Awareness Raising Workshop

Areas of Research in Green Chemistry: FEEDSTOCKS

GLOBAL GREEN CHEMISTRY INITIATIVE

EXPERT

YALE REPRESENTATVE

CENTER *for* GREEN CHEMISTRY
and GREEN ENGINEERING *at* YALE

UNITED NATIONS
INDUSTRIAL DEVELOPMENT
ORGANIZATION

Agenda

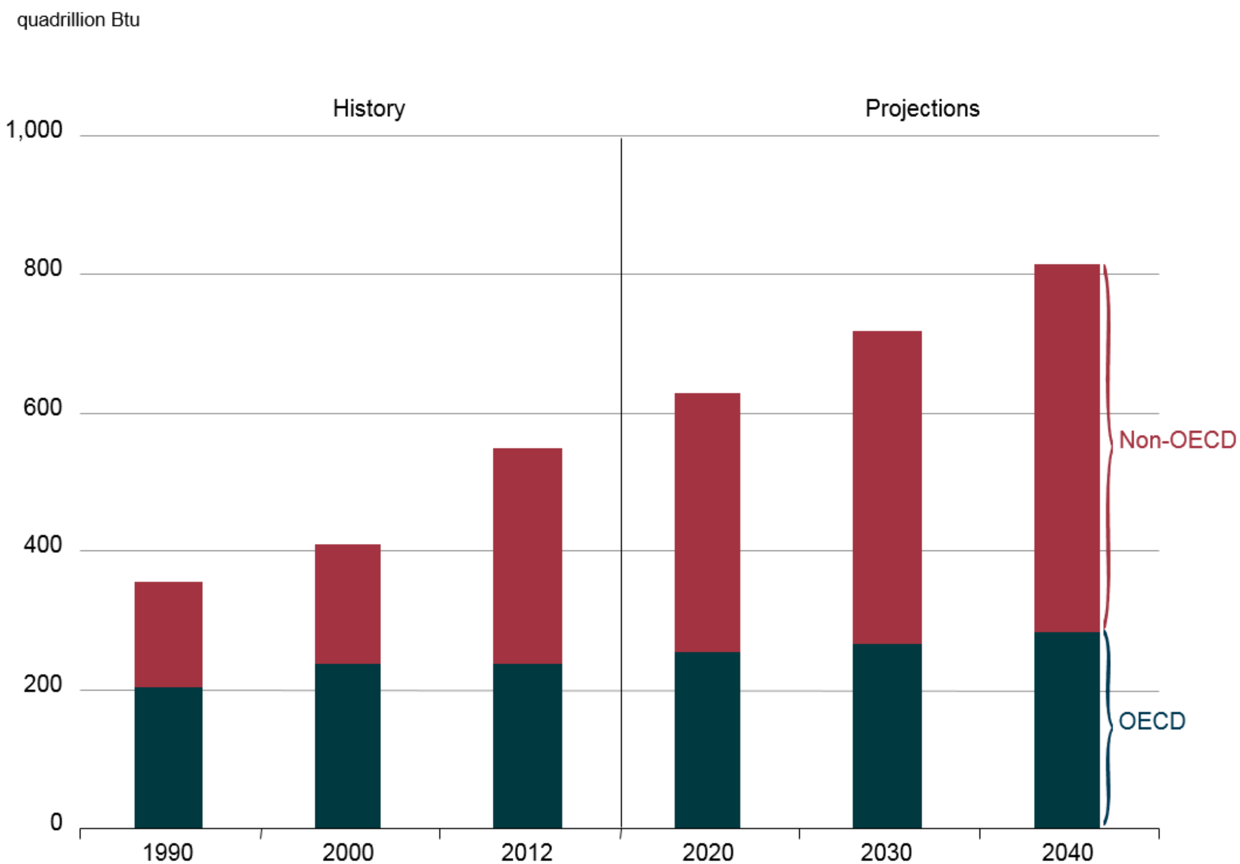
- 8:30 Welcome Remarks
- 9:00 – 10:00 Introduction
- 10:00 – 10:20 Break
- 10:20 – 12:00 Fundamentals of Green Chemistry
- 12:30 – 12:45 Lunch and Networking
- 12:45 – 14:15 Areas or Research in Green Chemistry
- 14:15 – 14:30 Break
- 14:30 – 16:00 Case Study examples
- 16:00 Closing Remarks

Recap…

PRINCIPLE 7

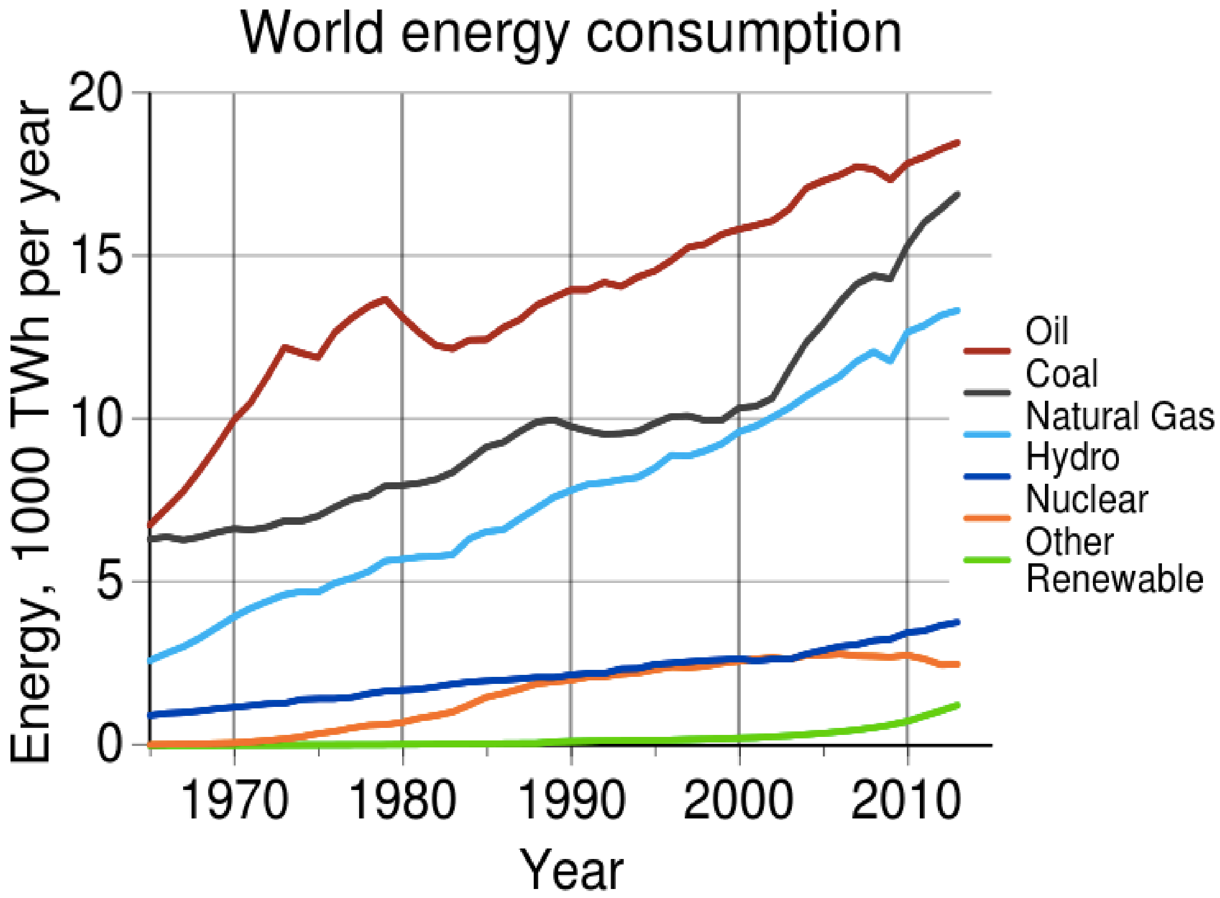
A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.

Energy Consumption: data and projections



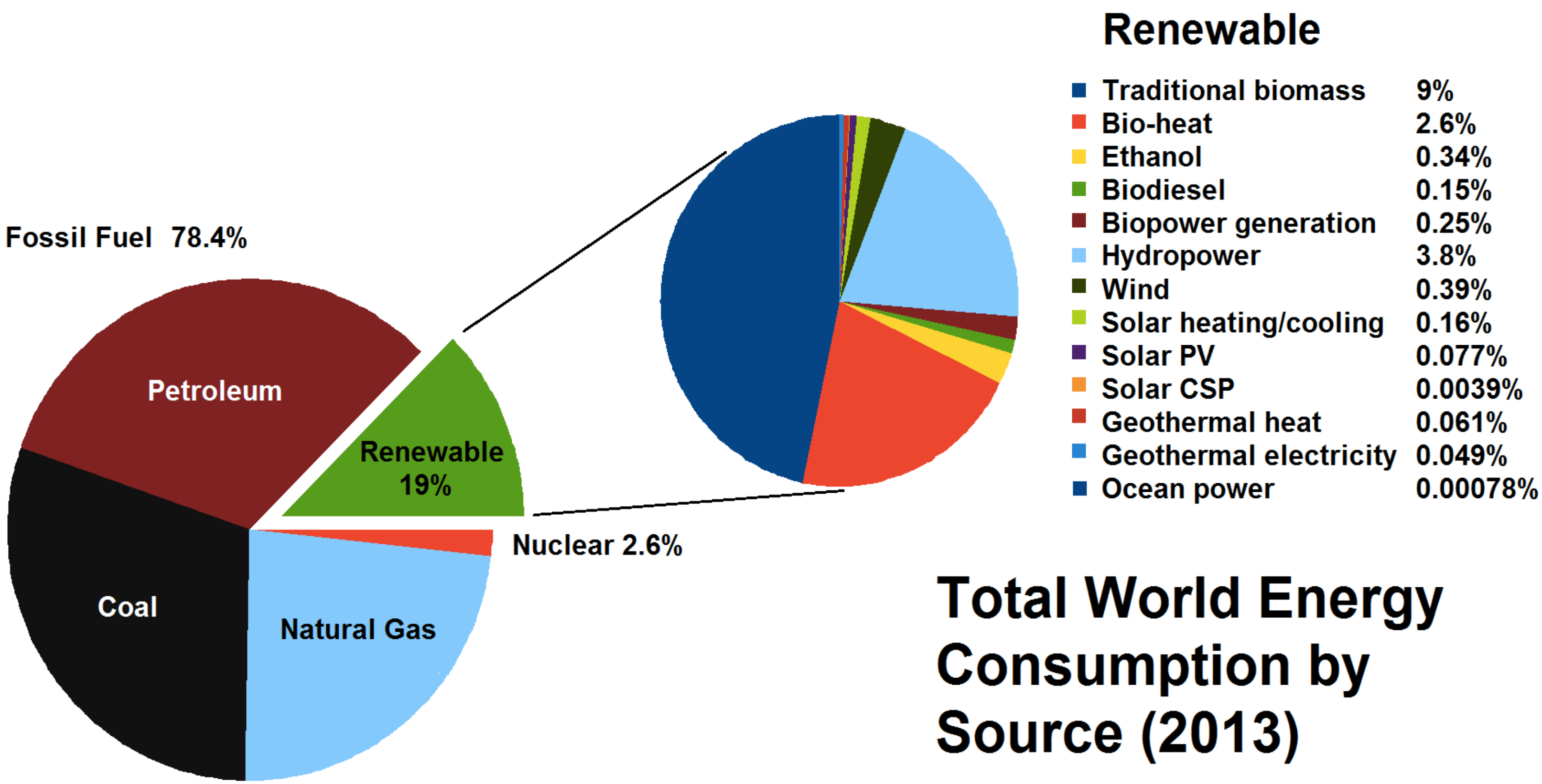
Increasing world energy consumption since 1990.
The graph includes prediction for year 2035, where the use will reach 770 quadrillion British Thermal Unit [BTU]. Source: U.S. Energy Information Administration [U.S. EIA].

Energy Feedstocks Consumption



Increasing world energy consumption years 1970-2010. Oil, coal and natural gas are still predominant sources of energy, but renewables are on the increase too. Source: Statistical Review of World Energy.

Energy Feedstocks Sources



World energy consumption by source reported in 2013. While fossil fuel is still predominant, in 2013 there has been an increase in renewable source of energy. Most renewable energy comes from biomass. Source: REN21 Renewables 2014 Global Status Report.

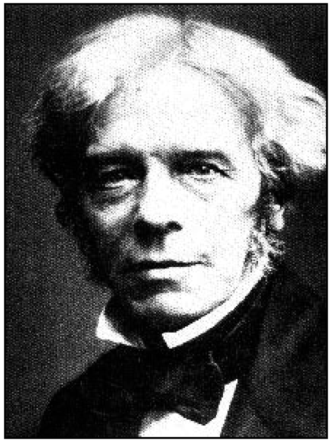
Renewable vs. Depleting feedstocks

Feedstock

- A raw material to supply or fuel or industrial process
- A renewable resource is determined to be renewable if it can be replenished in a relevant amount of time

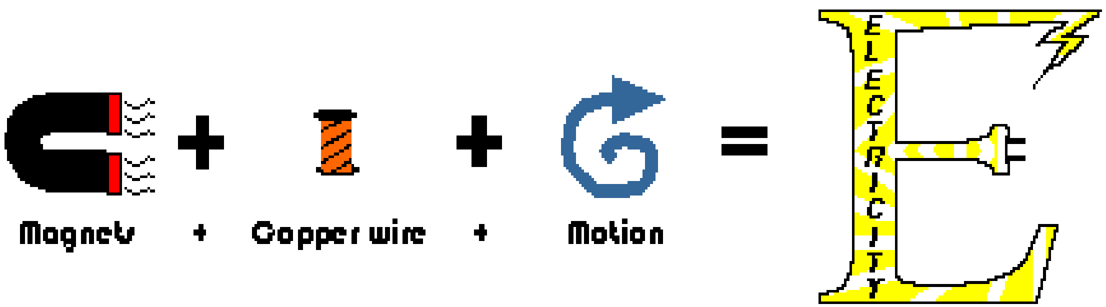
Renewable or Depleting:

- How far do we push the analysis?



Faraday Effect

- **Faraday Effect**



- **Basic Concepts**
  - Voltage – V – Potential to Move Charge (volts)
  - Current – I – Charge Movement (amperes or amps)
  - Resistance – R – V = IxR (R in =ohms)
  - Power – P = IxV = I^2xR (watts)

Periodic Table of Elements

C Solid
Hg Liquid
H Gas
Rf Unknown

Metals: Alkali metals; Alkaline earth metals; Lanthanoids; Actinoids; Transition metals; Poor metals

Nonmetals: Other nonmetals; Noble gases

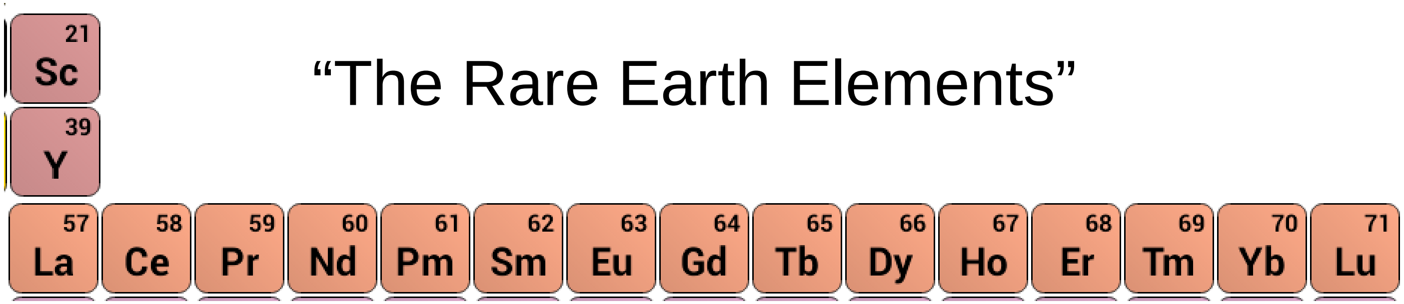
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogen 1.00794	Atomic # Symbol Name Atomic Mass																2 He Helium 4.002602
2	3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
3	11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050											13 Al Aluminium 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
4	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.96	43 Tc Technetium (97.9072)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293
6	55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57–71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (208.9824)	85 At Astatine (209.9871)	86 Rn Radon (222.0176)
7	87 Fr Francium (223)	88 Ra Radium (226)	89–103	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium	118 Uuo Ununoctium (294)

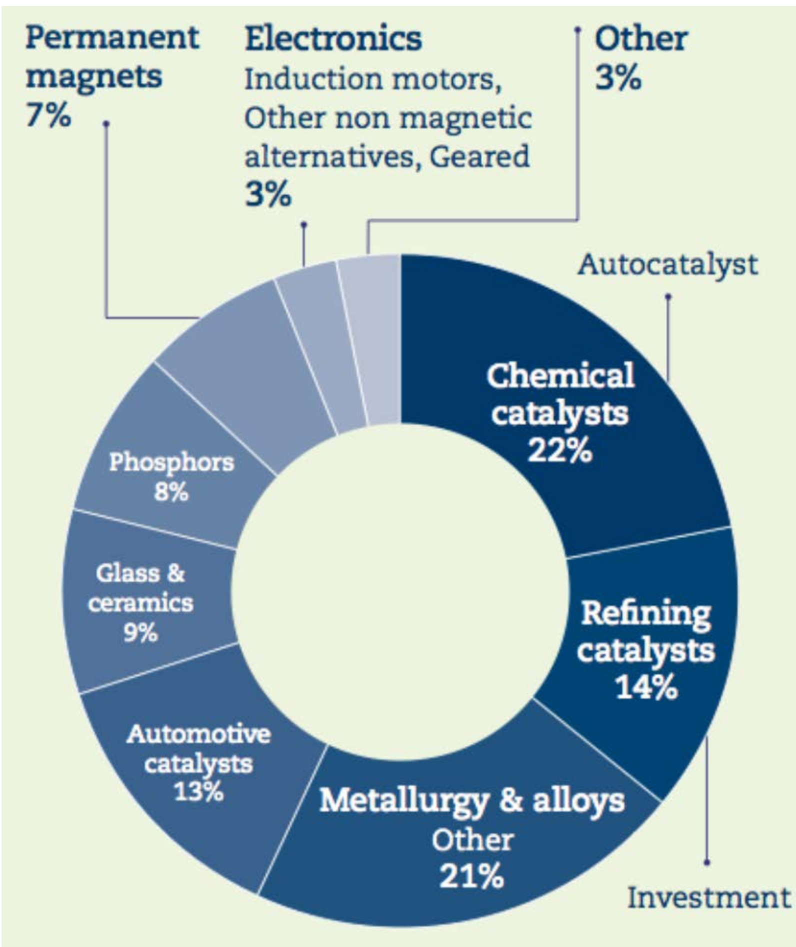
For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

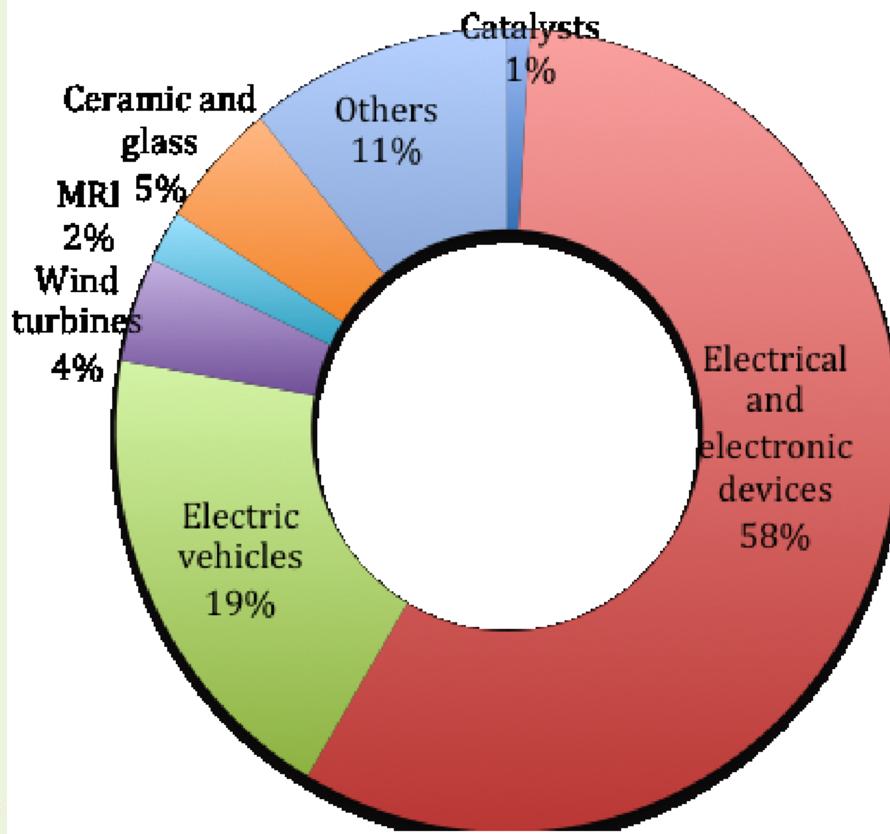
57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

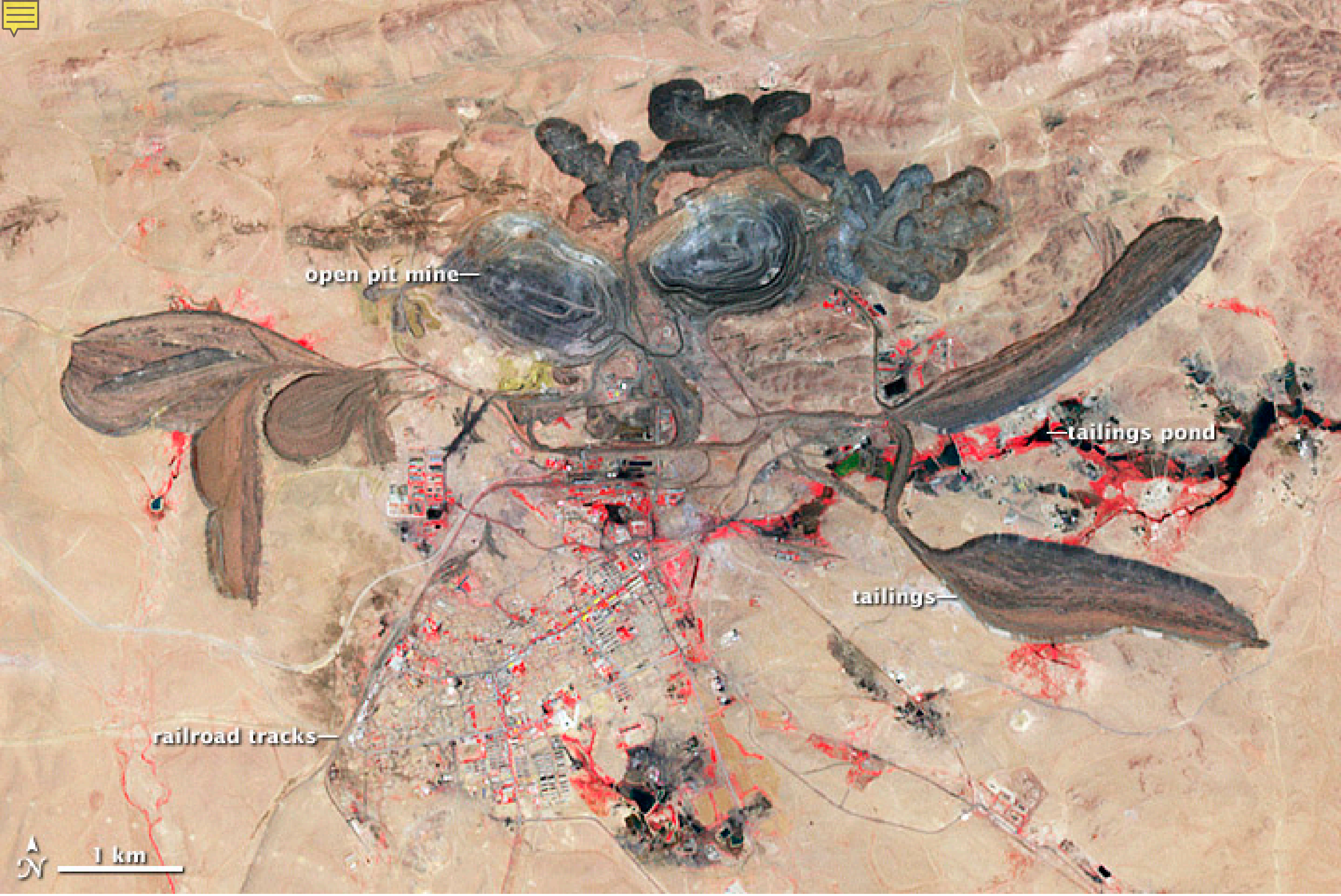
Ptable.com

“The Rare Earth Elements”









Bayan Obo – Outer Mongolia – Largest deposit of REE (Nd)

“The true cost of the clean, green wind power experiment: Pollution on a disastrous scale”

“This toxic lake poisons Chinese farmers, their children and their land. It is what’s left behind after making the magnets for Britain’s [plus the rest of the world's] latest wind turbines, and is merely one of a multitude of environmental sins committed in the name of our new green Jerusalem”

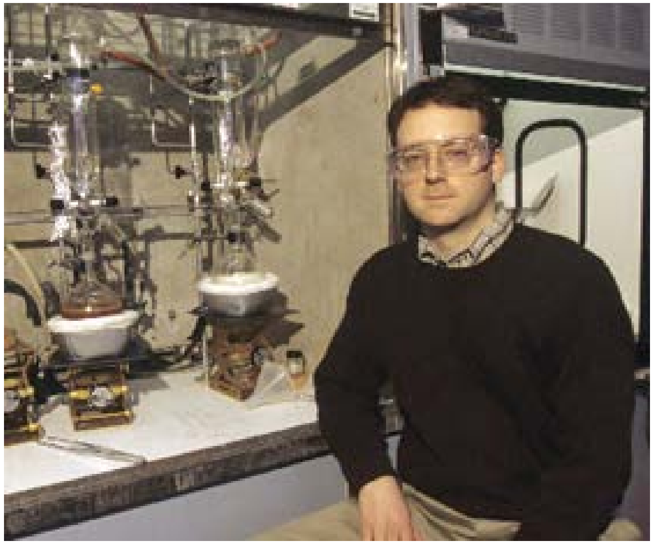
Simon Parry in China & Ed Douglas in Scotland, **The DailyMail, (29/1/11)**

Renewable feedstocks

Renewable feedstocks include the following materials:

- CO_2
- Biomass (algae, corn, switchgrass, poplar, willow, sorghum, and bamboo)
- Agricultural waste (ex. manure)

Using CO_2 as a feedstock: Prof. Geoffrey W. Coates

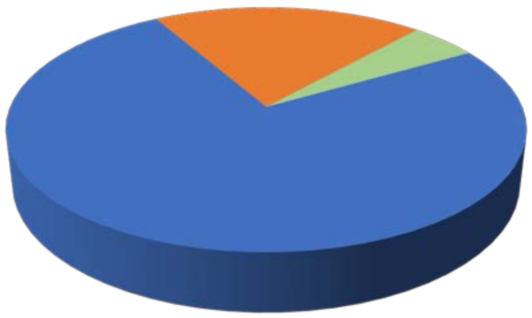


- Development of catalysts able to incorporate carbon monoxide and dioxide into polymers
- Utilize renewable sources of carbon monoxide and dioxide gases such as biomass (agricultural waste) and other low-cost sources such as coal or industrial waste
- High turnover numbers, frequencies, and selectivities
- Polycarbonate coatings manufactured with these catalysts have the potential to sequester or avoid up to 180 million metric tons of CO_2 emissions

Biomass platforms

Biomass production in nature:
180 billion metric tons/yr

Only about 4% utilized by humans
(food, ethanol, sweeteners)



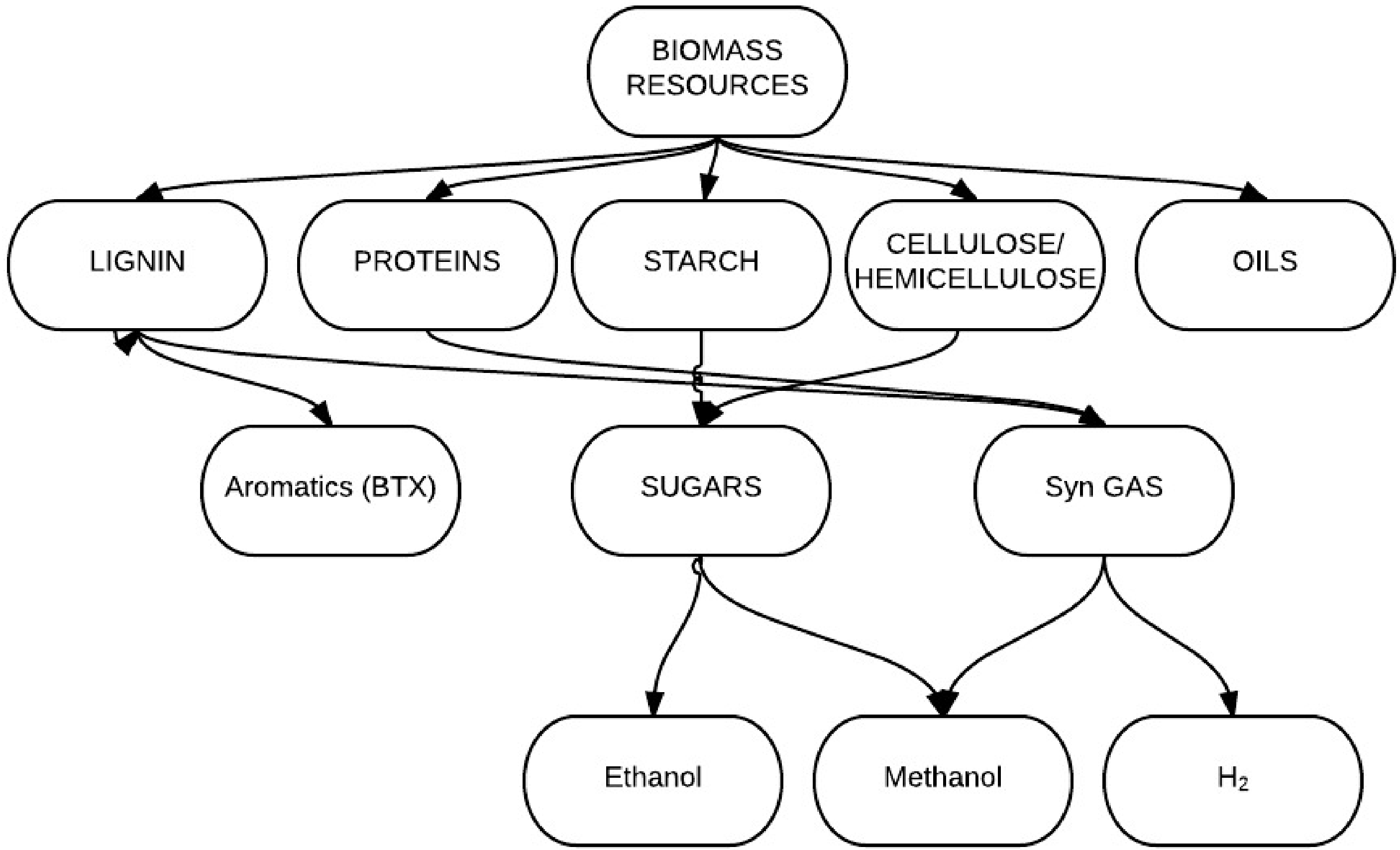
Carbohydrates Lignin Fats, proteins, terpenes, etc.

Building blocks for a diverse chemical platform.

Nature's richest source of aromatic carbon. Used in polymers, adhesives, production of phenolic chemicals.

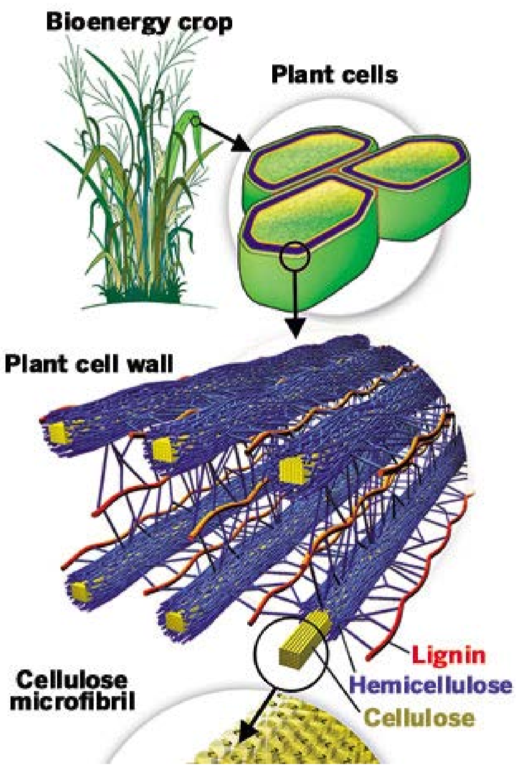
Converted into polymers, lubricants, and detergents.

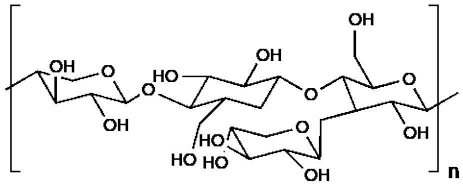
Biomass valorization today



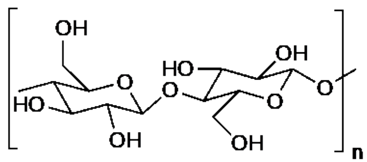
Biomass is a robust feedstock and can be used as a source of proteins, starches, cellulose and oils.

Lignocellulose Biomass

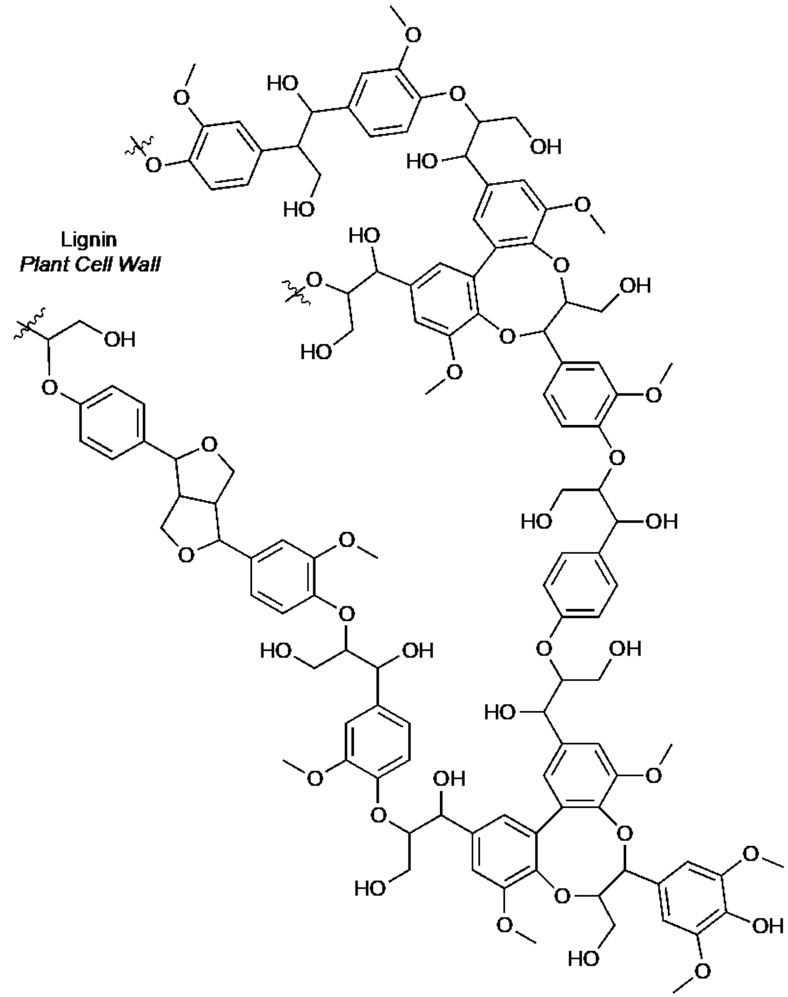




Hemicellulose
Plant Cell Wall



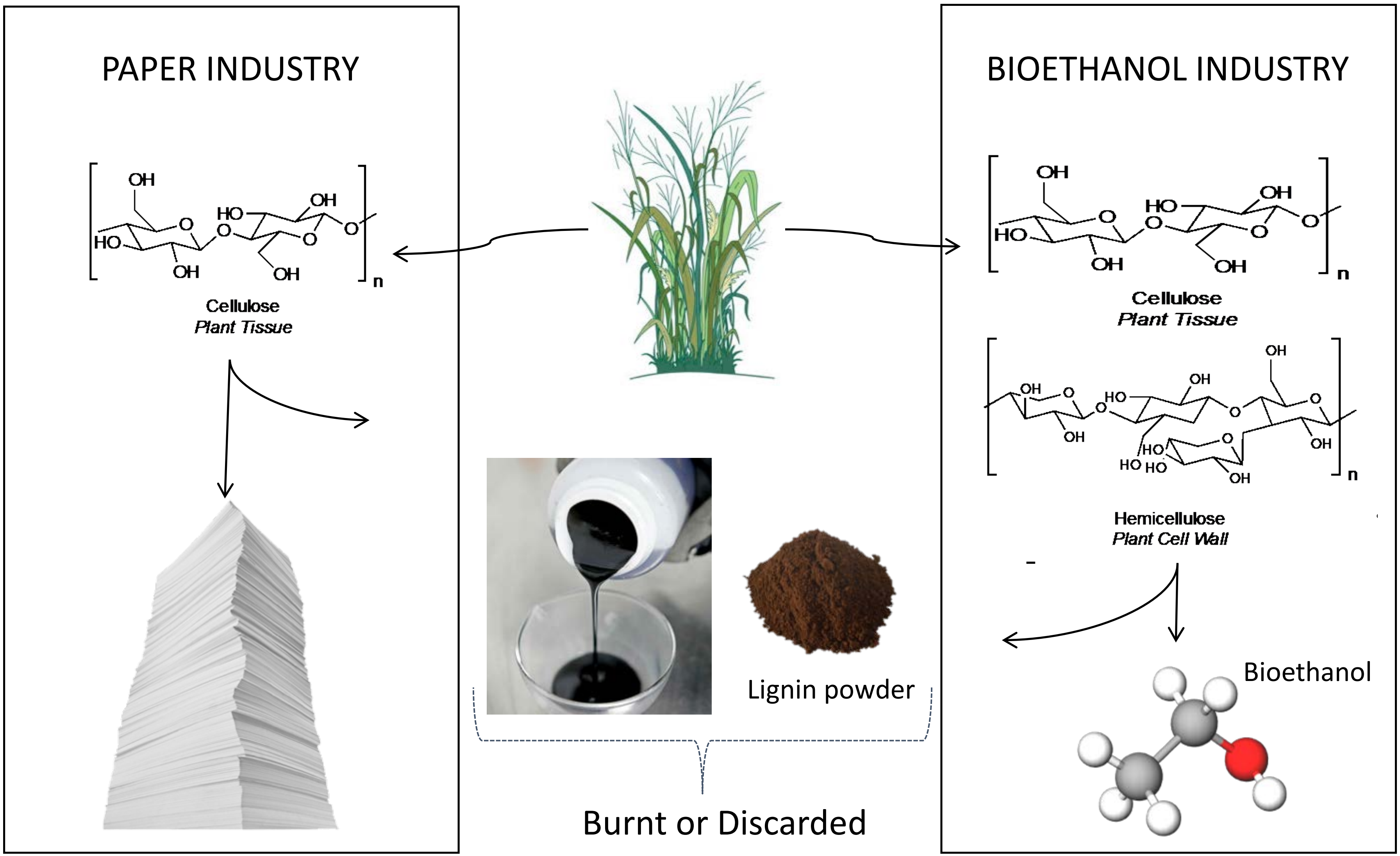
Cellulose
Plant Tissue



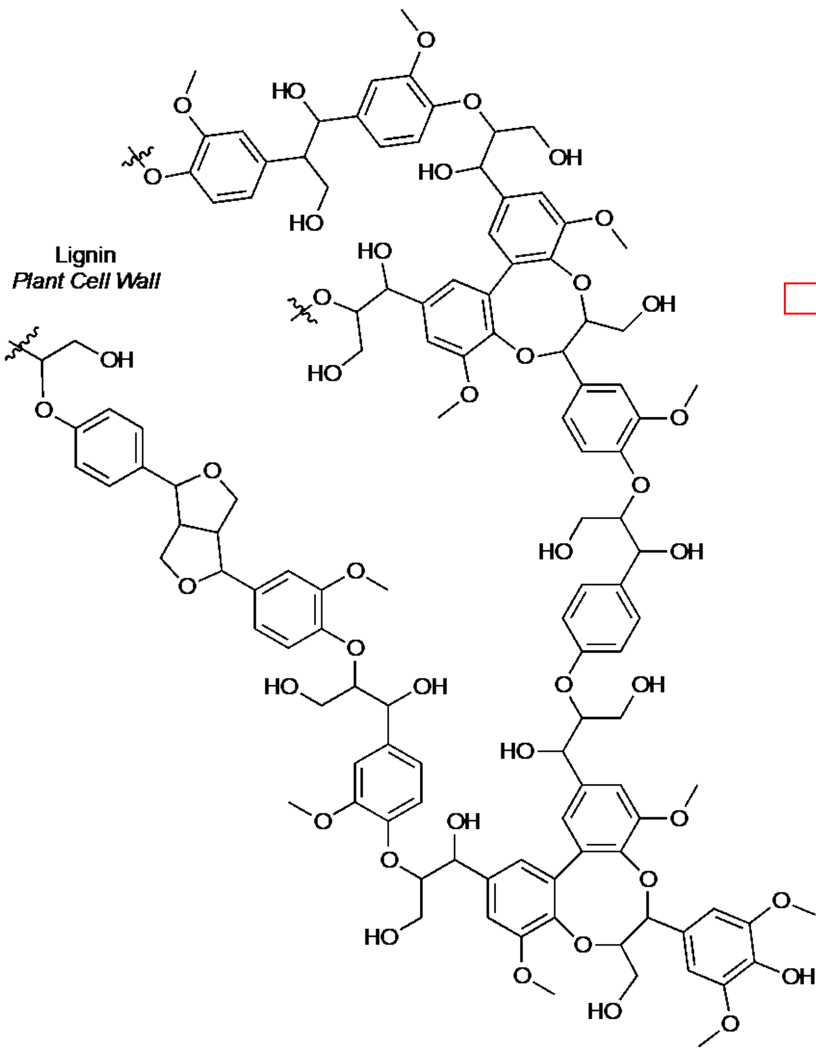
Lignin
Plant Cell Wall

Lignocellulose is a complex polymer obtained from plant cell walls.

Main Industries for Lignocellulose

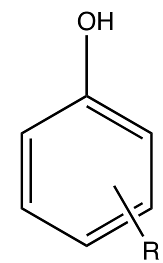


Lignin – Source of Renewable 'Drop-in' Platform Chemicals



A Need of New Technology:

Economical
Sustainable
Selective
Efficient

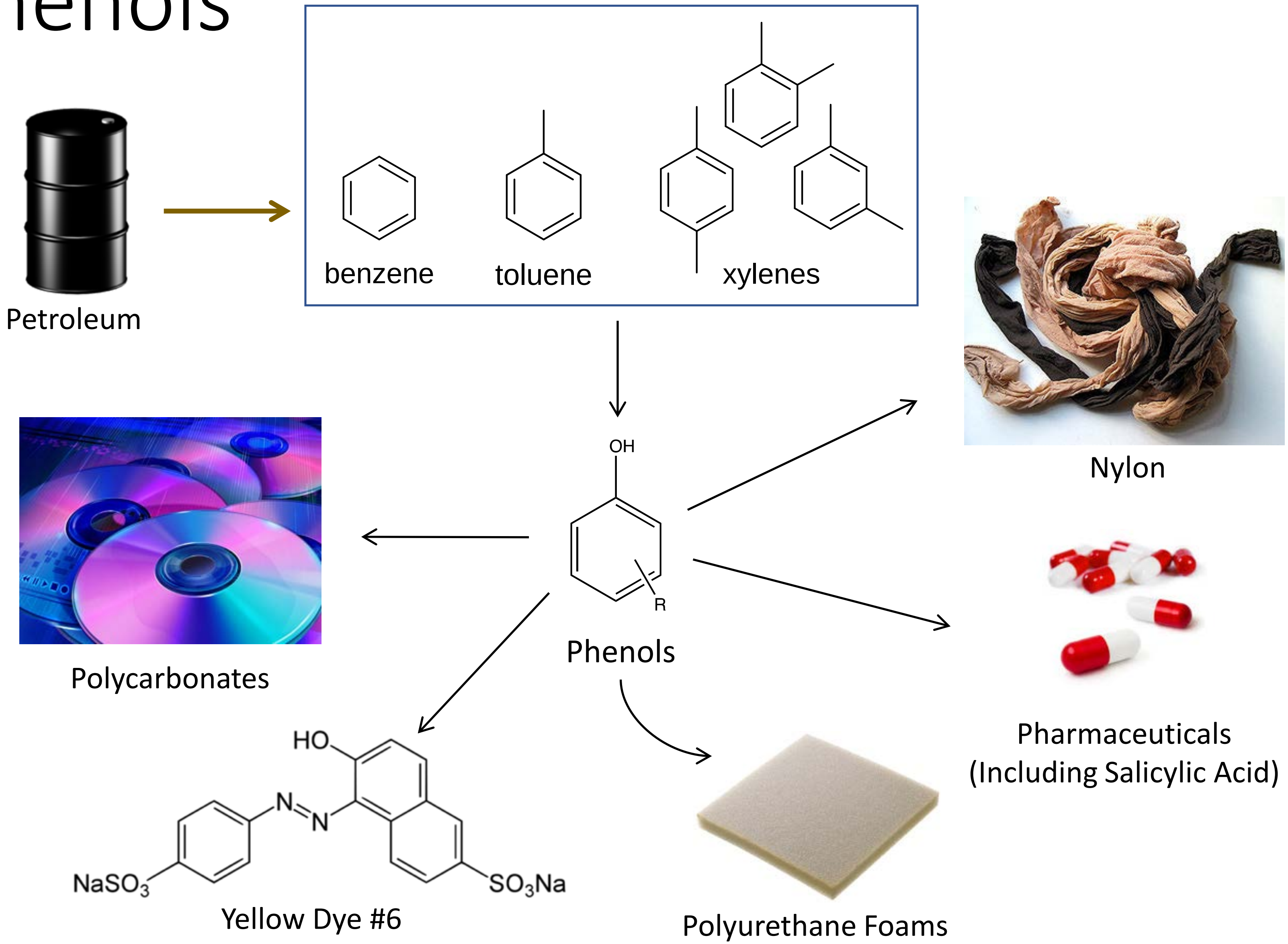


phenol

Lignin structure includes aromatic (ring) structures.

If broken down selectively, it can be a source of drop –in platform chemicals such as phenol

Traditional synthesis and use of phenols



Why use renewable feedstocks?

- Economic reasons:
  - Inherent long-term tendency for petroleum price increases
  - A fluctuation of a few cents in crude oil price can result in massive price swings for downstream products
  - Constant decrease on cost of renewable resources
- Scientific reasons:
  - Constant improvement of quality of renewable feedstocks
  - Modern plant breeding
  - Genetic manipulation
  - Breakthroughs in catalysis (enzymes, etc.)
- Environmental reasons:
  - Biological compatibility (to an extent)
  - Use of waste streams (wood pulping, agriculture, etc.)

Challenges with Renewables

- Feedstock cultivation
    - Competition with food supply
    - Land demand
    - Nutritional needs
    - Diseases
    - Initial investment
- Harvesting method to maximise yields and minimise degradation of product
- Post harvest processing
- Product extraction and purification
- Product standardization
- Complexity
- Product storage, packing, and distribution
- New methodologies for alternative feedstocks

Areas of Research in Green Chemistry

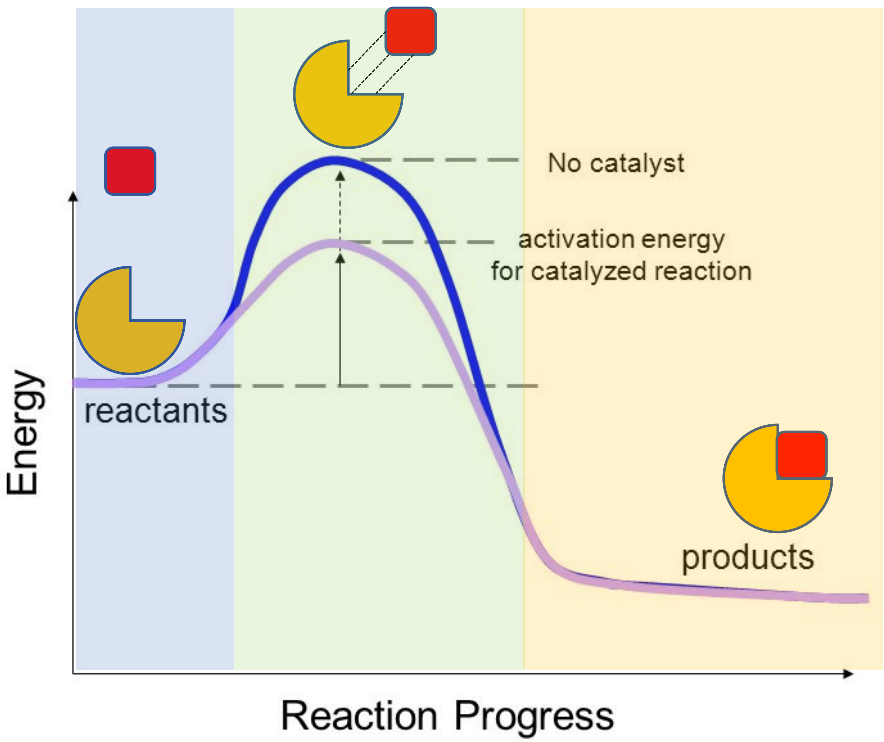
CATALYSIS

PRINCIPLE 9

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

What is a Catalyst?

→ A substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.



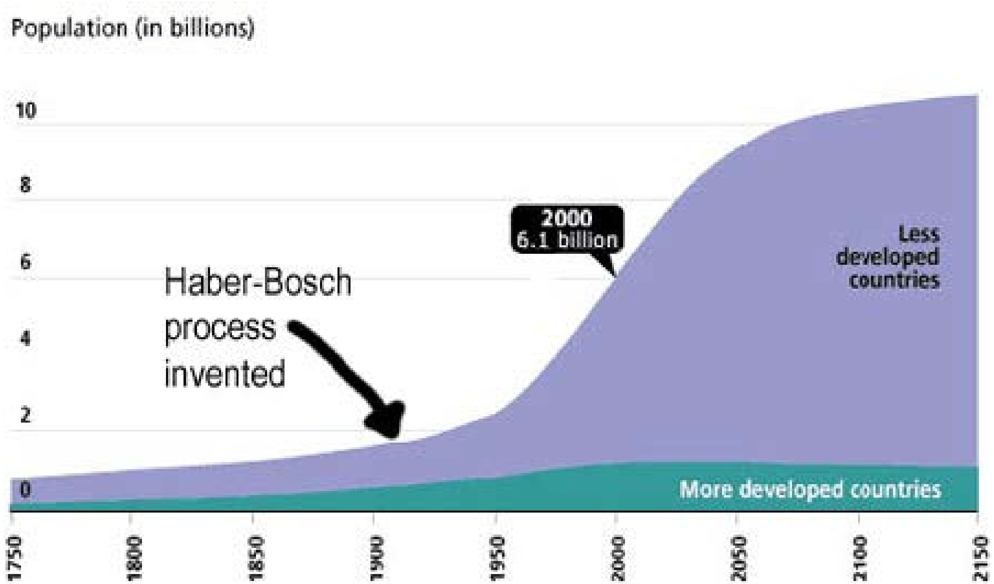
Advantages:

- Lowers activation energy of the reaction
- Can be recycled and reused
- It is used in minuscule amounts
- Shortens reaction time

Source: Wikipedia

Catalysts are widely used by industry and by nature

Catalyst	Reactions catalyzed
Iron oxide	Ammonia from nitrogen and hydrogen
Chromium-Molybdenum Alloy Nickel-Molybdenum Alloy Zeolite (Porous Aluminum and Silica Oxide)	Petroleum Industry
Acid (HCl, H_2SO_4, HNO_3)	Many organic reactions
Enzymes	Starch into sugars and sugars to ethanol



Haber-Bosch process, which allows fertilizer production, is facilitated by a catalyst.

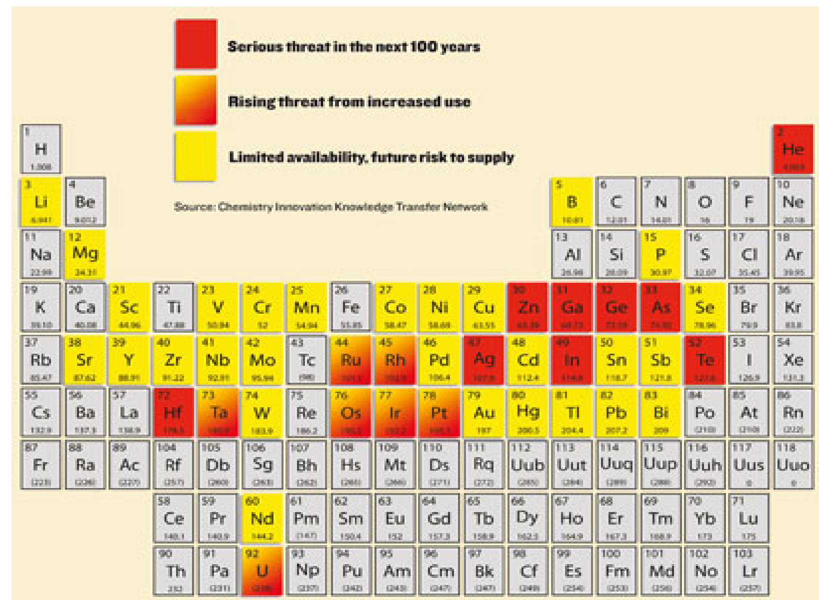
The reaction led to a global increase in human population.

Source: Wikipedia

Designing a Green Catalyst

Not all catalysts are created equal. Chemists need to consider various factors when deciding on the catalyst.

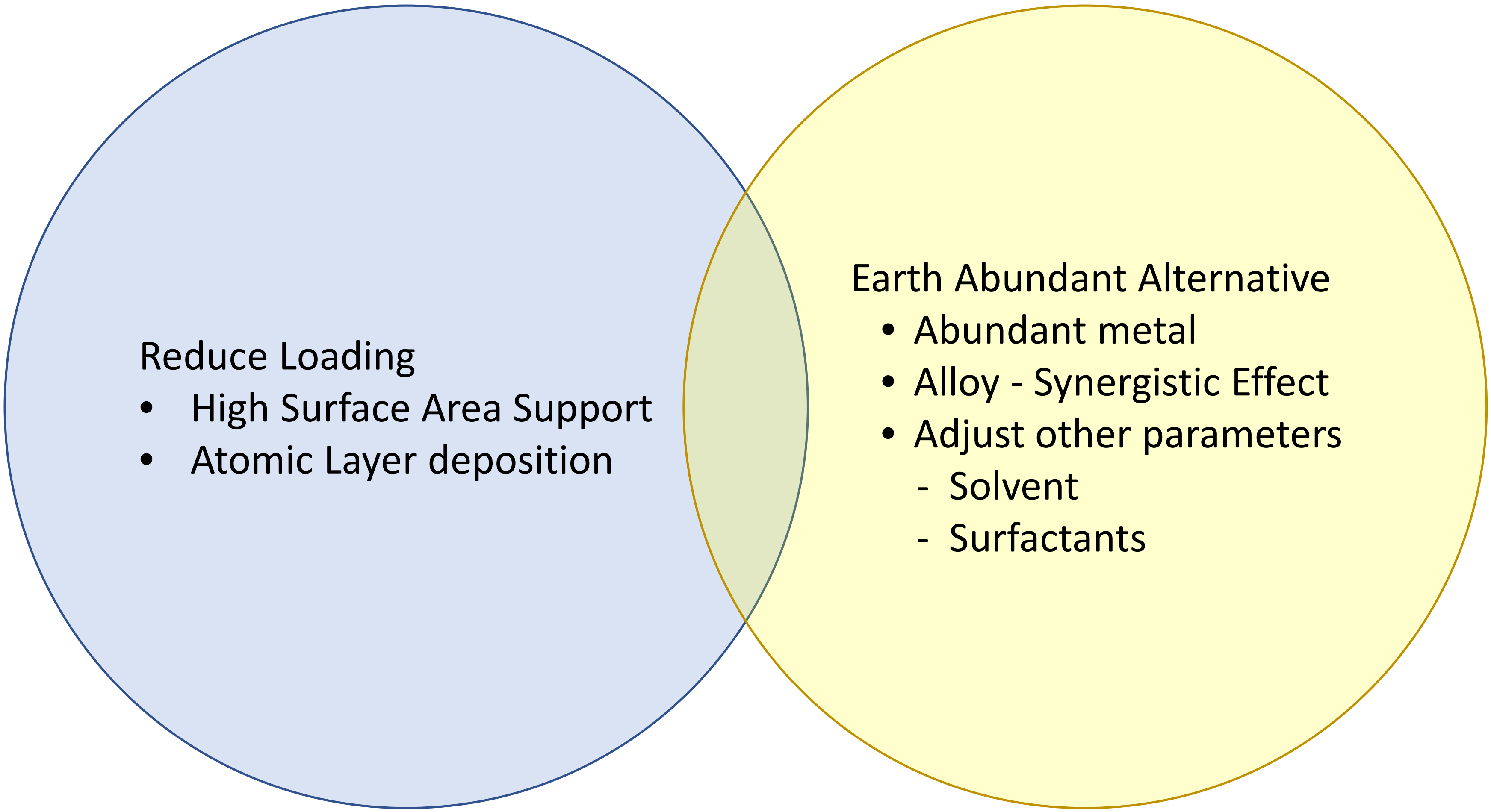
- Low toxicity
- Earth abundance
- Efficiency
  - Rate and energy input
- Compatible with green solvent
- Longevity and Recyclability
- Ease of production
  - Large volume and consistent in quality
- High selectivity for desired product(s)



Many metals which are used as catalysts are depleting

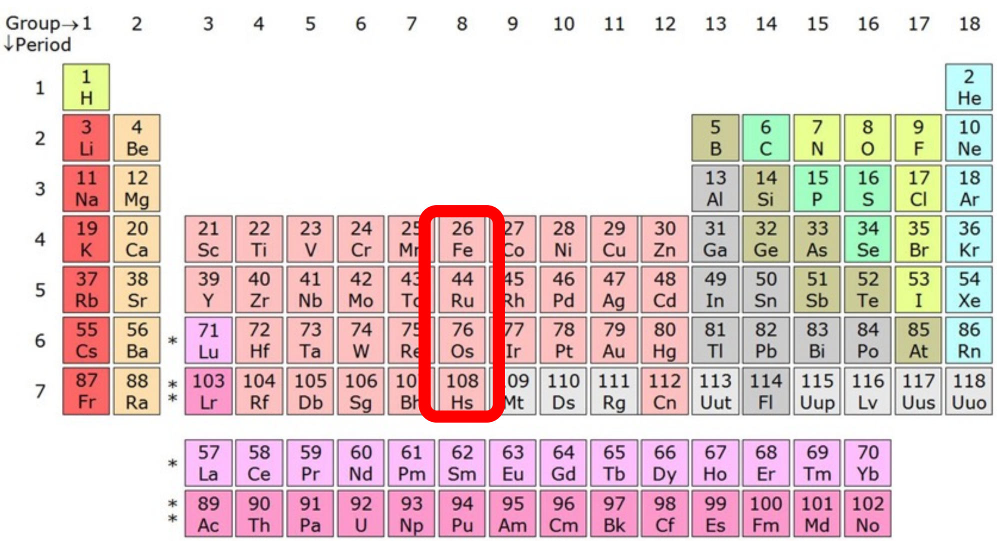
http://www.rsc.org/chemistryworld/Issues/2011/January/CriticalThinking.asp

Current trend in catalyst design



Improving the Haber-Bosch process using iron catalyst

$$N_2 + 3H_2 \rightarrow 2NH_3$$

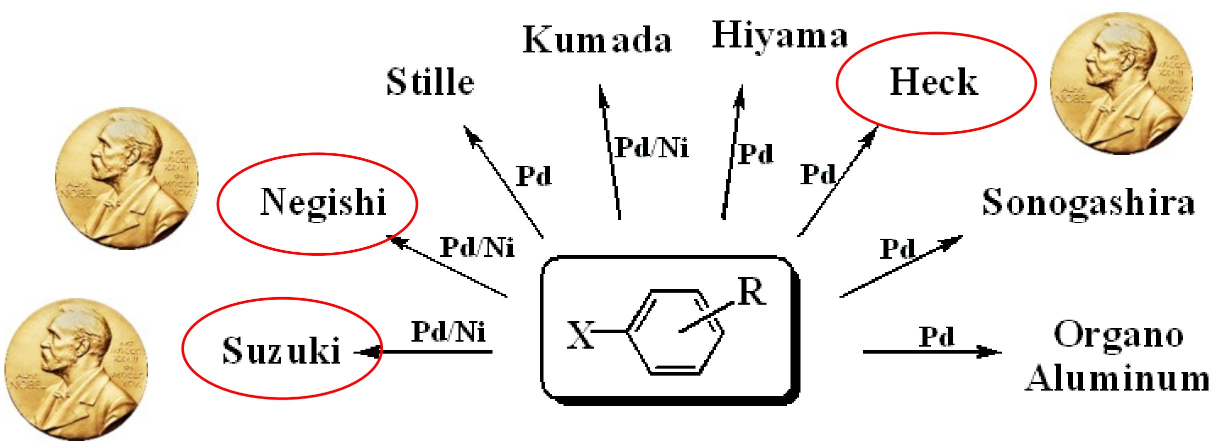


- Traditionally the HB reaction was made using Osmium metal as catalyst.
  - Osmium metal is rare and toxic, which made the reaction unsustainable.
- Because Iron is in the same column as Osmium, its properties are similar
- (Fe_3O_4) can be an alternative catalyst to provide comparable yield.

Other catalyst improvements: from Palladium to Nickel

Cross Coupling Reactions

→ Connect two separate organic molecules together with high selectivity and high yield



	USD mol^{-1}
Ni	$1.20
Pd	$1,500

Other catalyst improvements: alloys

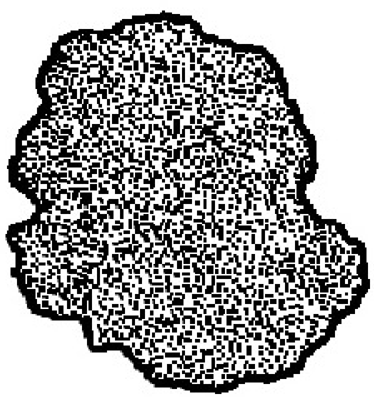
In addition to moving away from precious metals, scientists use metal alloys for synergistic effect:

- Alloying of multiple metals
  - Bronze – Copper + Tin (or Zinc)
  - Monel – Copper + Nickel
  - Stainless Steel – Steel (Iron + C) + Chromium with many others
- The surface area
  - Thin layer deposition
  - Ultra high area support

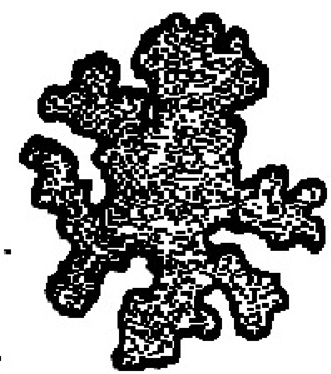
Increase Surface Area

High surface area porous support

<50 $cm^2\ g^{-1}$



50 – 4000 $cm^2\ g^{-1}$



Non-porous solid

- Low specific surface area
- Low specific pore volume

Porous solid

- High specific surface area
- High specific pore

Porous materials have highly developed internal surface area that can be used to perform a specific function. Almost all solids have some amount of porosity.

Areas of Research in Green Chemistry

SOLVENTS

PRINCIPLE 5

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

What is a solvent?

A solvent is any substance that dissolves another substance(s) so that the resulting mixture is a homogenous solution.

Ubiquitous across all sectors of economic activity
……..solvency??
In 2005, the worldwide market 17.9 million tons,
Revenue of about €8,000,000,000.

Typically > 60 % of the investment (in terms of atoms) in a process.

When solvents are used?

Solvents are used in all stages of a product's life-cycle:

- During manufacturing
  - To facilitate intermolecular chemical reactions via solute molecules & ions.
- During processing
  - To aid in manipulation of chemicals, but not as an integral part of the molecule itself.
- During extraction/separation
  - To separate or purify the chemical products from co-products, byproducts and impurities.
- During cleaning
  - To remove oil, grease and silica from mechanical parts.
- During product Formulation
  - To design a product and process (quantities, raw materials, mixture design and testing)

Uses of Solvents

<u>As a Solvent</u>

- Dissolution
- Extraction
- Degreasing
- Inks, dyes, paints, coatings
- Dilution, dispersal
- Dry cleaning

<u>As Something Else</u>

- Fuels
- Feedstocks
- Drugs of abuse
- Beverages
- Antifreeze
- Explosives
- Pollutants

Everything has been touched by a solvent

Traditional Solvents

- Volatile Organic Compounds
  - Chloroform, carbon tetrachloride, methylene chloride, perchloroethylene (PERC)
  - Benzene, Toluene, Xylene (BTX)
  - Acetone, Ethylene Glycol, methylethyl ketone (MEK)
- Chlorofluorocarbons (CFCs)

What are the concerns for solvents?

Inherent Toxicity

- Methylene chloride, chloroform, carbon tetra chloride and other halogenated solvents are suspected human carcinogens.

Flammability

- Because of their physicochemical properties (low flash point and autoignition temperatures), solvents are flammable.

Explosivity

- They can explode, and since they are used in large volumes, the explosion can be disastrous.

Stratospheric Ozone Depletion

- They reduce the ozone layer which protects the earth from the radiation.

Atmospheric Ozone Production

- CFCs contribute to ozone production which in turn increases a green house effect.

Global Warming Potential

Solvent Selection Process by ACS and GSK

- Screen solvents based on
  - reaction type
  - process requirements
  - reactant/product solubility
  - EHS
- Evaluate experimentally
- Review the entire route/ process and look for synergies
- Refine experimentation

American Chemical Society

GlaxoSmithKline

Solvent selection parameter

<u>Solvent Acceptability</u>

- Reactivity
- Compatibility
- Product quality
- Process safety
  - Vapor pressure
  - Odor threshold
  - Exposure limits
  - Autoignition temperature
  - Flash point complexity (number and nature of different solvents used)

<u>Mass</u>

- Total solvent mass
- Mass productivity or reaction mass efficiency

<u>Green Chemistry Metrics</u>

- greenhouse gas potential
- emissions on incineration
- Log K_{ow}
- aquatic toxicity
- acidification
- persistence
- eutrophication
- Total Organic Carbon (TOC)
- oil equivalents

<u>Energy</u>

- recovery (boiling point)
- heat of combustion
- ease of drying

GSK solvent selection guide ranking

Classification	Solvent	CAS number	Melting point °C	Boiling point °C	Waste recycling, incineration, VOC, and biotreatment issues	Environmental Impact fate and effects on the environment	Health acute and chronic effects on human health and exposure potential	Flammability & Explosion storage and handling	Reactivity/ Stability factors affecting the stability of the solvent	Life Cycle Score Environmental impacts to produce the solvent	Legislation Flag alerts regulatory restrictions
Greenest	Water	7732-18-5	0	100	4	10	10	10	10	10	
Alcohols	1-Butanol	71-36-3	-89	118	5	7	5	8	9	5	
	2-Butanol	78-92-2	-115	100	4	6	8	7	9	6	
	Ethanol/IMS	64-17-5	-114	78	3	8	8	6	9	9	
	t-Butanol	75-65-0	25	82	3	9	6	6	10	8	
	Methanol	67-56-1	-98	65	4	9	5	5	10	9	
	2-Propanol	67-63-0	-88	82	3	9	8	6	8	4	
	1-Propanol	71-23-8	-127	97	4	7	5	7	10	7	
	2-Methoxyethanol	109-86-4	-85	124	3	8	2	7	6	7	
Ester	t-Butyl acetate	540-88-5	-78	95	6	9	8	6	10	8	
	Isopropyl acetate	108-21-4	-73	89	5	7	7	6	9	7	
	Propyl acetate	109-60-4	-92	102	5	7	8	6	10	4	
	Dimethyl carbonate	616-38-6	-1	91	4	8	7	6	10	8	
	Ethyl acetate	141-78-6	-84	77	4	8	8	4	8	6	
	Methyl acetate	79-20-9	-98	57	3	9	7	4	9	7	

- Solvent selection guide in practice. Each solvent is ranked from 1-10 and color-coded for convenience (1 being the worst, 10 being the best). Ranking is across 6 different categories, which include waste production, environmental impact, human health, hazard, reactivity and life cycle.
- This effort took several years and it is still ongoing.

http://solventguide.gsk.com/

GSK Solvent Selection Guide

	Few issues (bp°C)	Some issues (bp°C)	*Major* issues
Chlorinated	....before using chlorinated solvents, have you considered TBME, isopropyl acetate, ethyl acetate, 2-Methyl THF or Dimethyl Carbonate?		Dichloromethane ** Carbon tetrachloride ** Chloroform ** 1,2-Dichloroethane **
Greenest Option	**Water** (100°C)		
Alcohols	**1-Butanol** (118°C) **2-Butanol** (100°C)	**Ethanol/IMS** (78°C) **1-Propanol** (97°C) **t-Butanol** (82°C) **2-Propanol** (82°C) **Methanol** (65°C)	2-Methoxyethanol **
Esters	**t-Butyl acetate** (95°C) **Isopropyl acetate** (89°C) **Propyl acetate** (102°C) **Dimethyl Carbonate** (91°C)	**Ethyl acetate** (77°C) **Methyl acetate** (57°C)	
Ketones		**Methyl isobutyl ketone** (117°C) **Acetone** (56°C)	Methyl ethyl ketone
Aromatics		**p-Xylene** (138°C) **Toluene** ** (111°C)	Benzene **
Hydrocarbons		**Isooctane** (99°C) **Cyclohexane** (81°C) **Heptane** (98°C)	Petroleum spirit ** 2-Methylpentane Hexane
Ethers		**t-Butyl methyl ether** (55°C) **2-Methyl THF** (78°C) **Cyclopentyl methyl ether** (106°C)	1,4-Dioxane ** 1,2-Dimethoxyethane ** Tetrahydrofuran Diethyl ether Diisopropyl ether **
Dipolar aprotics		**Dimethyl sulfoxide** (189°C)	Dimethyl formamide ** N-Methyl pyrrolidone ** N-Methyl formamide ** Dimethyl acetamide ** Acetonitrile

** = EHS Regulatory Alerts: please consult the detailed solvent guide and the GSK Chemicals Legislation Guide for more information

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PAPER

www.rsc.org/greenchem

GREEN CHEMISTRY CHALLENGE
A U.S. EPA Program

The development of an environmentally benign synthesis of sildenafil citrate (Viagra™) and its assessment by Green Chemistry metrics†

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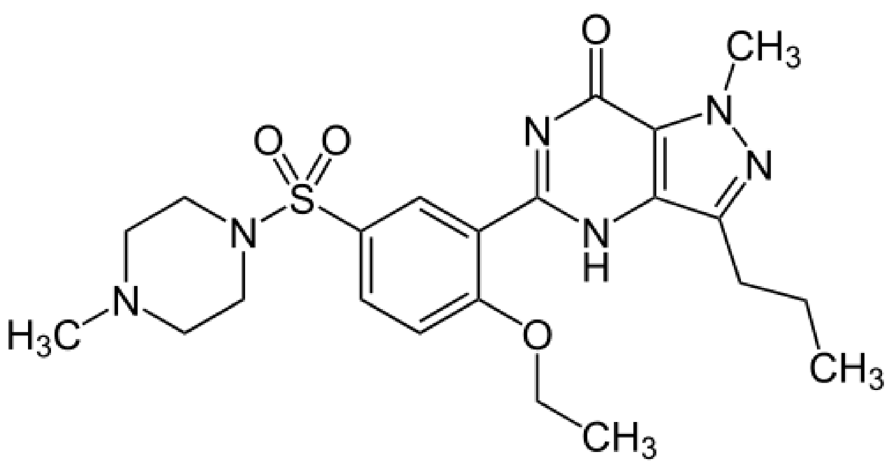
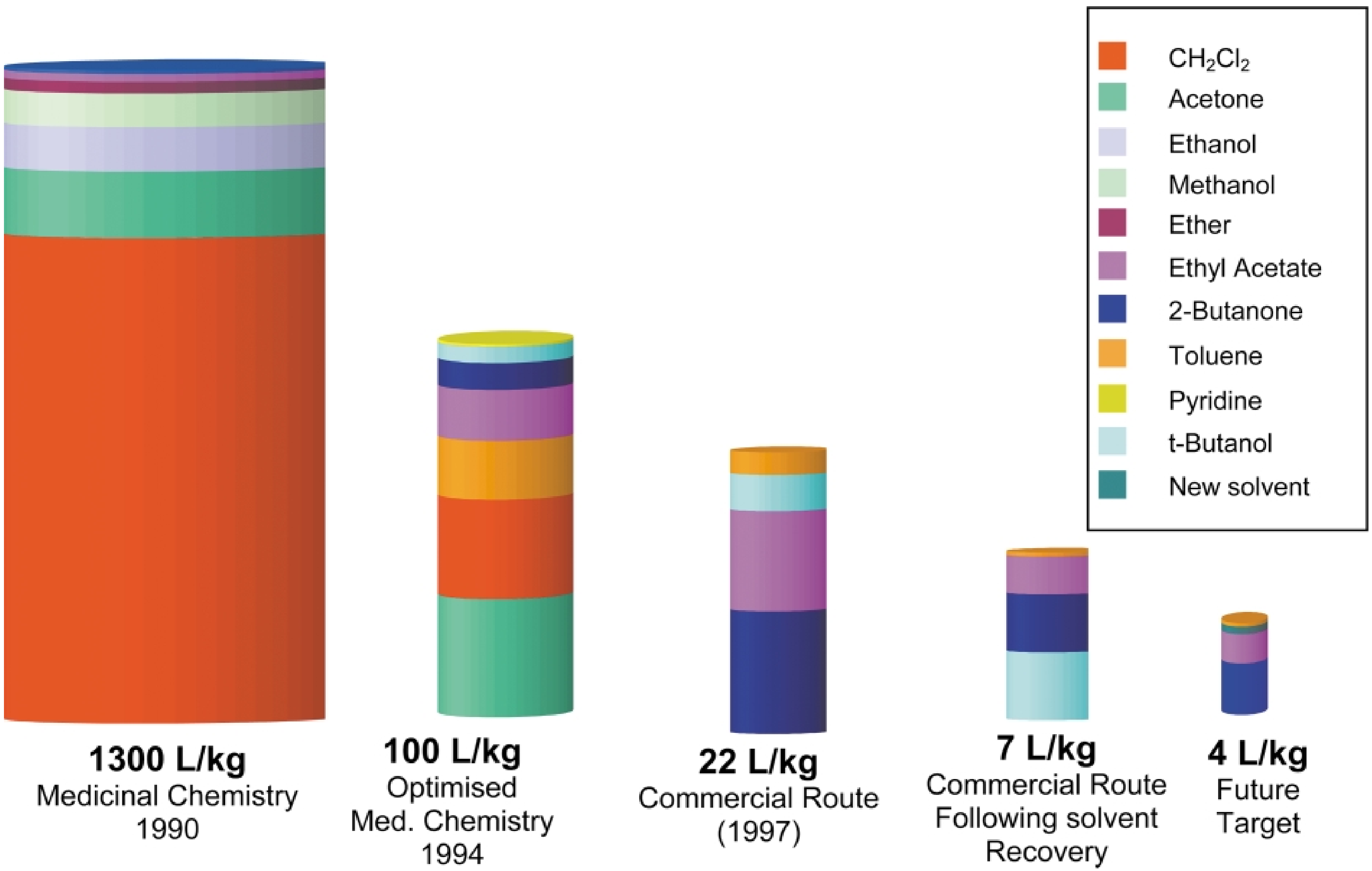


Dunn, P.J et al *Green Chem.*, 2004, **6**, 43-48



Dunn, P.J et al *Green Chem.*, 2004, **6**, 43-48

Other green chemistry solvents

- Aqueous Solvents
- Supercritical Fluids
- Ionic Liquids
- Solventless Conditions

Aqueous Solvents

Water based solvents with generalized applications.

Advantages

- Innocuous
- Inexpensive
- Well characterized
- Versatility among applications

Disadvantages

- High boiling point
- Separation difficulties
- Effluent contamination

Supercritical fluids

Small molecules (e.g., CO_2, H_2O) used under conditions of elevated pressure and temperature to form a fluid that is neither liquid nor gas.

Advantages

- Innocuous
- Inexpensive
- "Tunable" solvent properties
- Enhanced performance
- Versatility among applications
- Ease of separation

Disadvantages

- High pressure required
- Poor solvency
- Surfactants required

Ionic liquids

- Charged substance mixtures that form a liquid at ambient temperatures.
- "Salts whose crystal structure has been perturbed so they are a liquid at room temperature."

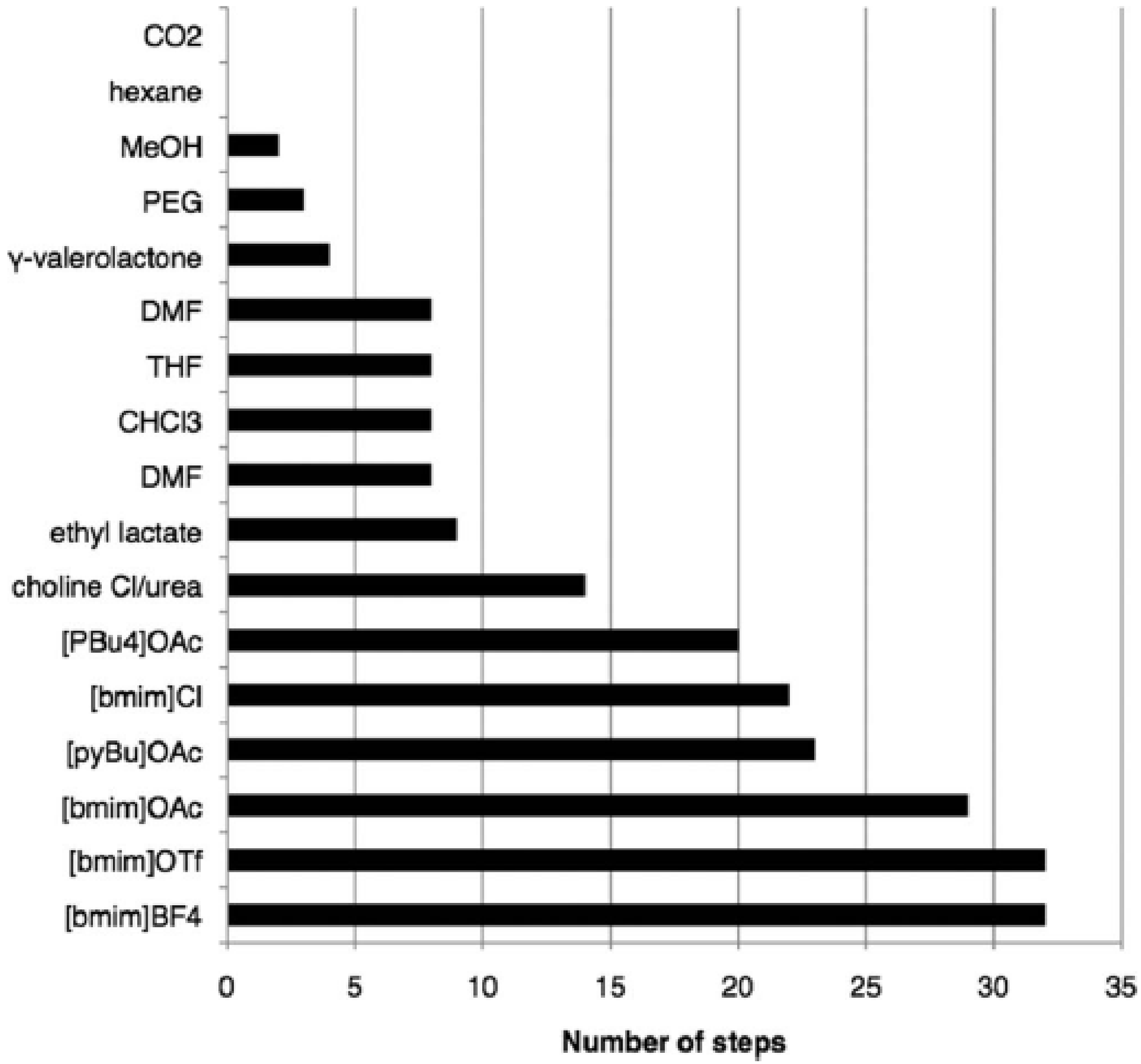
Advantages

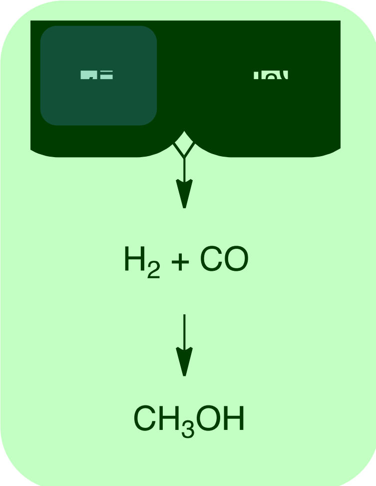
- Very low volatility
- Variable composition (high design potential - can be tailored for many applications)
- Easily recycled

Disadvantages

- Not necessarily benign
- Manufacture costs uncertain
- Ease of separation uncertain

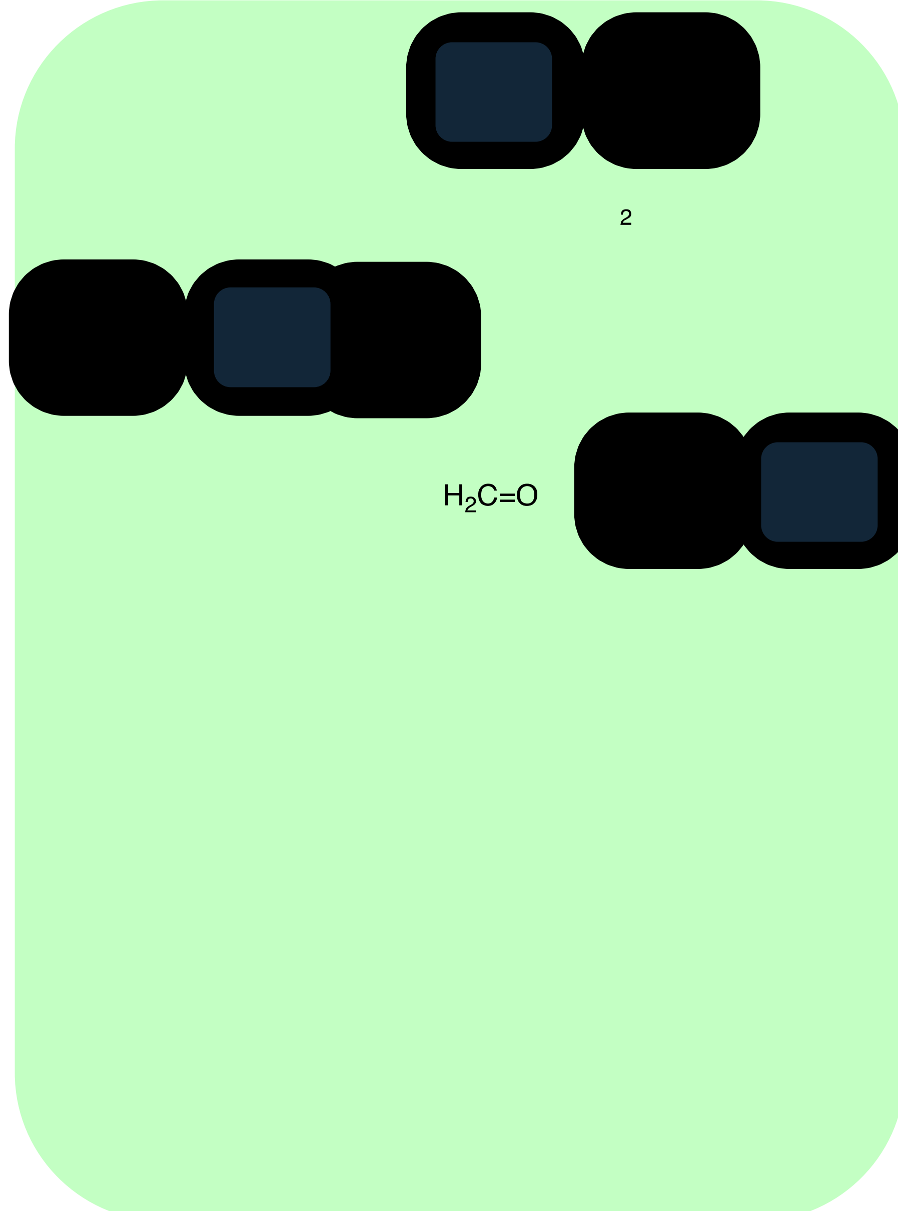
Preparation – so simple?



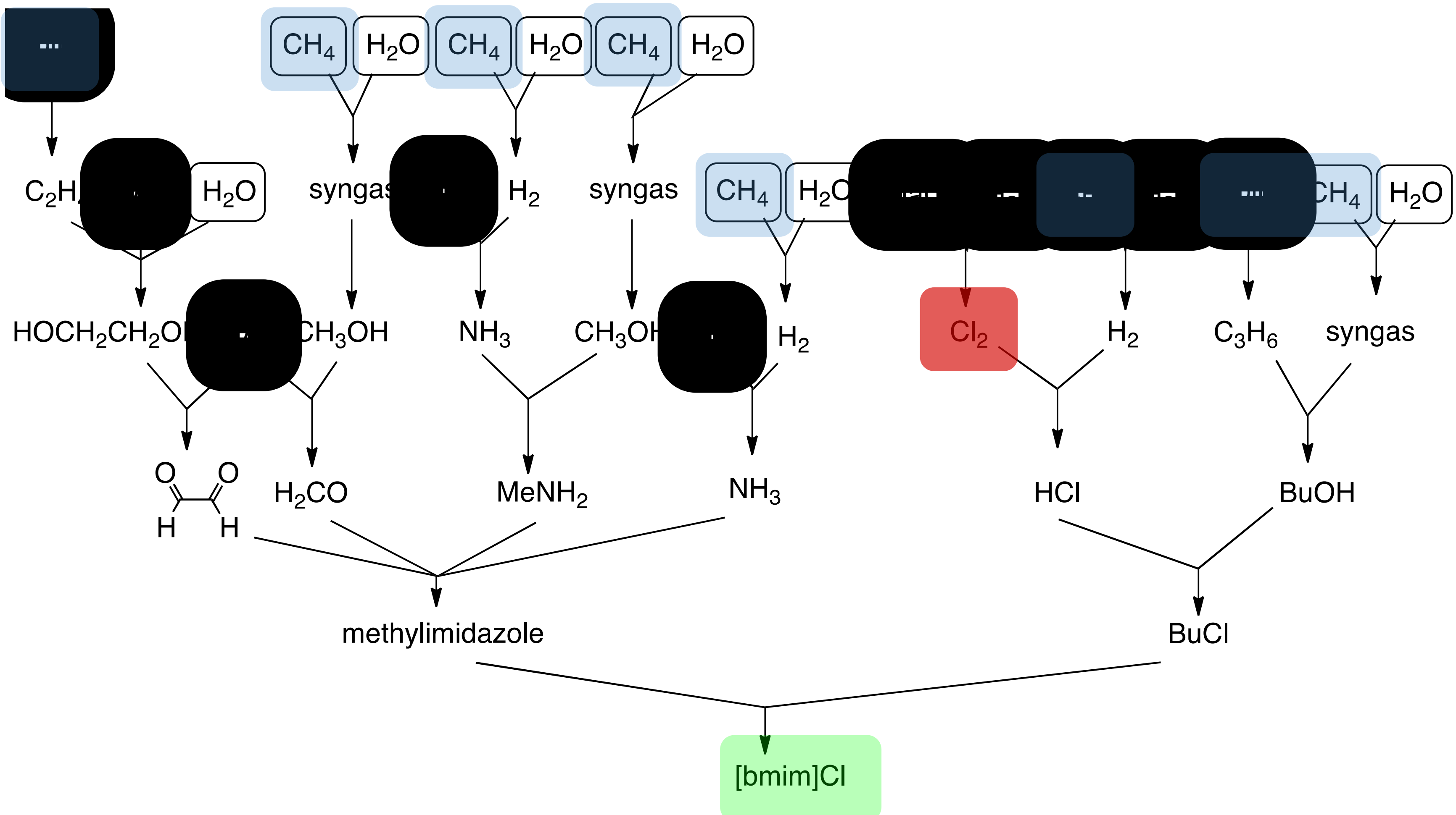


2 step

3 steps



8 steps


CH4
H2O
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C2H
H2O
syngas
H2
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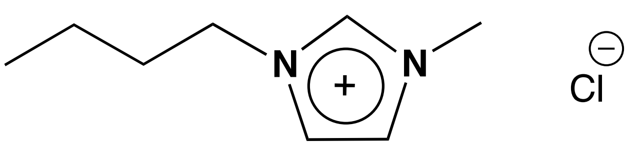
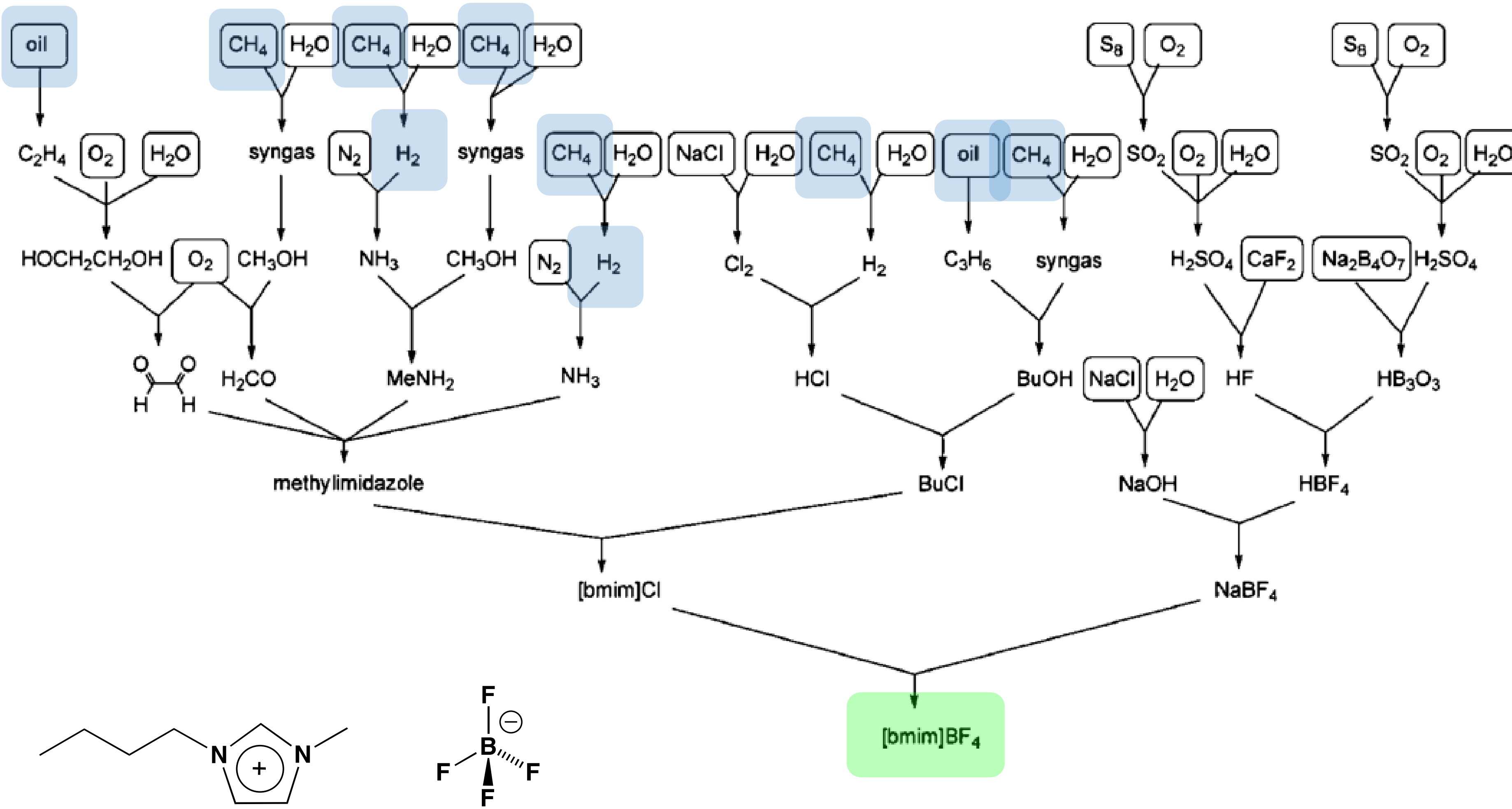
CH4
H2O
CH4
H2O
HOCH2CH2OH
CH3OH
NH3
CH3OH
H2
Cl2
H2
C3H6
syngas
H2CO
MeNH2
NH3
HCl
BuOH
methylimidazole
BuCl
[bmim]Cl



> 20 steps



Ionic Liquids – Advantage?

Solventless conditions

Use of neat conditions or solid state techniques

Advantages

- Solvent concerns eliminated
- Solvent costs eliminated

Disadvantages

- High temperature and/or pressure required
- Lower purity product obtained
- "Work-up"

Areas of Research in Green Chemistry

WASTE

PRINCIPLE 1

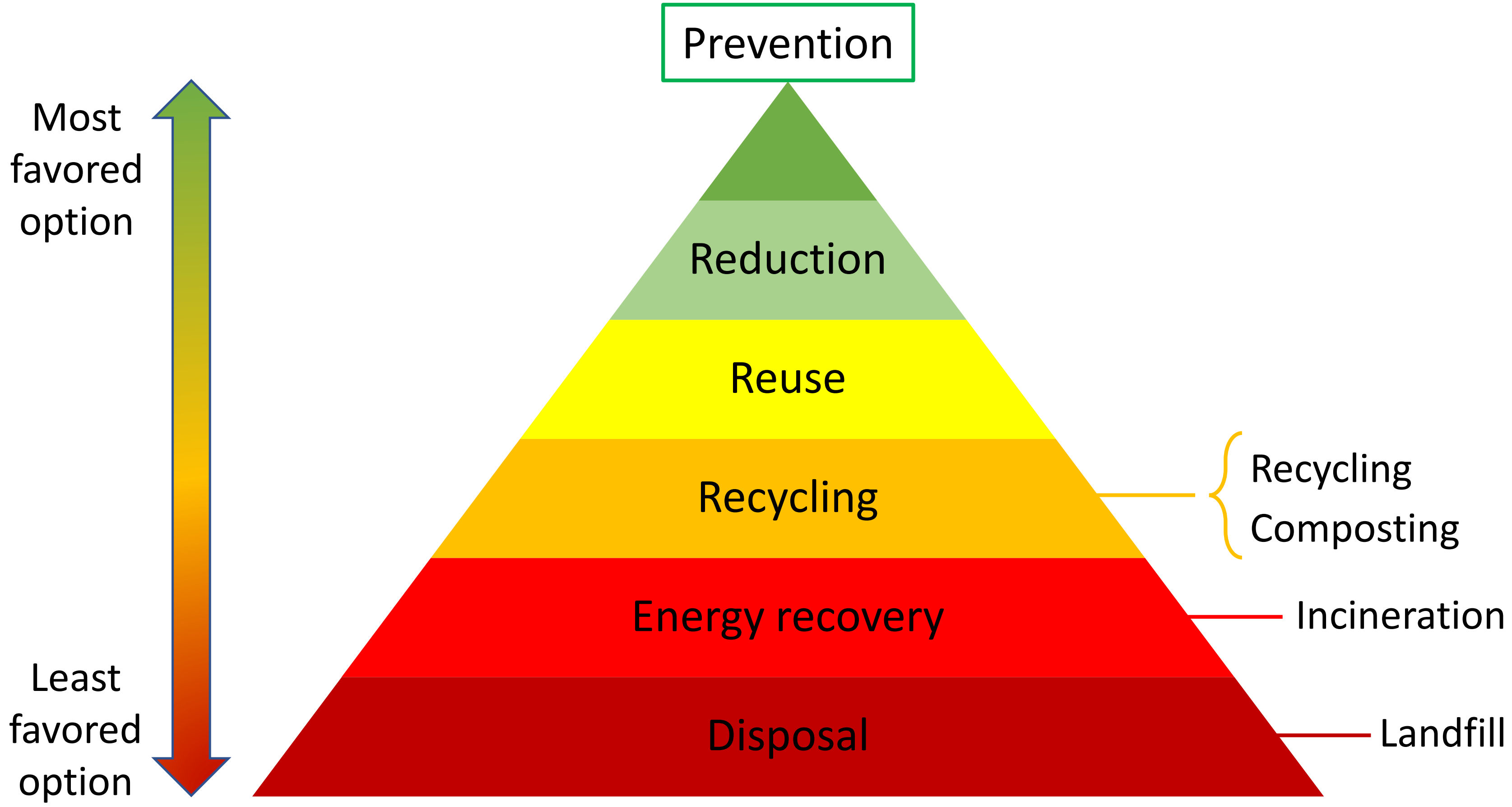
It is better to prevent waste than to treat or clean up waste after it is formed.

Types of waste

- Solid waste
- Liquid waste
- Animal by product
- Biodegradable waste
- Chemical waste
- Bulky waste

Waste treatment pyramid: 4 Rs

Reduce, Reuse, Recycle, Recover



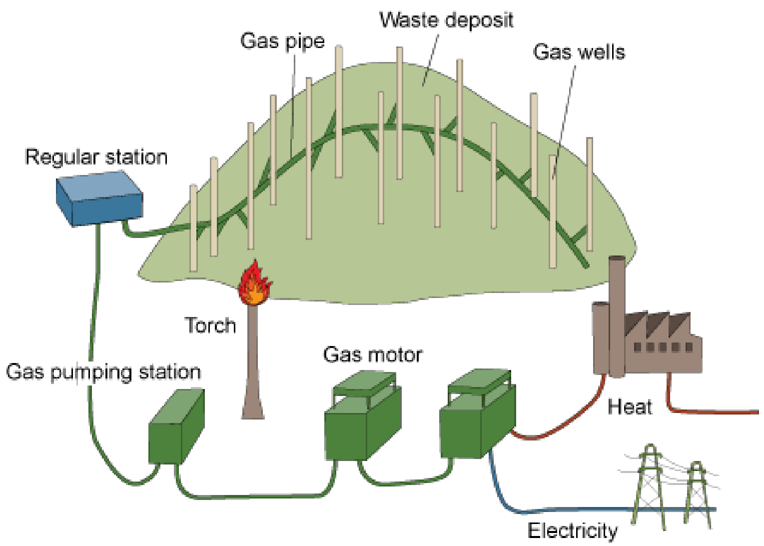
Established waste treatment technologies

Incineration

- Solid organic waste is combusted. Some thermal treatments allow energy capture.
- Solid mass reduction by 95-96%.

Landfill

- Consolidated material buried with mud and other sealing agents to enable chemical, bacteriological, and physical degradation
- Semi-anaerobic conditions lead to production of methane and CO_2
- If captured, landfill gas (methane) from decomposing garbage can be used to produce electricity, heat, fuels



http://vireoenergy.se/landfill-gas

Established waste treatment technologies

Recycling

- Converting waste materials into new materials and objects.
- Available for metals, plastic, paper, glass.

Composting

- Organics undergo a biological decomposition to form a material (compost) that is non-toxic to plant growth.
- By-product of the reaction are CO_2, water and heat.

Material	Energy savings
Aluminum	95%
Cardboard	24%
Glass	5-30%
Paper	40%
Plastics	70%
Steel	60%

Cost-benefit of recycling: energy savings

Alternative waste treatment technologies

Anaerobic conditions and biogas production.

- Adopted for farm waste.
- Can reduce greenhouse gas emissions and can provide a cost-effective source of renewable energy.
- Recovered biogas can be an energy source for electricity, heating or transportation fuel.

Pyrolysis

- Thermal decomposition 200–300 °C occurring in the absence of oxygen.
- Precursor of both the combustion and gasification processes.
- The products of biomass pyrolysis include biochar, bio-oil and gases like methane, hydrogen, carbon monoxide, and carbon dioxide.

Alternative waste treatment technologies

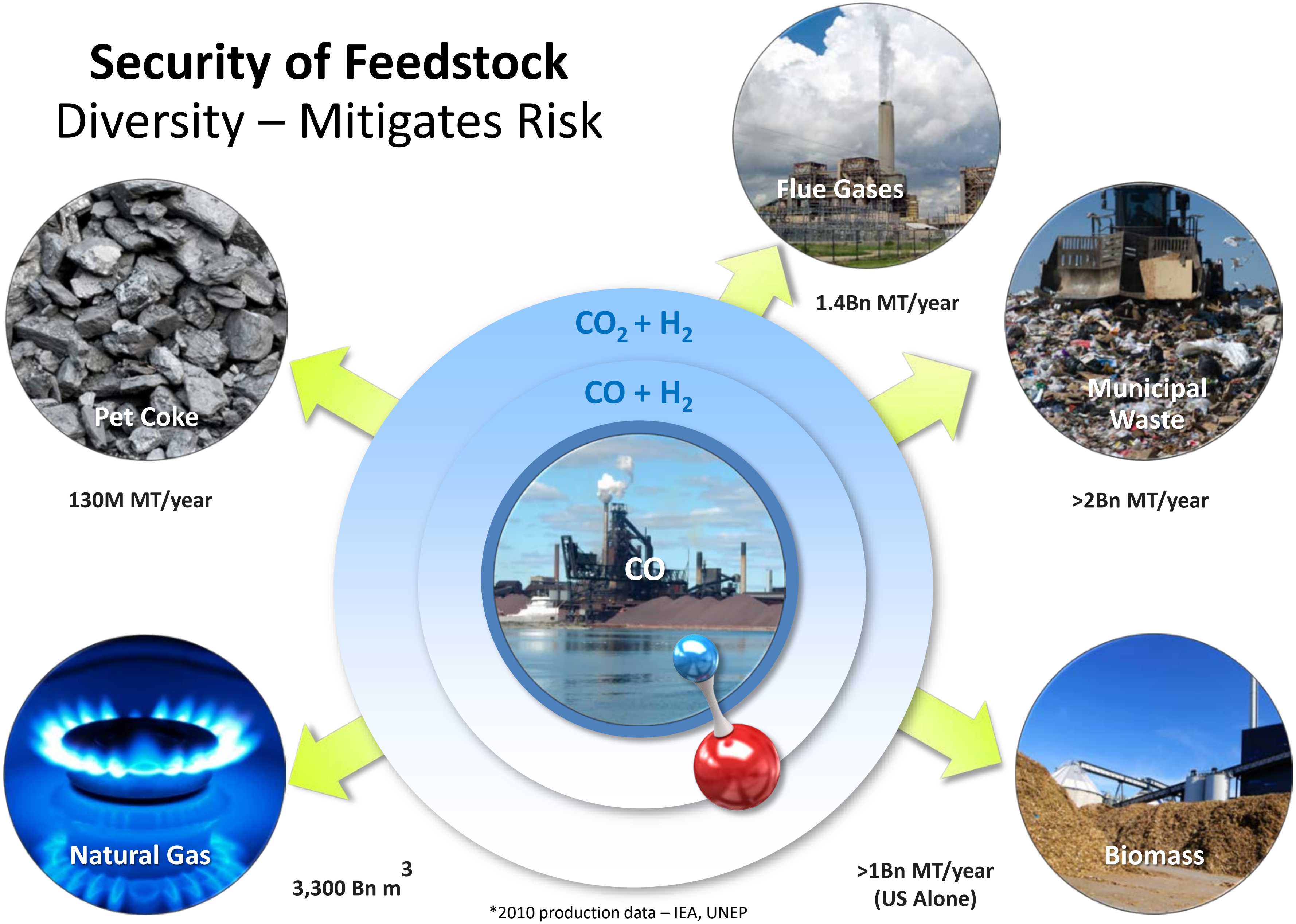
Gasification

- Converts organic based materials into CO, H_2 and CO_2.
- Achieved by reacting the material at high temperatures (>700 °C), without combustion, with a controlled amount of oxygen and/or stem.
- The resulting gas mixture is called syngas.
- Syngas is combustible and often used as a fuel.

Alcohol production (biomass conversion into mixed alcohol fuels)

- Biological/chemical method for converting any biodegradable material into useful chemicals, such as biofuels (e.g., ethanol, propanol, *n*-butanol, isopropanol, 3-pentanol).
- Made by enzymatic breakdown of biomass into simple sugars, followed by yeast fermentation into alcohols.

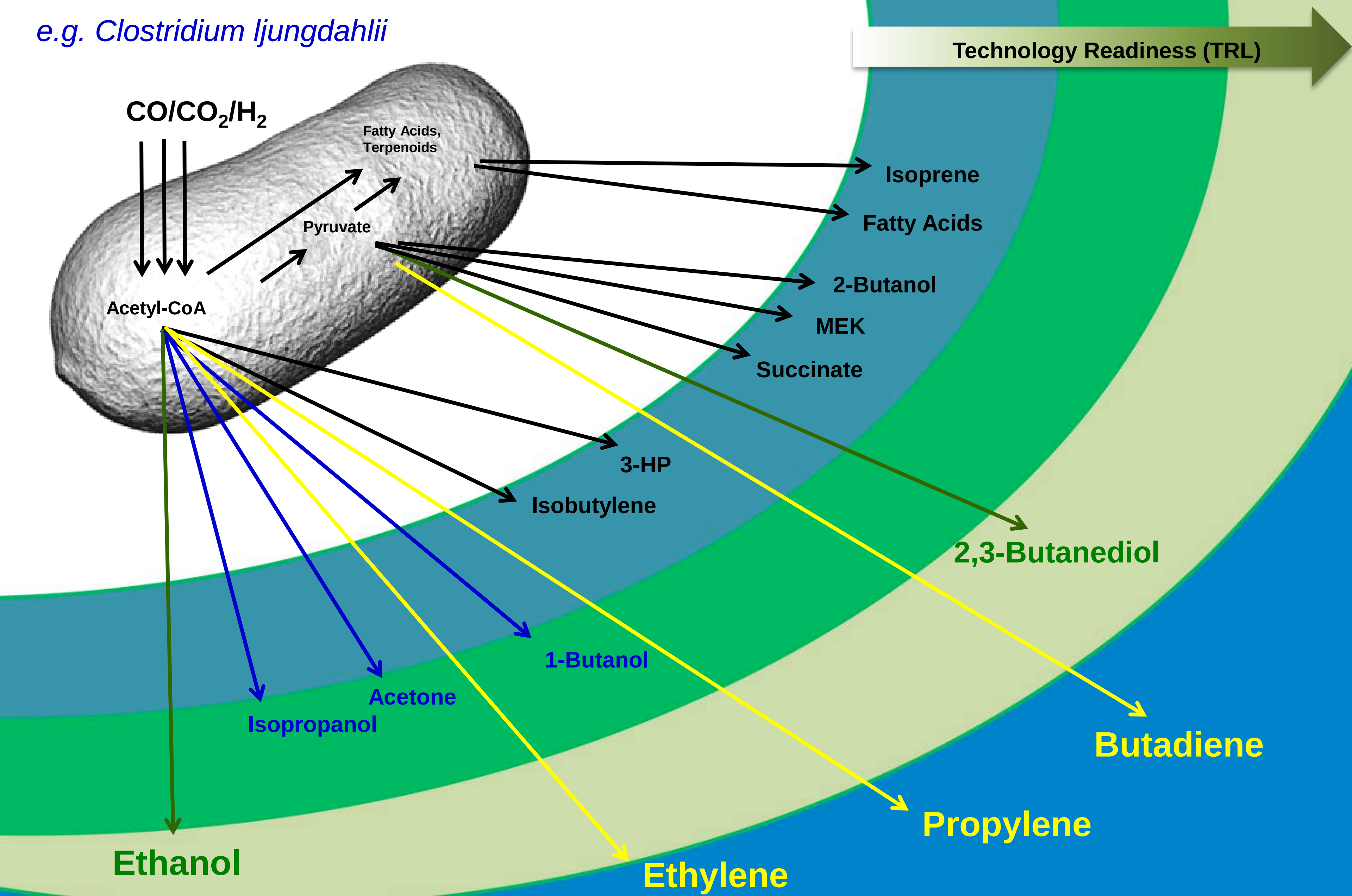
Security of Feedstock
Diversity – Mitigates Risk



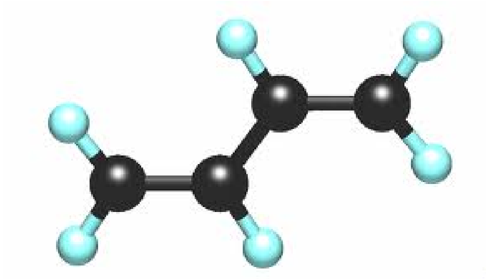
*2010 production data – IEA, UNEP

Gas Fermentation

e.g. Clostridium ljungdahlii



Example – Butadiene



Industrial Impacts

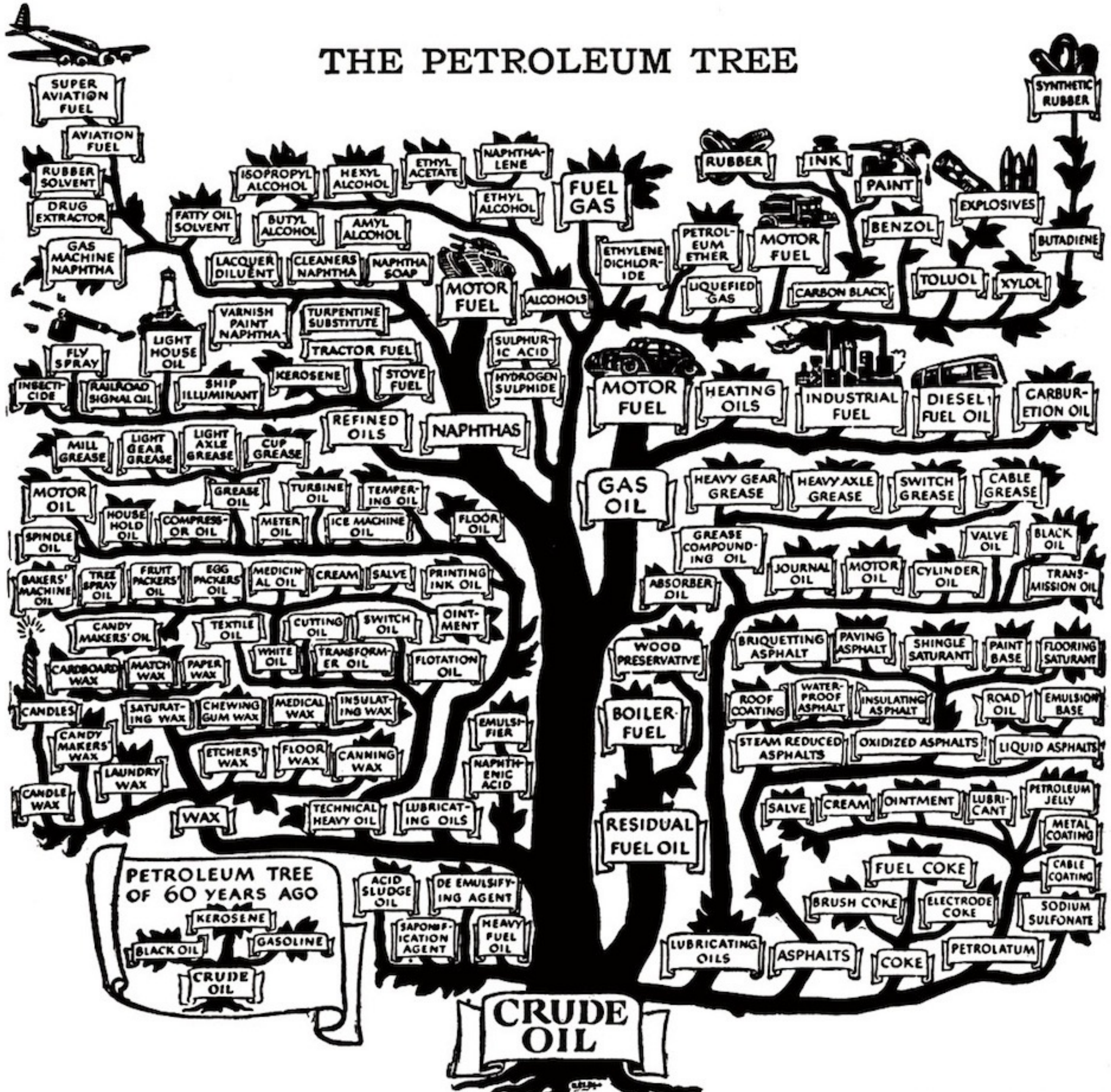
- Bulk & Fine Chemicals
- Pharmaceutical & Biotech
- Green Tyres
- Polymers and Resins (SBR, ABS)
- Electrical Insulators
- Nylon-6,6

$ 40 Bn World Market

Principal Driver – Bio Butadiene – Green Tyres

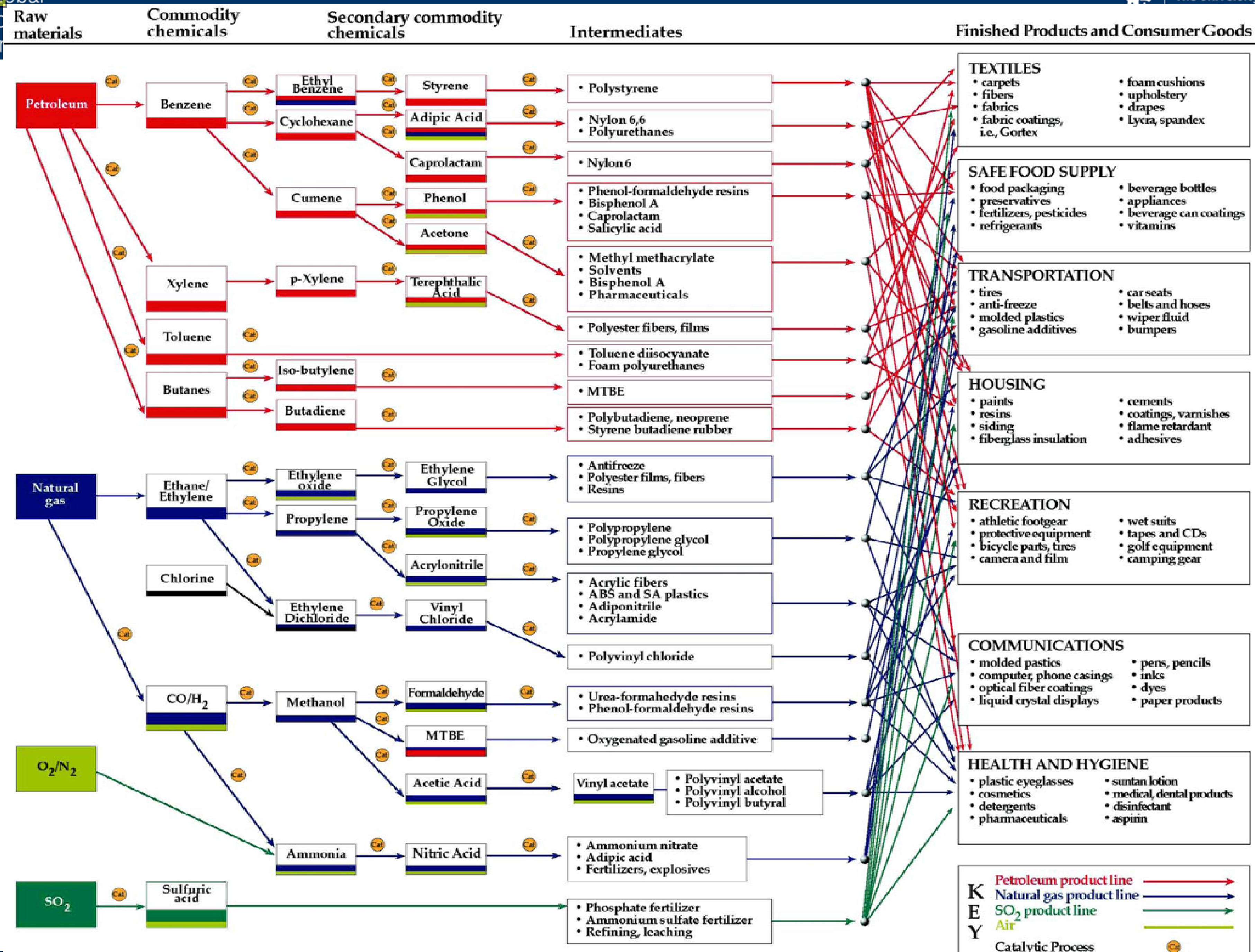
Semi-synthetic Styrene-Butadiene Rubber (SBR) – Green SBR

Butadiene is also key route to green adiponitrile – Green Nylon-6,6



Socony-Vacuum Oil Company

Crude oil has as many by-products as there are leaves on a tree. Sixty years ago, most of them were unknown.



Raw materials
Commodity chemicals
Secondary commodity chemicals
Intermediates
Finished Products and Consumer Goods
Petroleum
Benzene
Ethyl Benzene
Styrene
Polystyrene
Cyclohexane
Adipic Acid
Nylon 6,6
Polyurethanes
Caprolactam
Nylon 6
Cumene
Phenol
Phenol-formaldehyde resins
Bisphenol A
Caprolactam
Salicylic acid
Acetone
Methyl methacrylate
Solvents
Bisphenol A
Pharmaceuticals
Xylene
p-Xylene
Terephthalic Acid
Polyester fibers, films
Toluene
Toluene diisocyanate
Foam polyurethanes
Butanes
Iso-butylene
MTBE
Butadiene
Polybutadiene, neoprene
Styrene butadiene rubber
Natural gas
Ethane/ Ethylene
Ethylene oxide
Ethylene Glycol
Antifreeze
Polyester films, fibers
Resins
Propylene
Propylene Oxide
Polypropylene
Polypropylene glycol
Propylene glycol
Acrylonitrile
Acrylic fibers
ABS and SA plastics
Adiponitrile
Acrylamide
Chlorine
Ethylene Dichloride
Vinyl Chloride
Polyvinyl chloride
CO/H2
Methanol
Formaldehyde
Urea-formahedyde resins
Phenol-formaldehyde resins
MTBE
Oxygenated gasoline additive
Acetic Acid
Vinyl acetate
Polyvinyl acetate
Polyvinyl alcohol
Polyvinyl butyral
O2/N2
Ammonia
Nitric Acid
Ammonium nitrate
Adipic acid
Fertilizers, explosives
SO2
Sulfuric acid
Phosphate fertilizer
Ammonium sulfate fertilizer
Refining, leaching
TEXTILES
carpets
fibers
fabrics
fabric coatings, i.e., Gortex
foam cushions
upholstery
drapes
Lycra, spandex
SAFE FOOD SUPPLY
food packaging
preservatives
fertilizers, pesticides
refrigerants
beverage bottles
appliances
beverage can coatings
vitamins
TRANSPORTATION
tires
anti-freeze
molded plastics
gasoline additives
car seats
belts and hoses
wiper fluid
bumpers
HOUSING
paints
resins
siding
fiberglass insulation
cements
coatings, varnishes
flame retardant
adhesives
RECREATION
athletic footgear
protective equipment
bicycle parts, tires
camera and film
wet suits
tapes and CDs
golf equipment
camping gear
COMMUNICATIONS
molded pastics
computer, phone casings
optical fiber coatings
liquid crystal displays
pens, pencils
inks
dyes
paper products
HEALTH AND HYGIENE
plastic eyeglasses
cosmetics
detergents
pharmaceuticals
suntan lotion
medical, dental products
disinfectant
aspirin
KEY
Petroleum product line
Natural gas product line
SO2 product line
Air
Catalytic Process
Cat

Prevent waste

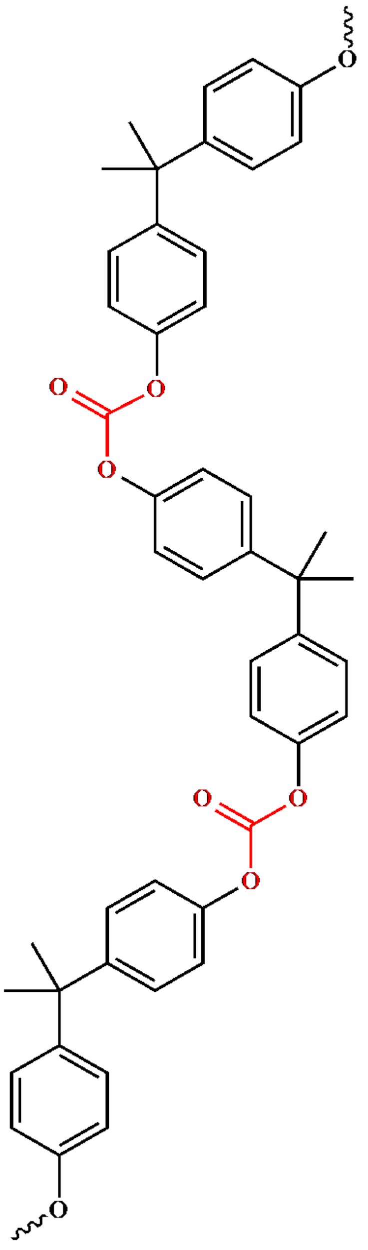
Design products which are biodegradable.

Use a waste as a feedstock for another process.

Waste reducing technology:
CO_2 utilization

CO_2 is a common byproduct (waste) of many reactions. It is also a green house gas. There are technologies which use CO_2 gas as a feedstock.

Carbonate materials – polycarbonate plastic



Carbonate

Newlight Technologies for *AirCarbon:*

Greenhouse Gas Transformed into High-Performance Thermoplastic

- Methane is emitted by natural sources such as wetlands. It is also the second most prevalent greenhouse gas emitted in the U.S. from human activities, such as leakage from natural gas systems and the raising of livestock.
- Newlight *AirCarbon* is a carbon capture technology that combines methane with air to produce to produce polymers at environmentally friendly, ambient conditions.
- This technology allows polymerization beyond previous maximum limits and generate a yield of nine kilograms of polymer for every one kilogram of biocatalyst (9:1) – nine times more material compared to previous technologies.
- The process matches the performance of a wide range of petroleum-based plastics while out-competing on price and it is being used to make bags, cell phone cases, containers, furniture and other products.

Sponsored by Yale-UNIDO Initiative

QUESTIONS?

CENTER *for* GREEN CHEMISTRY
and GREEN ENGINEERING *at* YALE

UNIDO
UNITED NATIONS
INDUSTRIAL DEVELOPMENT
ORGANIZATION