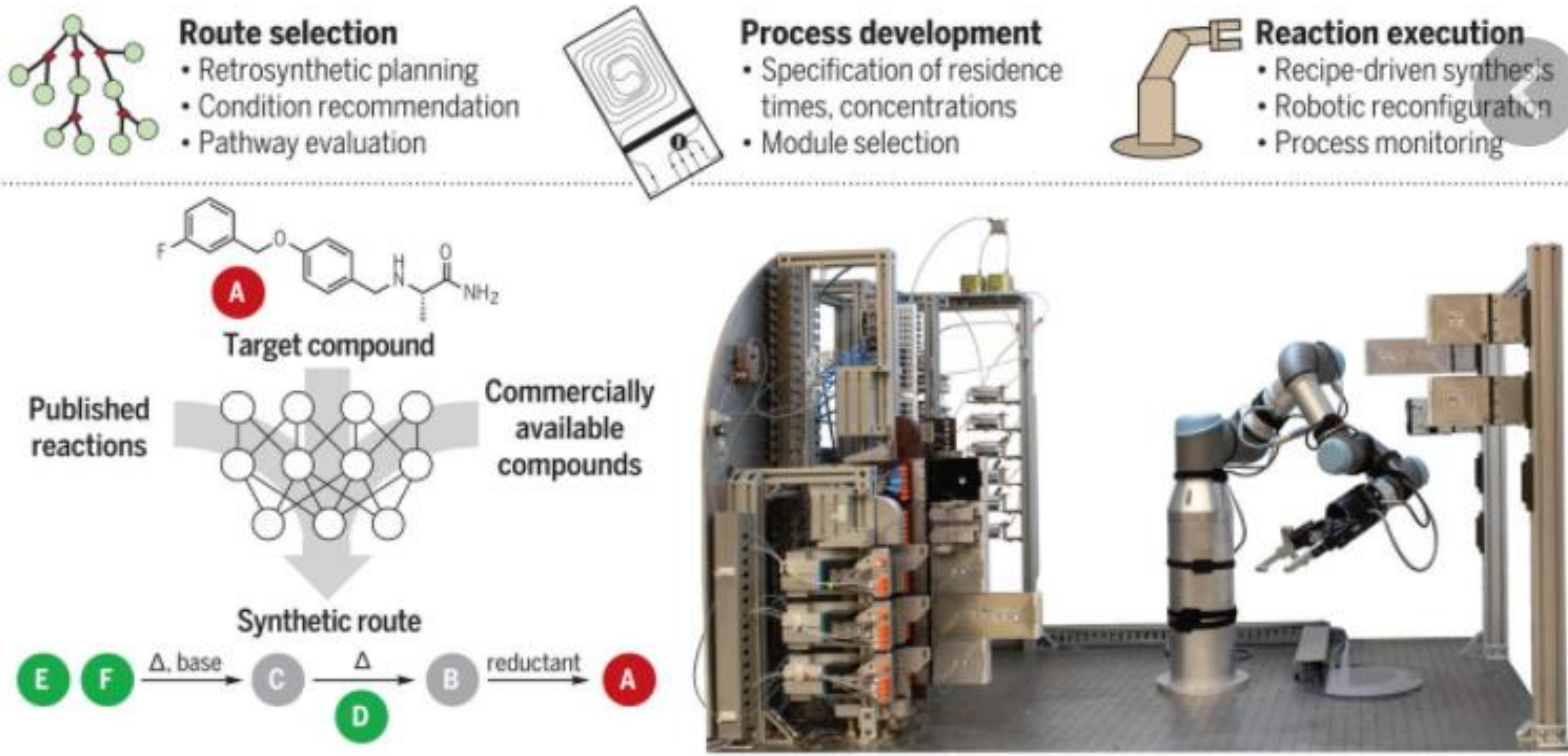
Circumventing lock-ins

11. Reject lock-in. Business and regulatory environment should be flexible to allow the implementation of innovations.

The lock-in problem: Because of the financial cost of adopting the new approach, which often involves the necessary development of supporting technology and infrastructure, the situation can be referred to as a 'lock-in'



Artificail Intelligence and Machine Learning in Organic Synthesis



Thus, circular chemistry innovations also need to promote transitions and overcome lock-ins to realize market opportunities for long-term sustainability ambitions

12. Unify industry and provide coherent policy framework. The industry and policy should be unified to create an optimal environment to enable circularity in chemical processes.

Key drivers to induce this transition are: enabling and rewarding chemical and environmental regulations; sustainable supply chains and chemical logistics and optimal university–industry–government relations

My Own Garden Using Scrap Materials


FEUTRE EXTRA
LANGE HALTBARKEIT
CamPure
Cone
Productivity
Estd: 1994
NATCOSEB XX
December 9-11, 2021