UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

Center For Green Chemistry
and Green Engineering at Yale

beyondbenign
green chemistry education

WEBINAR
Introduction to Green Chemistry

Presenter: Dr. Karolina Mellor

Yale Center for Green Chemistry and Green Engineering

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THE GLOBAL GREEN CHEMISTRY INITIATIVE

MISSION:

To increase the general global awareness and capacities on deployable Green Chemistry approaches for the design of products and processes that advance global environmental benefits throughout their life cycles.

https://www.global-green-chemistry-initiative.com

Brazil Colombia Egypt Serbia South Africa Sri Lanka

Peru* Uganda* Ghana* Rwanda* Ethiopia* FYR Macedonia* Jordan* Kenia*

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* Workshop participants

Welcome to the Introduction to Green Chemistry Webinar

Submit questions at any time during the webinar in the **Control/Chat** box on the **Control Panel**

Kimberly Chapman, B.A.
Administrative Assistant
Center for Green Chemistry and Green Engineering at Yale

Your Instructor: Dr. Karolina Mellor

Program Manager and Green Chemistry Educator at the Center *for* Green Chemistry *and* Green Engineering at Yale

Expertise in green chemistry research translation into educational materials including classes, workshops, publications, case studies, educational games and online certificates.

Received three National Science Foundation (NSF) educational grants.

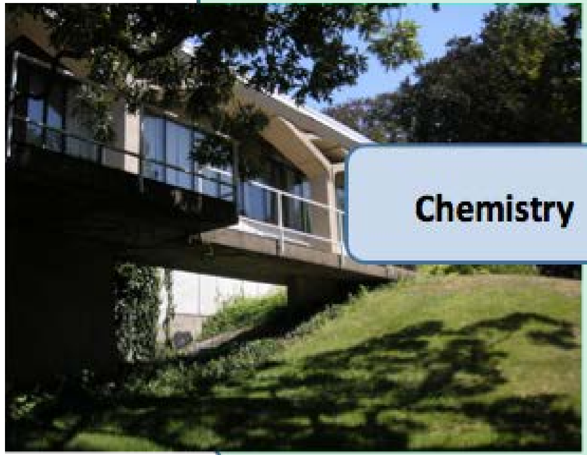
9 years of biotech academic and professional experience –MSc in biotechnology, PhD in molecular biology.

Technology transfer experience.

Currently co-leads operations, outreach and development of the Center for Green Chemistry and Green Engineering.

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

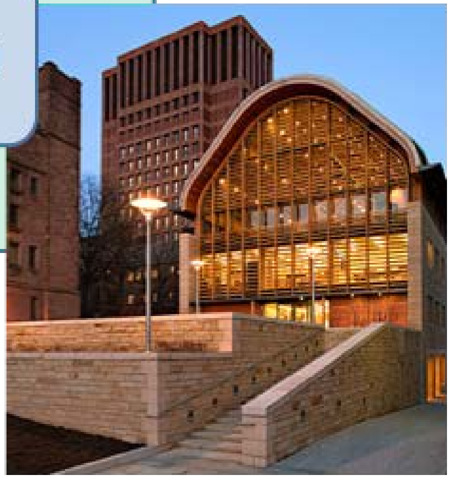
Core researchers



Chemistry

Chemical / Environmental Engineering

Forestry / Environmental Studies



School of Law, School of Medicine School of Management
School of Architecture
School of Divinity

Who is the webinar intended for?

Regulatory bodies, specifically government representatives.

Policy makers, who are now facing pressures to better control risk and provide guidelines to industries that need to be compliant with the international safety standards.

What can you expect to learn?

Benefits of green chemistry which can lead to a more efficient production process, less waste, better product design, and ultimately a healthier economy.

Overview of the science which will range from conceptual framework to social and environmental benefits which are aligned with SDG goals.

Schedule

- Session 1: The need for Green Chemistry (13:00 – 14:00)
- Questions
- Break
- Session 2: Green Chemistry Definition and Principles (14:00 – 15:00)
- Questions
- Break
- Session 3: Areas of Green Chemistry (15:00 – 16:00)
- Questions
- End

Session 1:
The need for Green Chemistry

Everything is a chemical

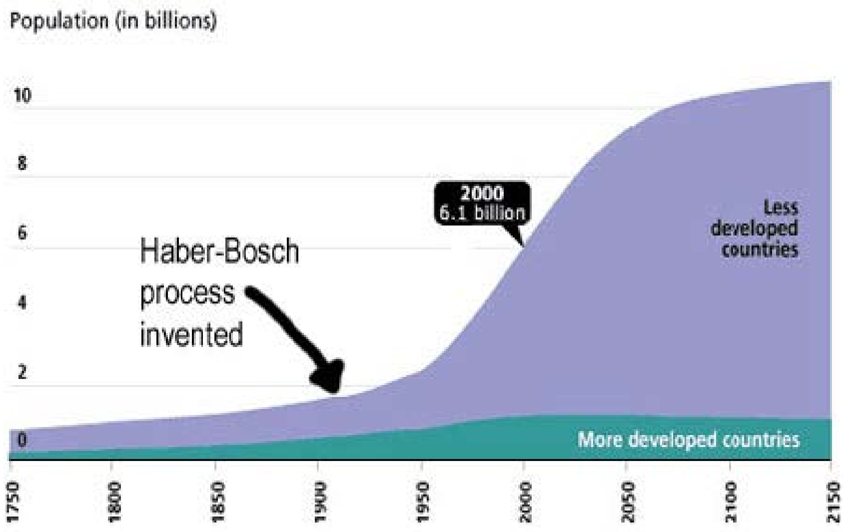
- Name everything in the room that is a chemical
- Name everything in the room that is not a chemical

Chemicals are related to:

- Food
- Transportation
- Communication
- Information Technology
- Economy

Chemicals and Food

- Fertilizers
  - More food can be grown for the population
  - Revolution came with the Haber Bosch process
- Pesticides
  - Mosquitos carrying deadly diseases can be controlled
  - Algal blooms which lead to eutrophication are controlled
- Food preservatives
  - Longer shelf life leads to population spreading to less favorable places



In the early 1900s, the Haber-Bosch process allowed incorporation of Nitrogen from the air and lead to population growth.

Image source: Wikipedia

Chemicals in Transportation

- Gasoline/Diesel
  - Fast ground transportation was enabled
- Jet Fuel
  - Air transportation was enabled
  - Globalization and international trade is possible
- Rocket Fuel
  - Satellites placed on the Earth's orbit allow communication and navigation
- Vulcanized Rubber
  - Tires, shoe soles, hoses and conveyor belts can be made
- Deicing of plane wings
  - Aviation in all conditions is made possible

Apollo 15 launching

Image source: Wikicommons

Chemicals in the Economy

- Chemical industry sector
  - Total pharmaceutical revenue had reached $3.6 trillion in 2019
- Petrochemicals
  - Global market is predicted to reach $958 billion by 2025
- Consumer products
  - Most products that we see, touch, and feel are petroleum based

Why is working towards Green Chemistry so important?

GREEN CHEMISTRY

Chemicals and Unintended Consequences

Chemicals can also negatively impact society.

How?

Unintended Consequences

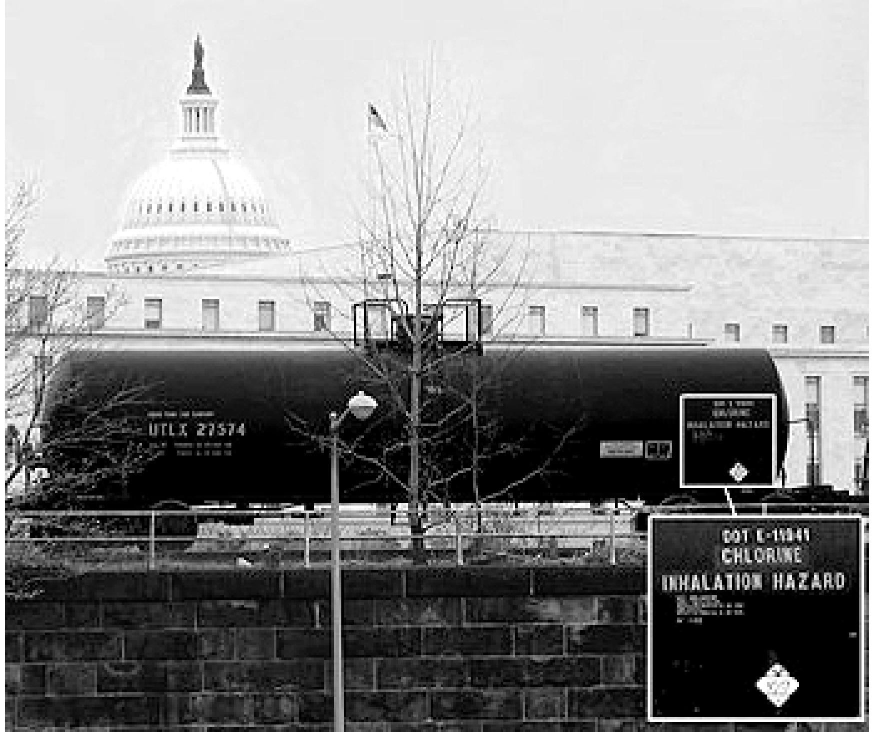
Biofuels made from corn that compete with food, feed, and land use.

Biofuels made from corn.

Image source: Adobe Stock

Unintended Consequences

Purifying water with acutely lethal substances.



Chlorine transported in Washington D.C.

Unintended Consequences

Renewable energy through the use of precious, rare, toxic metals in photovoltaics.

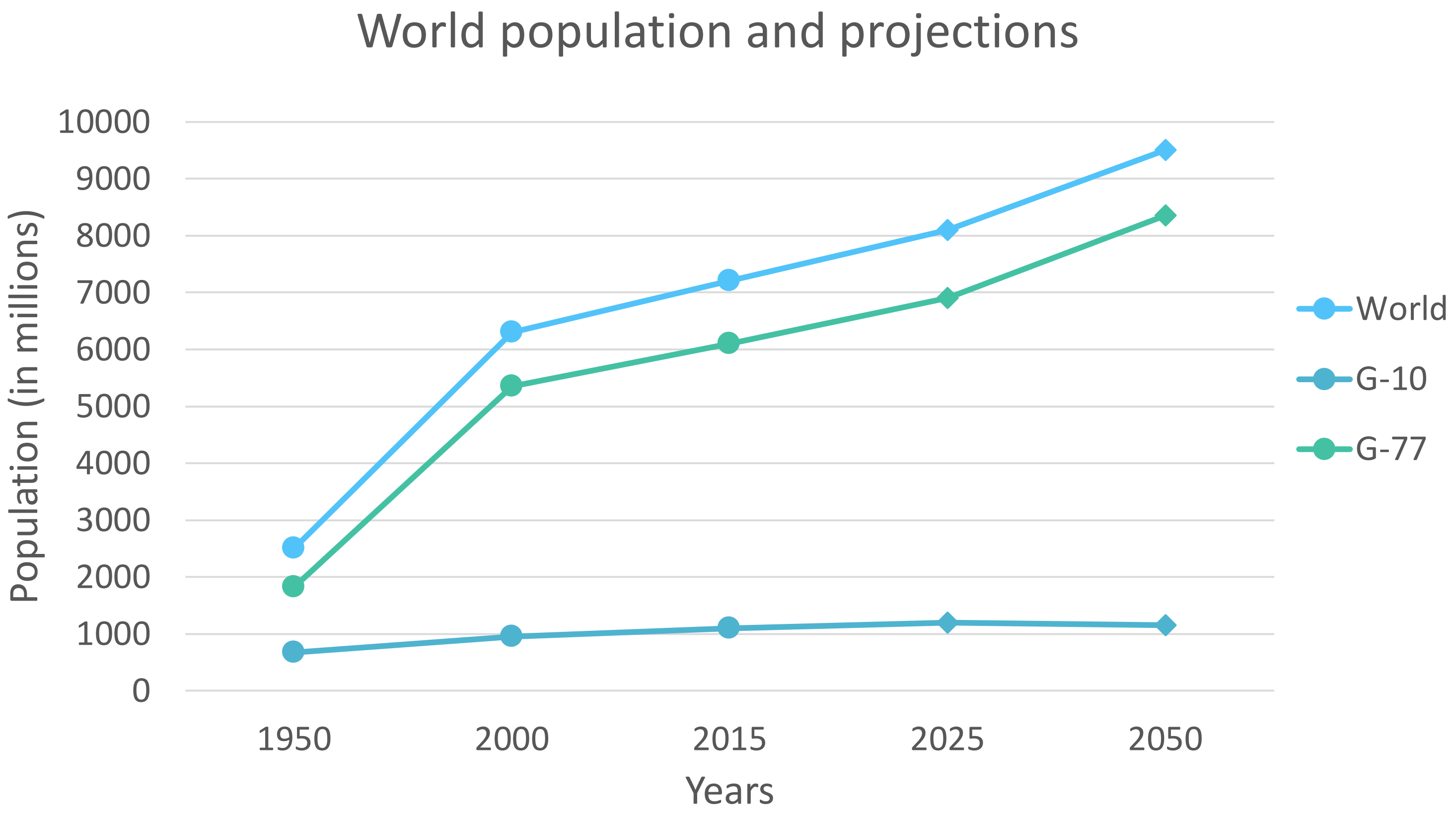
Solar panel installed on the roof of a building

Image source: Wikipedia

Other Environmental Challenges

- Population
- Energy
- Global Change
- Resource Depletion
- Food Supply
- Toxics in the Environment

Population



Source: U.N. World Population Prospects, *2000 Revision*

Population growth in developing countries is predicted to reach 7.8 billion by 2050. G-10 countries remain the same.

Populational challenge: how green chemistry can help

- **The challenge:** How to increase quality of life while minimizing detrimental effects to human health, the environment, and the biosphere
- **The solution:** Green Chemistry and Green Engineering provide a mechanism to address this challenge in very real terms: <u>less dependence on precious resources, tapping into unused or historically undervalued materials</u>

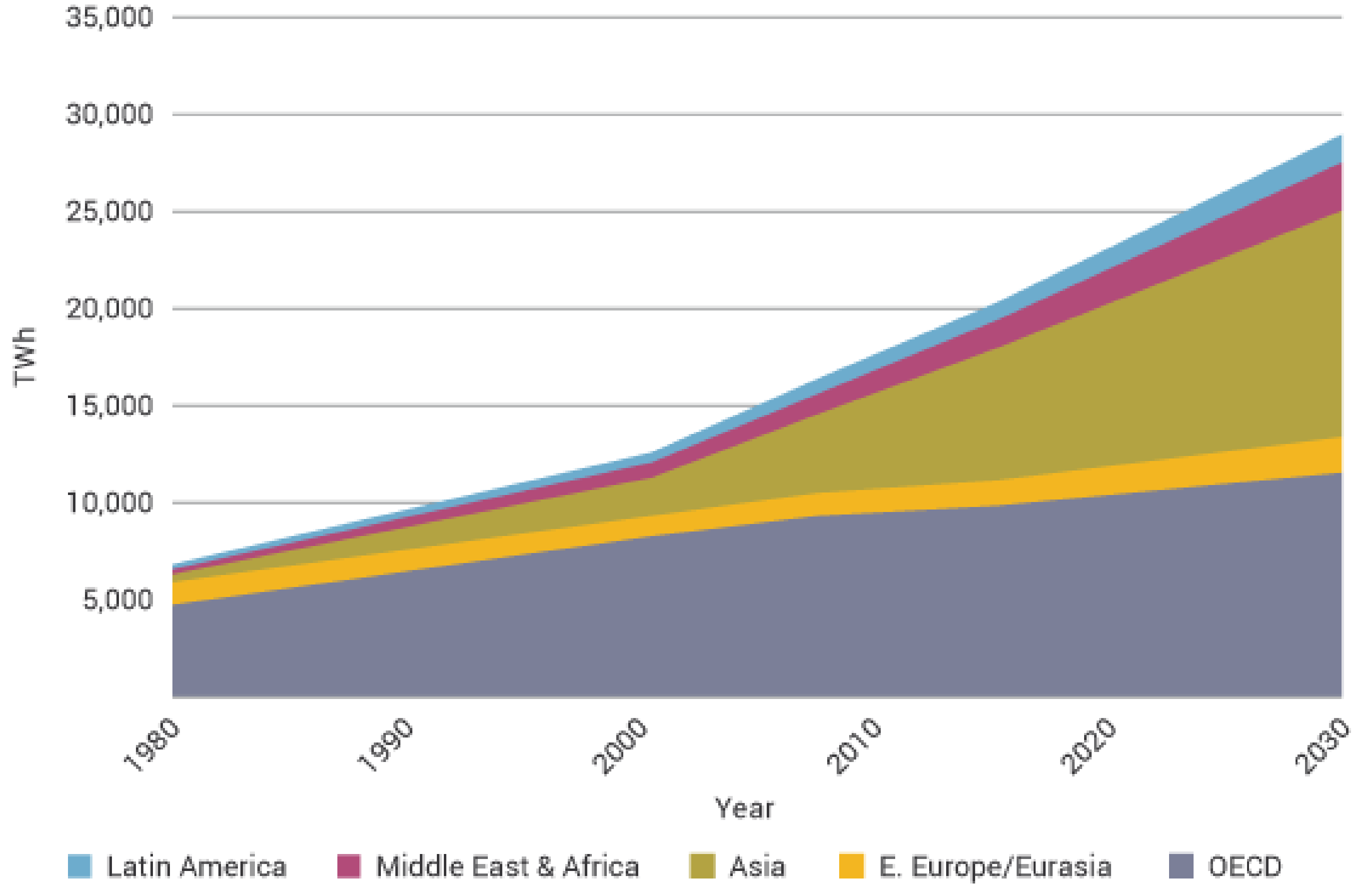
Energy

The vast majority of the energy generated in the world today is from non-renewable sources that damage the environment:

- Carbon dioxide and greenhouse gases
- Depletion of resources
    - Rare earth metals, fossil fuels
- Effects of mining, drilling
    - Contamination of streams, lakes and ground water by fracking fluid or Sulphur ores
- Toxics
    - Separation agents like benzene, toluene and xylene (BTX) which are shown to be carcinogenic.

Growing Energy Consumption

Energy use has approximately doubled in the past 30 years



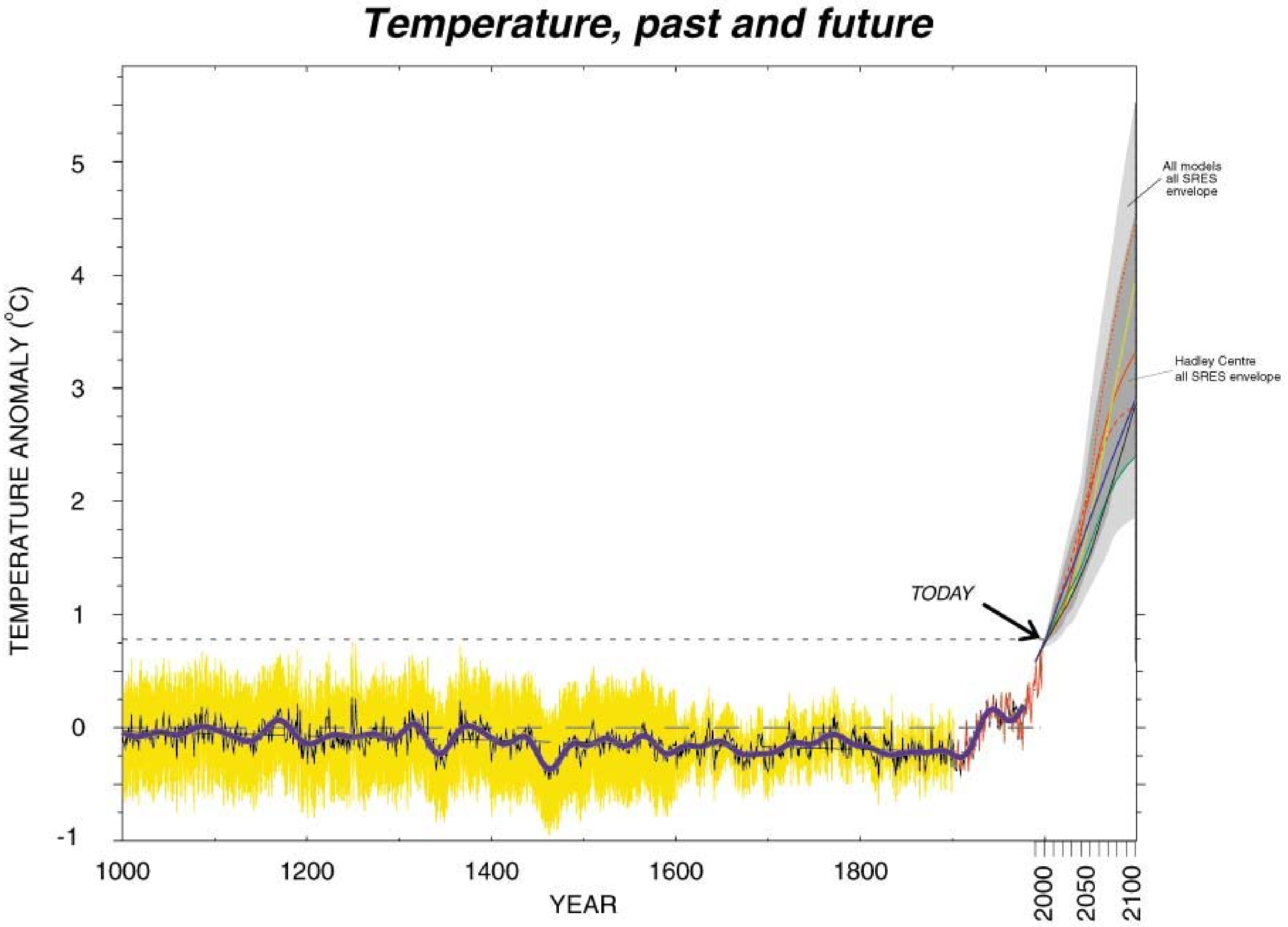
Source: OECD/IEA World Energy Outlook 2009 - Reference Scenario

Energy: how green chemistry can help

Green Chemistry will be essential in both:

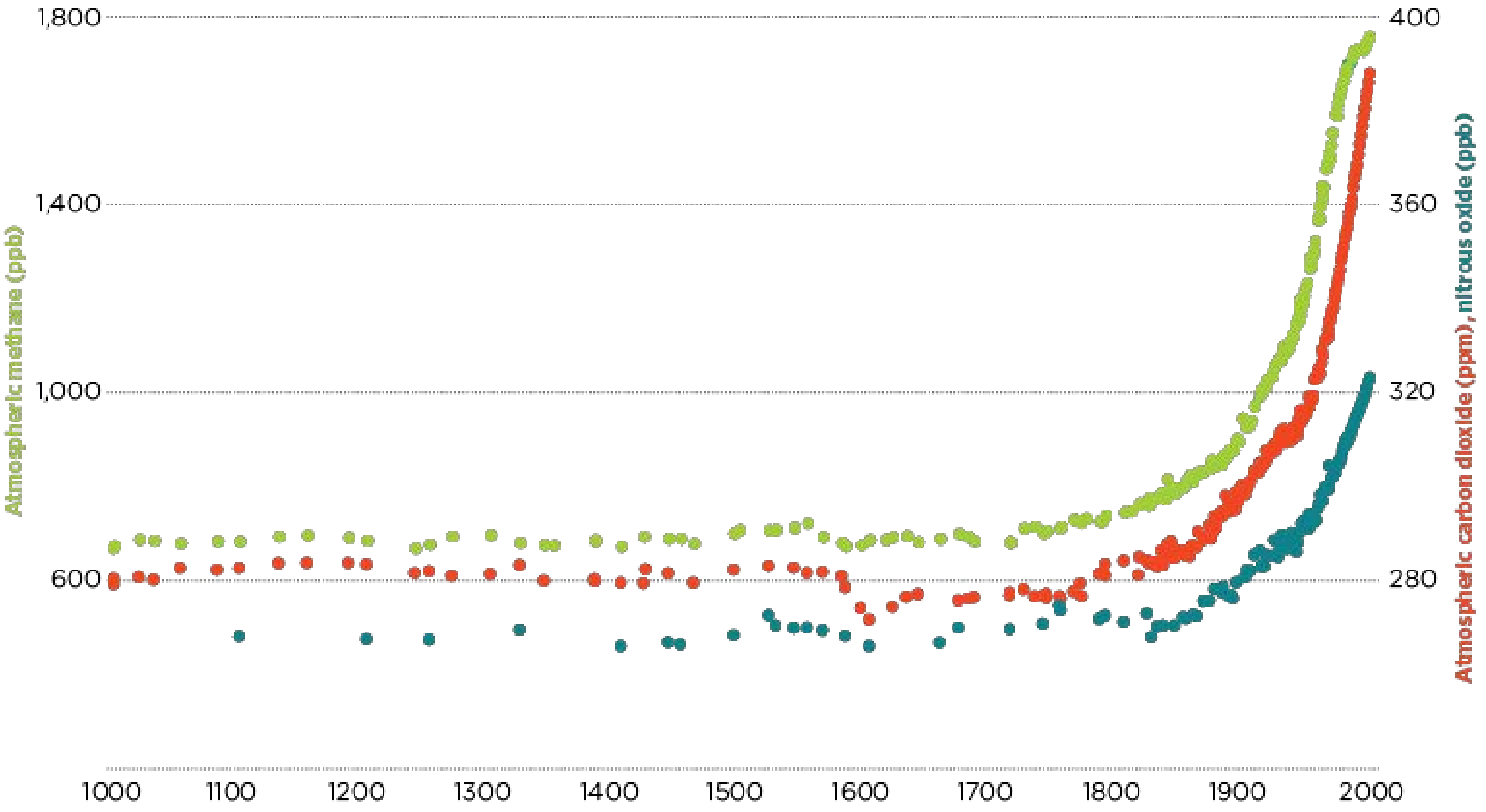
- Developing the alternatives for energy generation (photovoltaics, hydrogen, fuel cells, biobased fuels, etc.)
- Continuing the path toward energy efficiency with catalysis and product design at the forefront

Temperature change



Source: http://www.sustainablescale.org/

Carbon dioxide, methane and nitrous oxide concentrations over the past 1,000 years



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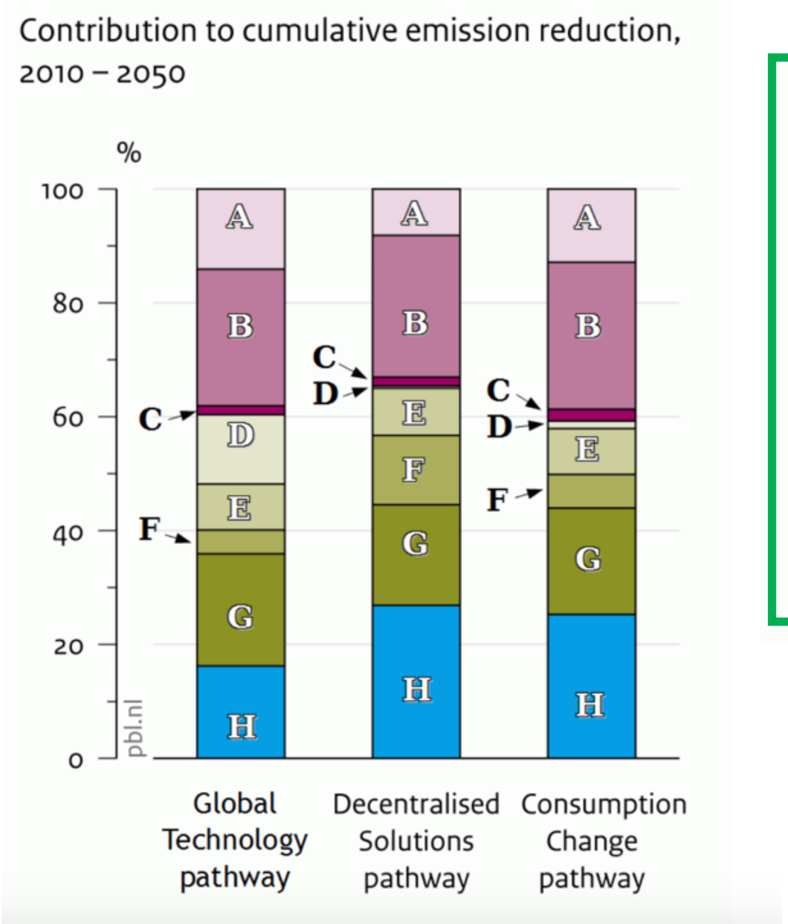
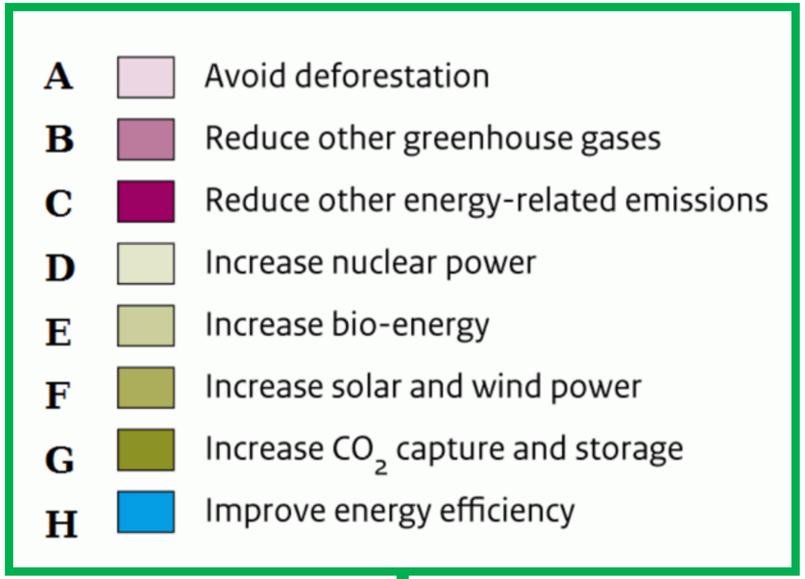
Upsala Glacier - Los Glaciares National Park
Patagonia, Argentina.

Factors involved in Global Warming: Reducing Carbon Emissions





All solutions involve the 12 Principles of Green Chemistry

The graph shows how a 2 °C target might be achieved. The target refers to the goal of limiting global warming. The graph shows three "pathways" to meet the 2 °C target, labelled "global technology", "decentralized solutions", and "consumption change".

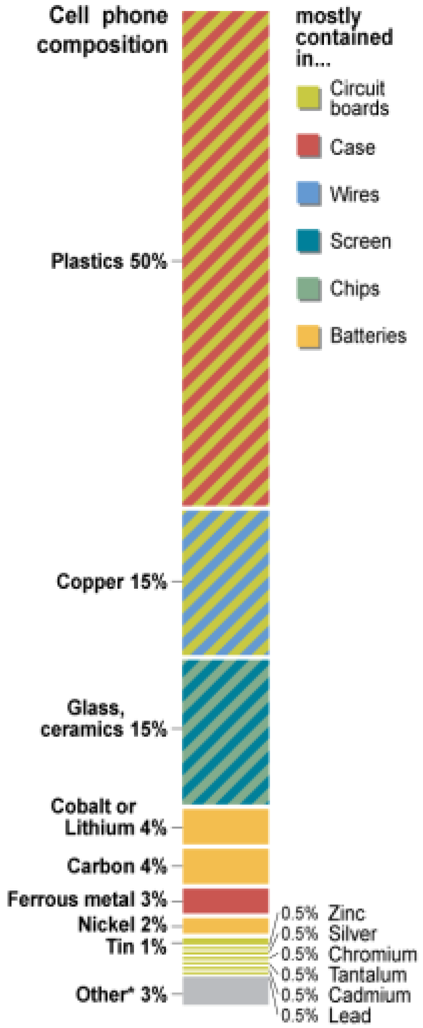
https://commons.wikimedia.org/wiki/File:Limiting_global_warming_to_2_degrees_Celsius_-_options_to_reduce_greenhouse_gas_emissions_(PBL).png

Resource Depletion

Due to the over utilization of non-renewable resources, natural resources are being depleted at an unsustainable rate.

- Examples of depleting resources: precious metals, fossil fuels
- These are used to support of our current life style, economy, etc

Elements in a Mobile Phone?



Roughly 40 different elements

H, Li, Be, C, N, O, F, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Br, Sr, Y, Zr, Ru, Pd, Ag, Cd, In, Sn, Sb, Ba, Ta, W, Pt, Au, Hg, Pb, Bi, Nd.

mobile phone weighing 100 grams, contains

- 13.7 g of copper
- 0.189 g of silver
- 0.028 g of gold
- 0.014 g of palladium

Source: Basel Convention, 2006; Lindholm (Nokia report), 2003


1kg Au
2 m tonnes waste
691,000 litres water
141 kg cyanide
Kalgoorlie gold mine, Australia

Resource Depletion: how Green Chemistry can help

Renewable resources can be made increasingly viable technologically and economically through green chemistry:

- Biomass
  - Algae for fuel, lignin for platform chemicals
- Transformations with visible light
  - Light rather than solvents
- Carbon dioxide as feedstock
  - In plastics
- Chitin as feedstock
  - In packaging
- Waste utilization
  - By biodegradation

Toxics in the environment

Substances that are toxic to humans, the biosphere and all that sustains it, are currently still being released at a cost of life, health and sustainability.

Body Burden

- In 2000-2001 the study showed that human body includes 148 xenobiotic.
- Of the chemicals found:
  - 76 suspect carcinogens in humans or animals,
  - 94 are identified neurotoxins, and
  - 79 are linked to reproductive/developmental toxicity.
- The synergistic effects of these chemicals in combination has not been studied.

One of Green Chemistry's greatest strengths is the ability to design for reduced hazard.

Reducing Costs

Source: iStock

Past & Present State to Environmental Problems

Waste Treatment → Waste Control → Waste Disposal

Past & Present State to Environmental Problems

Waste Treatment → Waste Control → Waste Disposal

Image Source: http://journalrecord.com/tinkertakeoff/2011/07/22/greening-tinker-water-treatment-plant-gushing-about-conservation-effort/

Past & Present State to Environmental Problems

Waste Treatment → Waste Control → Waste Disposal

Lab

Industry Offsite Waste

Image source: Wikipedia Commons

Past & Present State to Environmental Problems

Waste Treatment → Waste Control → Waste Disposal

Treated aqueous waste discharged

Waste Transported to be properly disposed

Image source: Wikipedia Commons and Flickr

Past & Present State to Environmental Problems

Other mechanisms to deal with end-of-pipe problems:

- Continuous pollutant monitoring
- Hazardous waste clean-up

Development of Standards to curb environmental problems:

- Air emission standards
- Release standards to water sources
- Land disposal standards

Past & Present State to Environmental Problems

Other mechanisms to deal with end-of-pipe problems:

- Continuous pollutant monitoring
- Hazardous waste clean-up

Development of Standards to curb environmental problems:

- Air emission standards
- Release standards to water sources
- Land disposal standards

→ **Highly Regulated**

The Cost of Using Hazardous Materials

- Storage
- Transportation
- Treatment
- Disposal
- Regulatory Costs
- Liability
- Worker Health and Safety
- Corporate Reputation
- Community Relations
- New Employee Recruitment

Image Sources: Wikipedia Commons, Public Domain Pictures

But things are changing!

Benefits of Green Chemistry?

The traditional approach to hazards focuses on reducing risk by minimizing exposure.

- For example, wearing personal protective equipment or space ventilation if the chemical is volatile.

Green chemistry focuses on reducing risk by reducing hazard.

- If there is no hazard, exposure becomes irrelevant.

↓Risk = ↓Hazard x Exposure

Green chemistry and engineering focus on reducing risk by reducing hazard.

Green Chemistry Across Industrial Sectors

Defense and aerospace
- Adhesives
- Coatings
- Corrosion, inhibitors

Automotive
- Solvents
- Polymers
- Fuels

Household cleaners
- Surfactants
- Fragrances
- Dyes

Electronics
- Solder
- Housings
- Displays

Agriculture
- Pesticides
- Fungicides
- Fertilizers

Cosmetics
- Builders
- Chelating agents
- Dyes

Pharmaceuticals

Headlines

IT'S NOT EASY BEING GREEN
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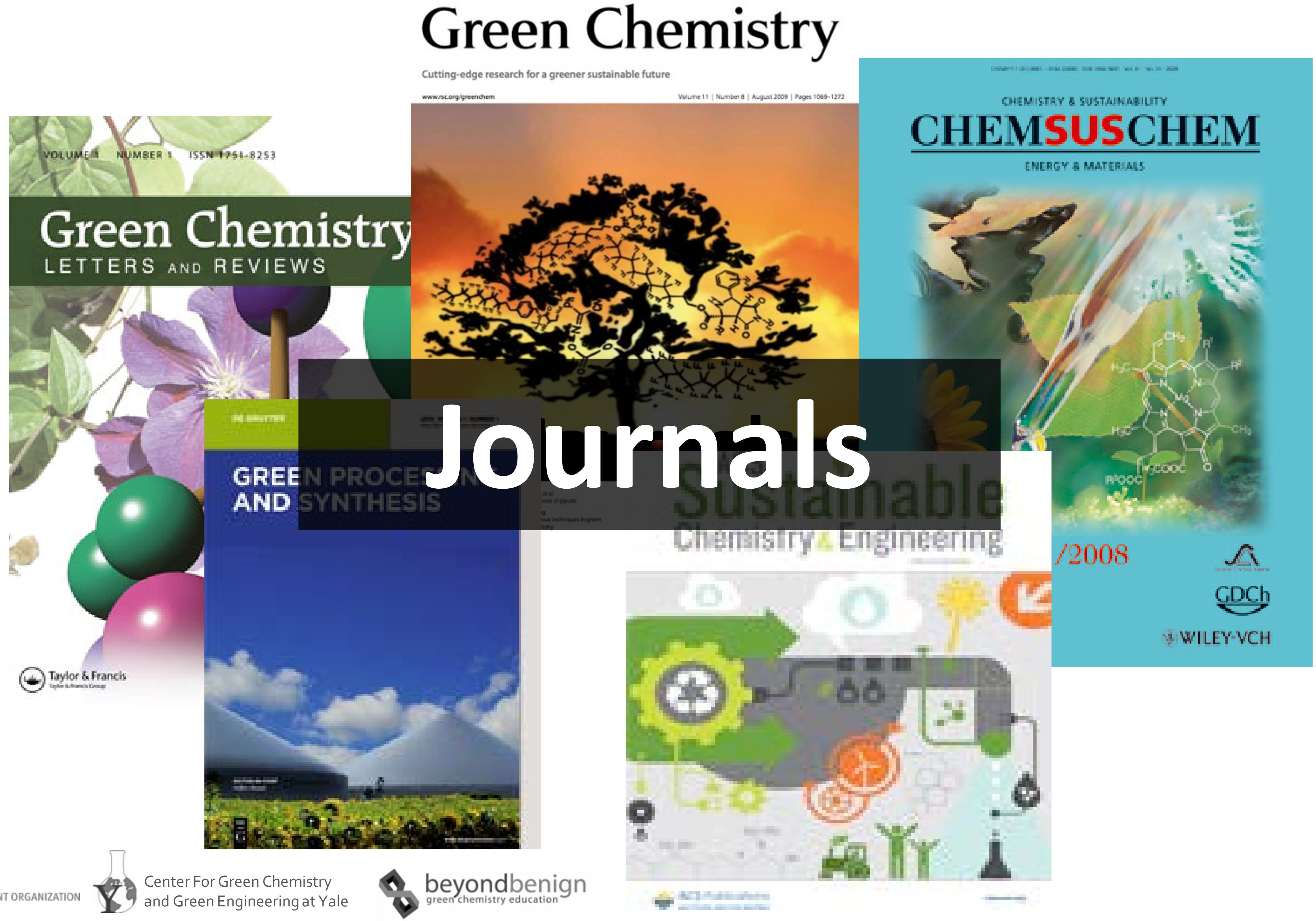
DISCOVER
Health & Medicine | Mind & Brain | Technology | Space | Human Origins | Living World | Environm
Green Chemistry Company Turns Sugar Into an Industrial Chemical
C&EN
CHEMICAL & ENGINEERING NEWS
SERVING THE CHEMICAL, LIFE SCIENCES,
2011 Green Chemistry Awards
Los Angeles Times
Green chemistry
USA TODAY Classifieds:
Posted 11/22/2004 12:25 AM
Green chemistry takes root
By Elizabeth Weise, USA TODAY
Greenwire
EPA: 'Green chemistry' guru charting new course for agency science
(06/20/2011)
Environmental Health News
Published by Environmental Health Sciences
Green Chemistry: Real world solutions for real environmental problems.
npr
CHINADAILY
From fibers to green chem
(China Daily)
Updated: 2011-03-11 08:06
GreenBiz
ntial to Reverse Job Losses
'Green chemistry' movement sprouts in colleges, companies
By SARA GOODMAN, Greenwire
Published: March 25, 2009
E-MAIL

Networks

Conferences

Journals


Green Chemistry
Cutting-edge research for a greener sustainable future
www.rsc.org/greenchem
Volume 11 | Number 8 | August 2009 | Pages 1069–1272
Green Chemistry
LETTERS AND REVIEWS
Taylor & Francis
CHEMISTRY & SUSTAINABILITY
CHEMSUSCHEM
ENERGY & MATERIALS
/2008
GDCh
WILEY-VCH
GREEN PROCESSING AND SYNTHESIS
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Articles

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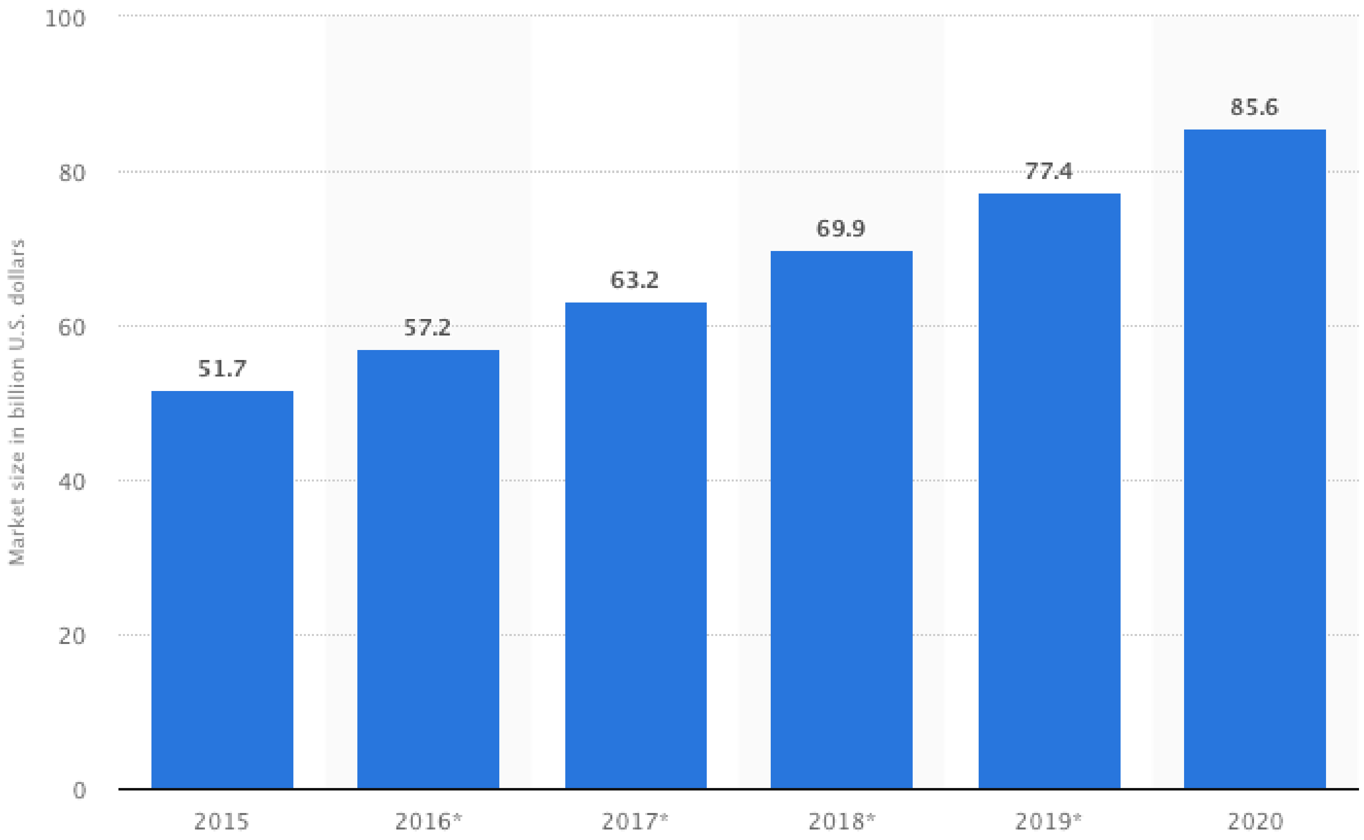
Business

Green Chemistry Market Predictions



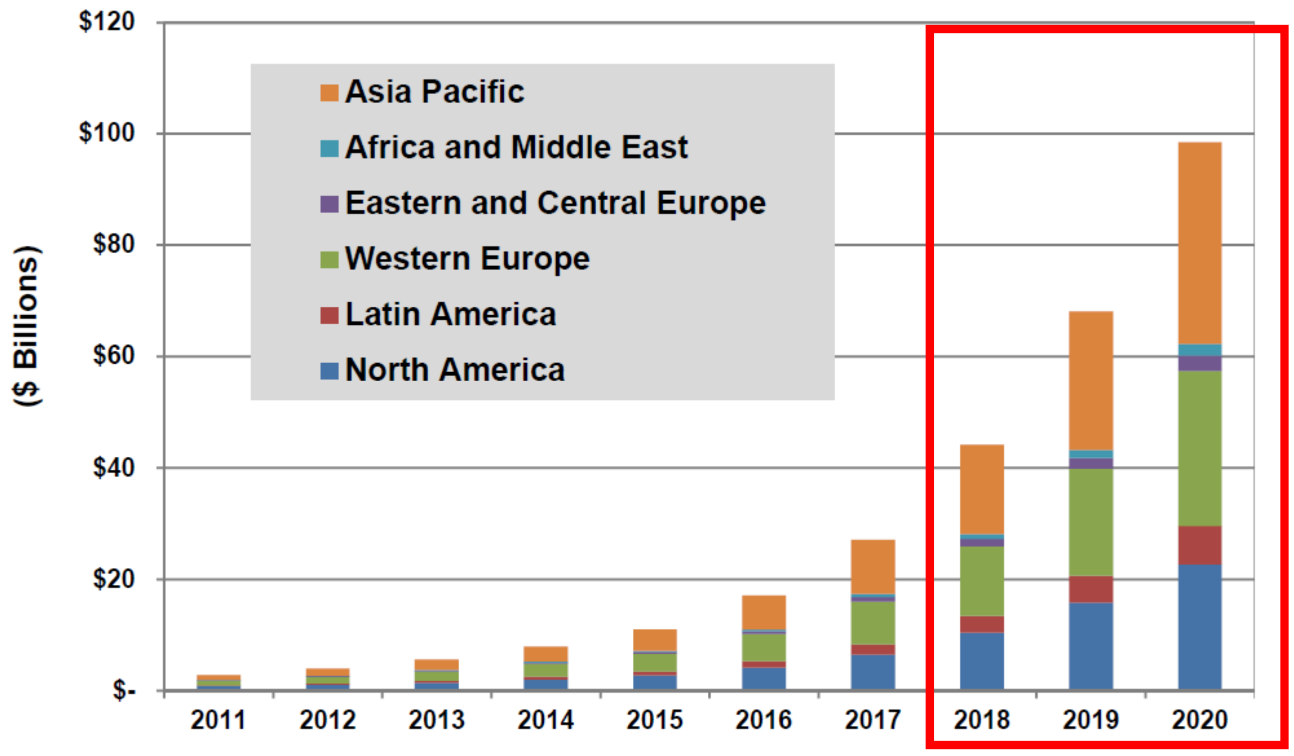
Forecasted market size of the green chemistry industry worldwide from 2015 to 2020 (in billion U.S. dollars).

* Calculated based on the compound annual growth rate (CAGR) of 10.6 between 2015 and 2020, as stated by the source. Figures from 2016 to 2020 are forecasted.

Source: statista.com

Future Growth of Green Chemistry Market

Chart 1.1 Green Chemical Market by Region, World Markets: 2011-2020



(Source: Pike Research)

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PikeResearch Cleantech Market Intelligence

Designing Products with the Intention of Reduced Hazards

One of Green Chemistry's greatest strengths is the ability to design products and processes for reduced hazard.

More specifically, designing for hazard reduction at the discovery phase of future products and process.

Time for Questions

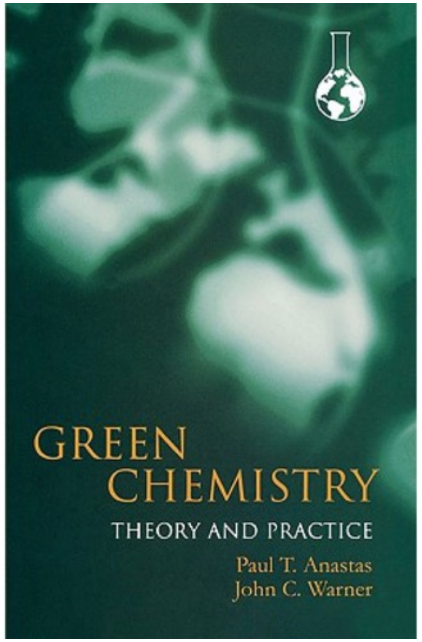
Break

- We will be back shortly!

Session 2:
Green Chemistry
Definition and Principles

What is Green Chemistry?

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

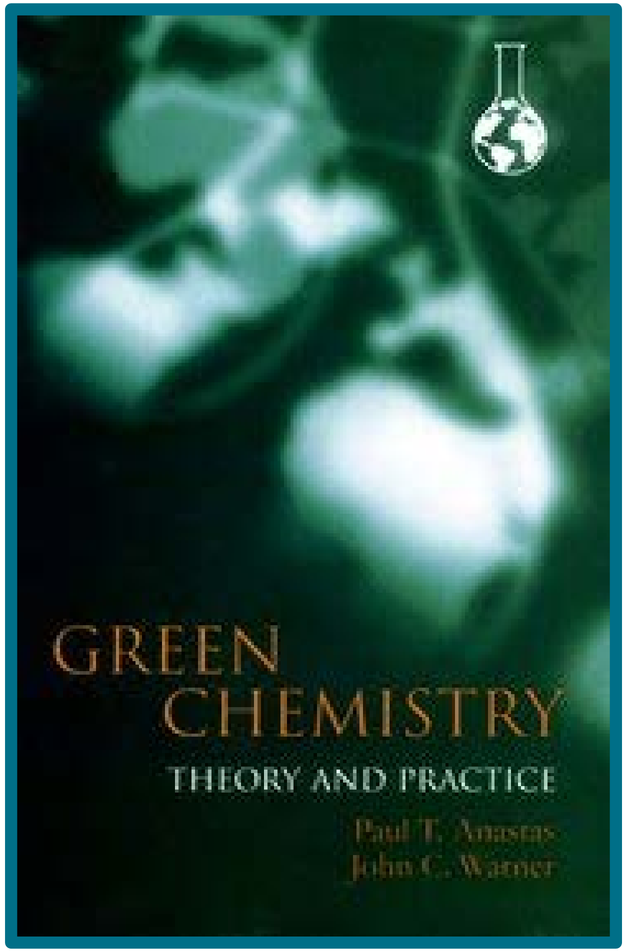


Anastas, P. T., Warner, J. C. (2000). Green chemistry: Theory and Practice. New York; Oxford University Press.

12 Principles of Green Chemistry

The principles address:

- Toxicity
  - Reducing the hazard
- Feedstocks
  - Use of renewable resources
- Designing safer products
  - Non toxic products by design
- Biodegradability
  - Enhancing breaking down at the end of life
- Energy
  - Reducing the energy needs
- Accidents
  - Eliminating accidents
- Efficiency
  - Shorter processes and synthesis



Anastas, P. T.; Warner, J.C. Green Chemistry: Theory and Practice, Oxford University Press,1998

Isn't This How It's Done Now?

Currently:

- Entire industries are geared toward cleaning up after wasteful chemical syntheses
- Today's scientific literature is filled with synthetic pathways that are inefficient in terms of design
- Reagents are seldom selected with regard to hazard
- Industrial chemicals do not have minimal hazard as a performance criterion
- Persistence of chemicals in the biosphere and in our bodies is a major global health issue (250 chemicals are still present since 1945)
- The vast majority of organic chemicals are made by depleting (non-renewable) feedstocks
- Our chemical industry deals with safety through engineering and security through barricades.

Benefits of Green Chemistry?

- The environment: → Products which will biodegrade and won’t persist in the environment
- Human health: → Products with won’t cause toxicity to humans
- The economy: → Novel products which boost competitiveness
- For sustainability: → Products made from renewable resources
- For science: → Fundamental new insights

Benefits of Green Chemistry?

- **A fundamental change of thinking**
- Green Chemistry moves our consideration of how to deal with environmental problems from the ***circumstantial*** to the ***intrinsic.***

Circumstantial		Intrinsic
- Use - Exposure - Handling - Treatment - Protection - Recycling - Costly	→	- Molecular design for reduced toxicity - Reduced ability to manifest hazard - Inherent safety from accidents or terrorism - Increased potential profitability

- Hazard must be recognized as a ***flaw in the designing process***.

The 12 Principles
of
Green Chemistry

1. Waste Prevention

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

$$A + B \longrightarrow P + W$$

Ways to prevent waste?

1. Avoid the generation of W.
2. Find alternatives to A & B to improved overall efficiency of a reaction.

Waste Prevention

Environmental Factor (E-Factor) among the scientific community

Industry sector	Annual production (t)	E-factor	Waste produced (t)
Oil refining	10^6-10^8	Ca. 0.1	10^5 – 10^7
Bulk chemicals	10^4-10^6	<1–5	10^4 – 5×10^6
Fine chemicals	10^2–10^4	5–50	5×10^2 – 5×10^5
Pharmaceuticals	10–10^3	25–100	2.5×10^2 – 10^5

Sheldon, R. *Chem Tech*, 1994, **24**, 38

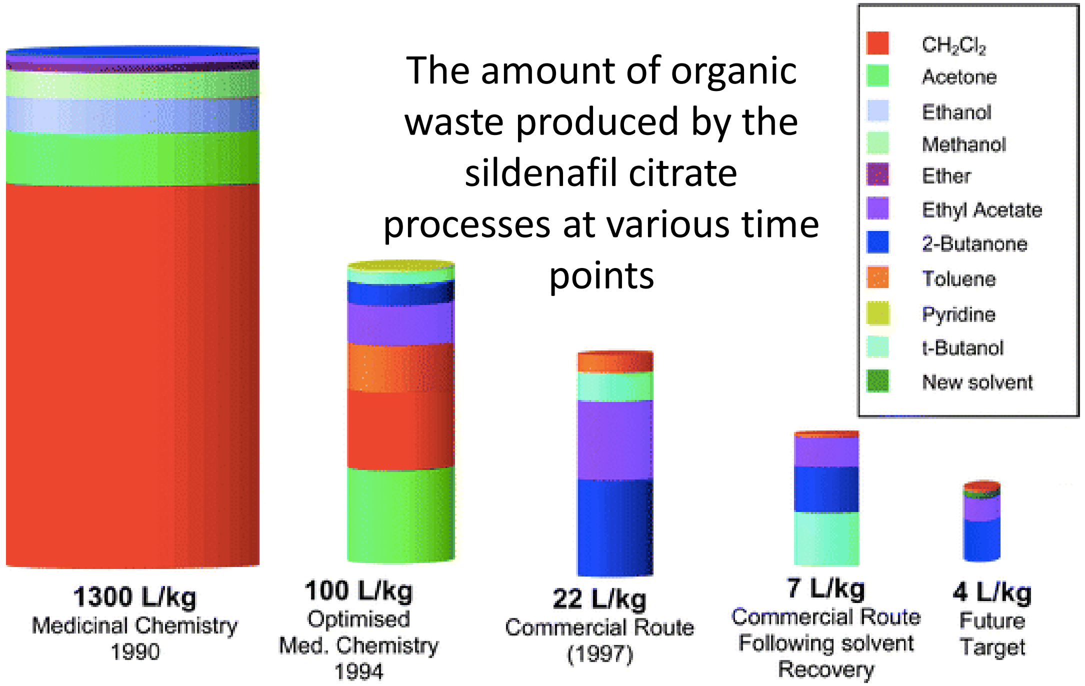
Waste Prevention

Case study: Sildenafil citrate production

Sildenafil citrate, commonly known as Viagra, is a selective inhibitor of phosphodiesterase 5 (PDE5). This new drug immediately became a major seller, achieving sales of more than $1 billion during its first year on the market. With such a rapid sales take off it was critical that the environmental performance of the synthesis was good from the outset.

Conventional sildenafil citrate synthesis included:

- 11 step synthesis, which gave a 4.2% overall yield.
- Tin chloride, a heavy metal and a major environmental polluter.
- The use of stoichiometric quantities of thionyl chloride in a solvent. This has a high environmental impact.
- Hydrogen peroxide, which causes burns upon skin contact and is a fire and transportation hazard, especially when in contact with organic materials.
- Produced over 1300 L of waste per 1 kg of product.



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

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

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

Atom Economy

More Simply…

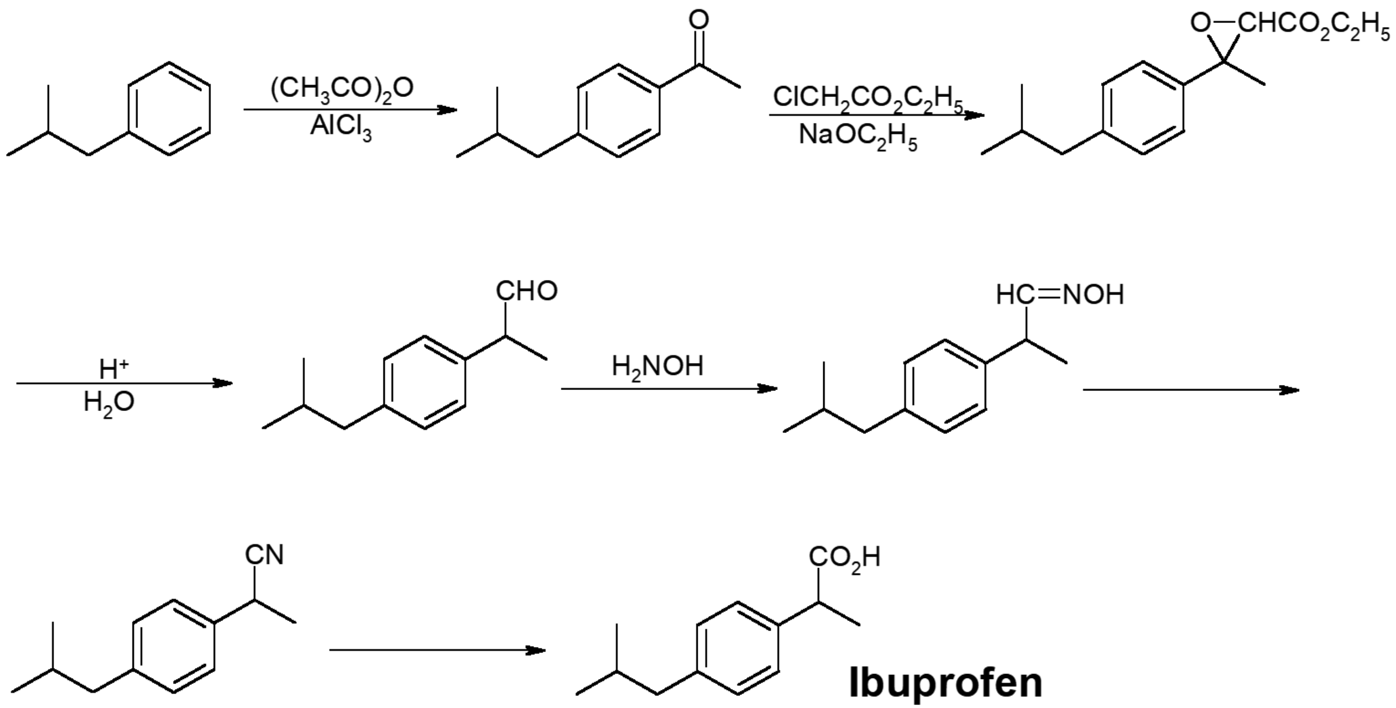
- Ideally all atoms from the reagents are incorporated into a final product.
  - High atom economy ↔ less waste production
- There are no co-products or byproducts in the reaction.
- The molecular waste is therefore reduced.

Atom Economy

Case study: Ibuprofen

Traditional synthesis of ibuprofen was inefficient:

- 6 stoichiometric steps
- <40% atom utilization

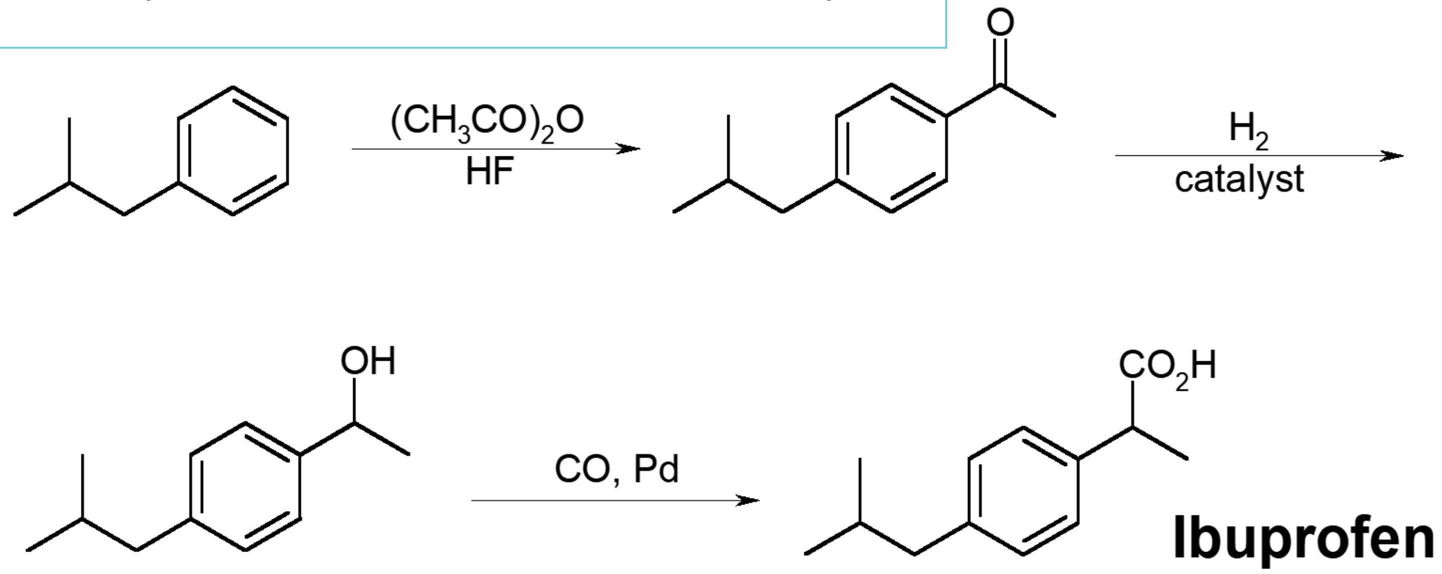


Atom Economy

Case study: Ibuprofen

Catalytic synthesis of ibuprofen using Green Chemistry:

- 3 catalytic steps
- 80% atom utilization (99% with recovered acetic acid)



3. Less Hazardous Chemical Synthesis

Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Less Hazardous Chemical Synthesis

Case study: Paper Bleaching

Conventional paper bleaching with Chlorine dioxide (ClO_2):

- Produces unacceptable quantities of chlorinated pollutants.
- Many of these pollutants are exceptionally toxic.

Alternative technology for paper bleaching with TAML/H_2O_2:

- Alternative catalytic breakdown of H_2O_2 provides the oxidative equivalent.
- Lower temperature and time requirements.

Image: Wikimedia Commons, Author: Sammutawe

Designing Safer Chemicals

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

Designing Safer Chemicals

Hazard types to avoid:

- **Toxicological/Eco-toxicological**
  - Carcinogenicity
  - Reproductive
  - Developmental
  - Neurological
  - Global warming potential
  - Ozone depleting potential
  - Bioaccumulation
  - Persistence
- **Physical**
  - Explosivity
  - Flammability
  - Corrosivity

Physical/Chemical Properties to consider:

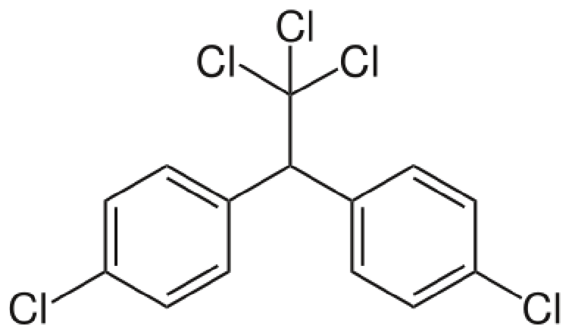
- Water solubility
- Log Kow
- Volatility
- Molar volume
- Aspect ratio
- Radical formation
- Nucleophilicity
- Electrophilicity
- pH/pKa
- Surface area
- Reducing potential
- Oxidizing potential
- Polarizability

Designing Safer Chemicals

Case study: Pesticides

Conventional use of agricultural pesticide and a malarial control agent Dichlorodiphenyltrichloroethane (DDT):

- Carcinogenic.
- The threat to wildlife - especially birds – has almost led to the extinction of a bald eagle population.



DDT

Image Source: http://www.avoidingregret.com/2014/06/photo-essay-eggs-and-nests-of-bird.html

Designing Safer Chemicals

Case study: Pesticides

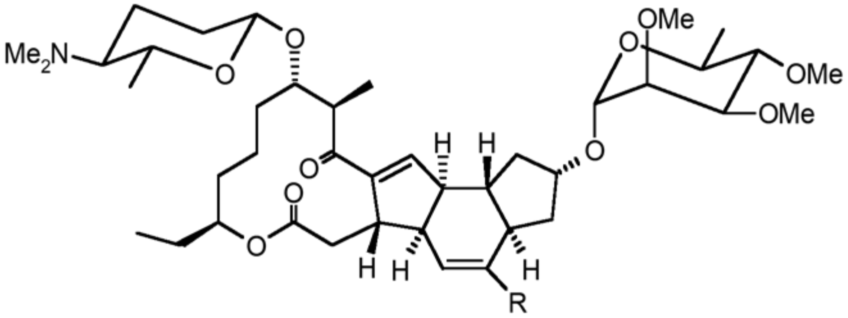
***Alternative (and natural) use of Spinosad* for insect control:**

- Produced by bacteria *Saccharopolyspora spinosa.*
- Isolated from Caribbean soil samples (sugar mill).
- It selectively targets nervous system of insects.
- Demonstrates high selectivity, low mammalian toxicity, and a good environmental profile.

Toxicity scorecard

Rat: LD_{50}>5000 mg/kg
Duck: LD_{50}>5000 mg/kg
Fish: $LC_{50\text{-}96h}$=30.0 mg/L
Bee: LD_{50}=0.0025 mg/bee

Saccharopolyspora spinosa



Spinosyn A: R = H
Spinosyn D: R = CH_3

5. Safer Solvents and Auxiliaries

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

Safer Solvents and Auxiliaries

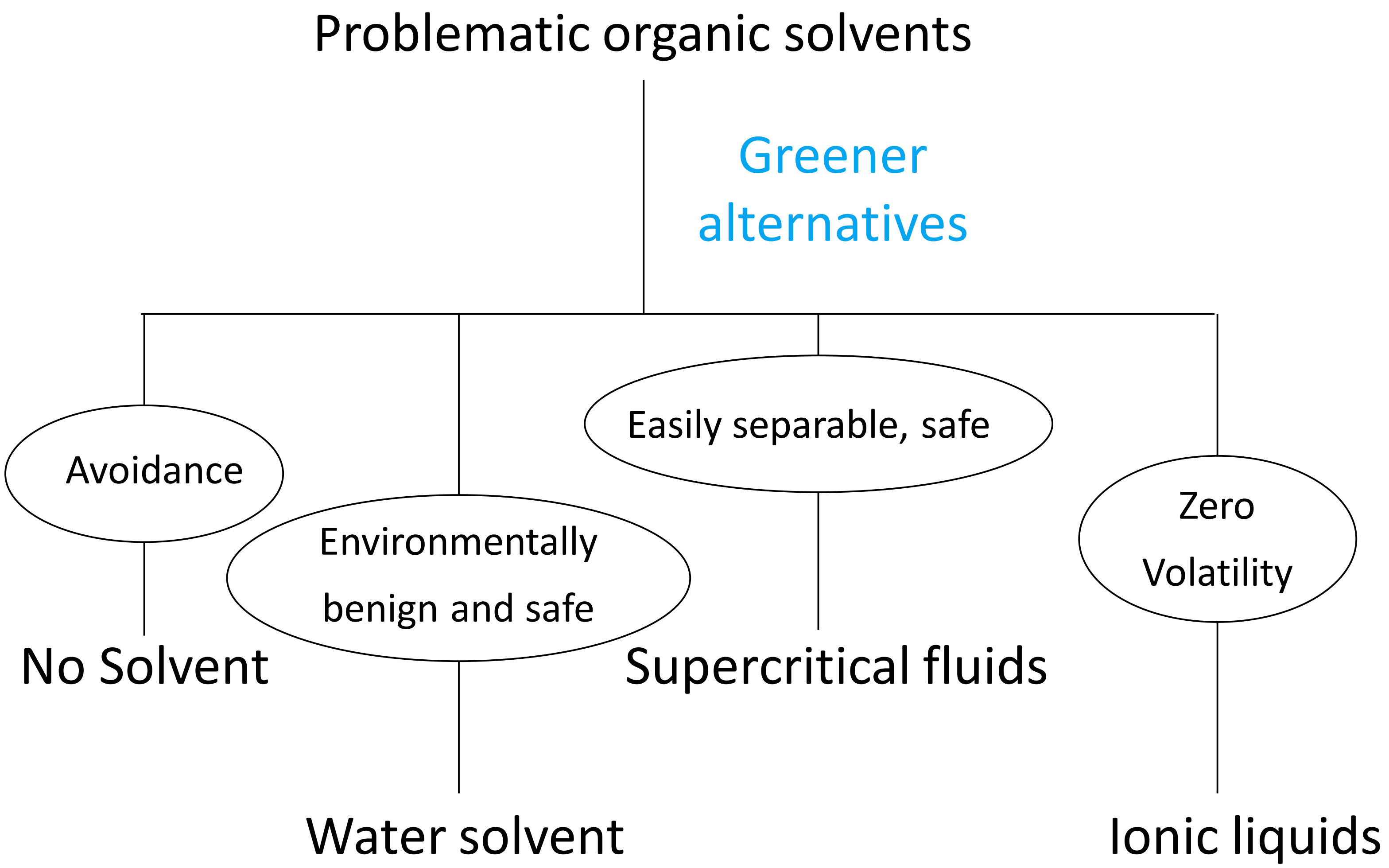
Solvents account for the vast majority of mass wasted in syntheses and processes. Moreover, many conventional solvents are toxic, flammable, and/or corrosive.

Solvents volatility and solubility have contributed to air, water and land pollution, have increased the risk of worker exposure, and have led to serious accidents.

Recovery and reuse, when possible, is often associated with energy-intensive distillation and sometimes cross contamination. In an effort to address all those shortcomings, chemists have started to search for safer solutions.

Image: Adobe Stock

Safer Solvents and Auxiliaries



Safer Solvents and Auxiliaries

Case study: Coffee decaffeination

Conventional method of coffee decaffeination:

- Coffee decaffeination was performed in a chlorinated organic solvent, dichloromethane (DCM), exposure to which can lead to headaches, mental confusion, nausea, vomiting, dizziness and fatigue.
- Coffee beans were heated with steam and then exposed to DCM for decaffeination.

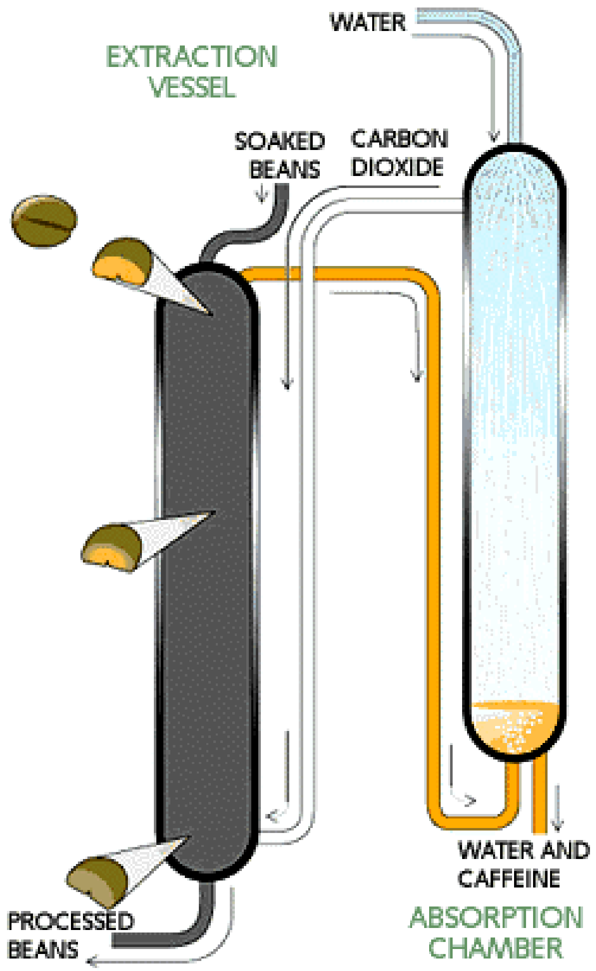
Image: Wikimedia Commons, Coffee Mechanical Separator, Aquapulp

Safer Solvents and Auxiliaries

Case study: Coffee decaffeination

Alternative method for coffee decaffeination:

- Soaking green coffee beans in water doubles their size, allowing the caffeine to dissolve into water inside the bean.
- Caffeine removal occurs in an extraction vessel (70 feet high,10 feet in diameter), suffused with carbon dioxide at roughly 90 °C and 250 atm. Caffeine diffuses into this $scCO_2$. The beans enter at the top of the chamber and move toward the bottom over 5 hours.
- Decaffeinated beans at the bottom of the vessel are removed, dried and roasted.
- Recovery of dissolved caffeine occurs in an absorption chamber. A shower of water droplets leaches the caffeine out of the supercritical carbon dioxide. The caffeine in this aqueous extract is then often sold to soft-drink manufacturers and drug companies. The purified carbon dioxide is recirculated for further use.



Zosel, K. Practical Applications of Material Separation with Supercritical Gases. *Angew. Chem., Int. Ed.* **1978**, *17*, 702-709

6. Design for Energy Efficiency

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.

Design for Energy Efficiency

Most energy is used for heating, cooling, separations and pumping.

Ideally, all reactions are performed at 'ambient' conditions – room temperature and atmospheric pressure – in order to minimize energy usage.

Image: Wikimedia Commons, Janicki Omni Processor Pilot Plant in Dakar, Senegal, Author: Janicki Bioenergy

Design for Energy Efficiency

Sono-, microwave-, and photo-assisted chemistry are known to save energy, improve reaction time, and catalytic activity.

Sonochemistry:

- Uses of high frequency (20-100 kHz) sound waves to promote chemical reaction.
- The collapse of bubbles formed in a solution generates a very high temperature and a higher pressure than conventional heating.
- Used in the production of triglycerides from methyl transesterification.

Microwave:

- Uses a high-frequency electric field to heat or cool the local environment with electrical charges.
- Avoids unnecessarily prolonged residence time at a given temperature.

Photo-assisted:

- Naturally occurring, such as using the sun as a catalyst.
- Used in photo-driven acylation for the production of valuable synthetic intermediates and commercial fragrances in bulk.
- Used by BASF to develop automotive primer coating, a precursor readily able to be crosslinked under photo irradiation, as opposed to its conventional energy-intensive thermally driven variation.

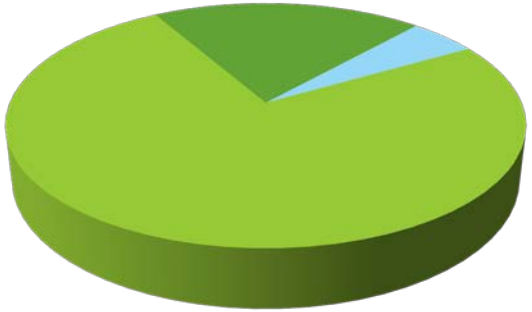
7. Use of Renewable Feedstocks

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

Use of Renewable Feedstocks

Biomass production in nature:
180 billion metric tons/year

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.

Use of Renewable Feedstocks

Case study: Development and commercialization of toners

Conventional synthesis:

- Over 400 million pounds of toner are consumed in the U.S. each year.
- Conventional petroleum-based resin toners are difficult to remove from paper, making paper recycling more intensive.

Image: Wikimedia Commons, Black toner container, Author: Adamantios

Use of Renewable Feedstocks

Case study: Development and commercialization of toners

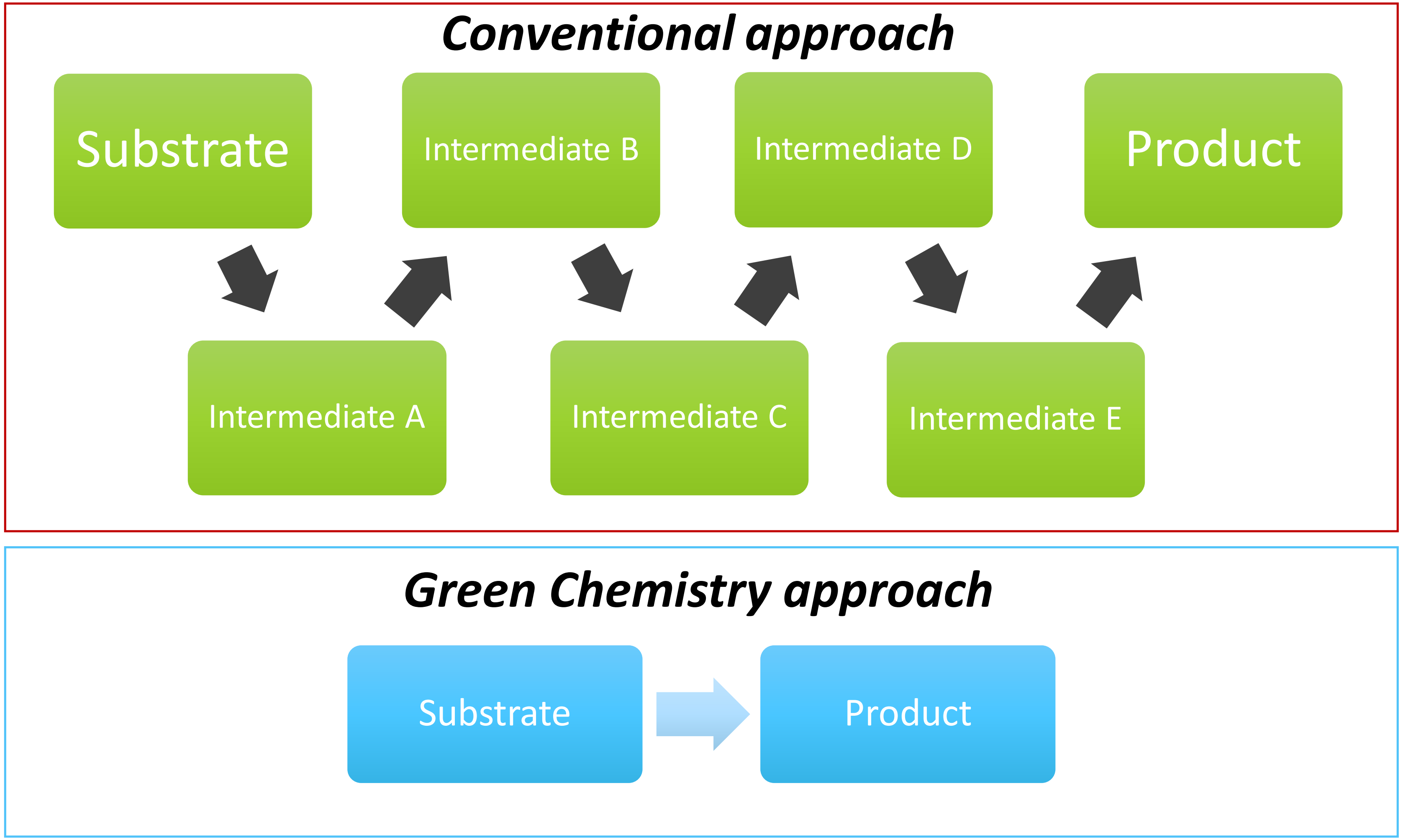
Alternative process:

- The development of a novel, bioderived printer toner that is easier to deink from paper.
- These toners are biobased, derived from soybean oil and corn.
- At 25% market penetration, this technology could reduce CO_2 emissions by 360,000 tons/year.

8. Reduce Derivatives

Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

Reduce Derivatives

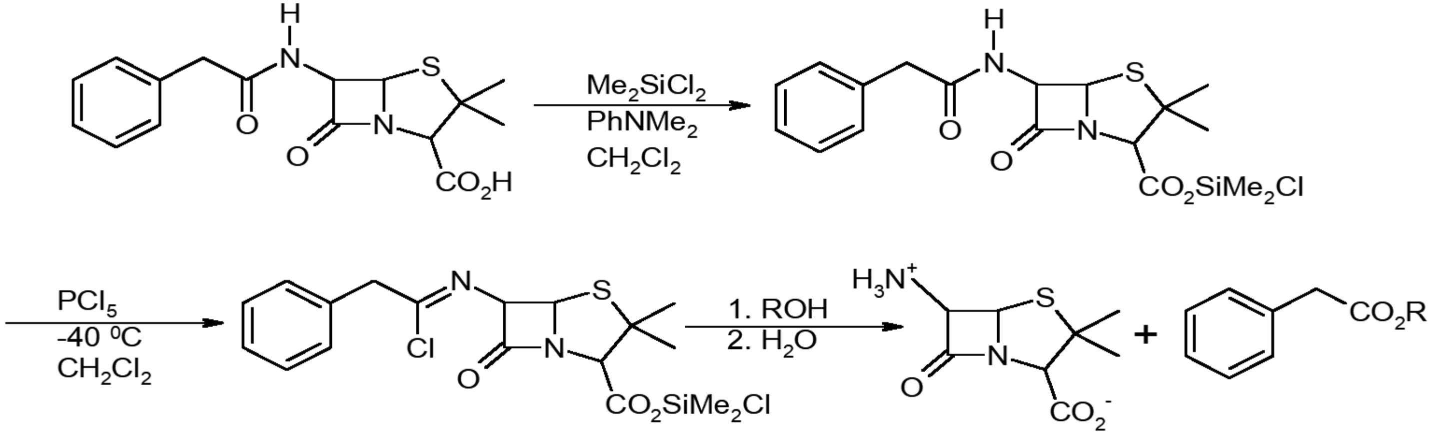


Reduce Derivatives

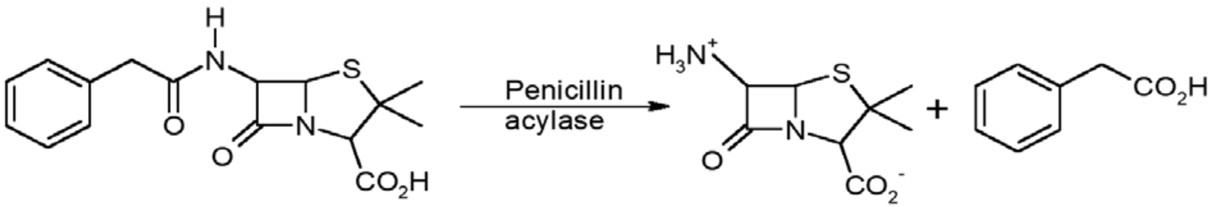
Case study: 6-aminopenicillanic acid

Synthesis of 6-aminopenicillanic acid – core moiety of penicillin

Conventional synthesis of 6-aminopenicillanic acid using 3 steps and intermediate products:



Alternative synthesis using enzyme and fewer derivatives:



9. Catalysis

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

Catalysis

Catalysts can facilitate complex reactions by:

- Lowering the activation energy of the reaction.
- Reducing temperature necessary to achieve a reaction.
- Controlling the site of the reaction (selectivity enhancement).

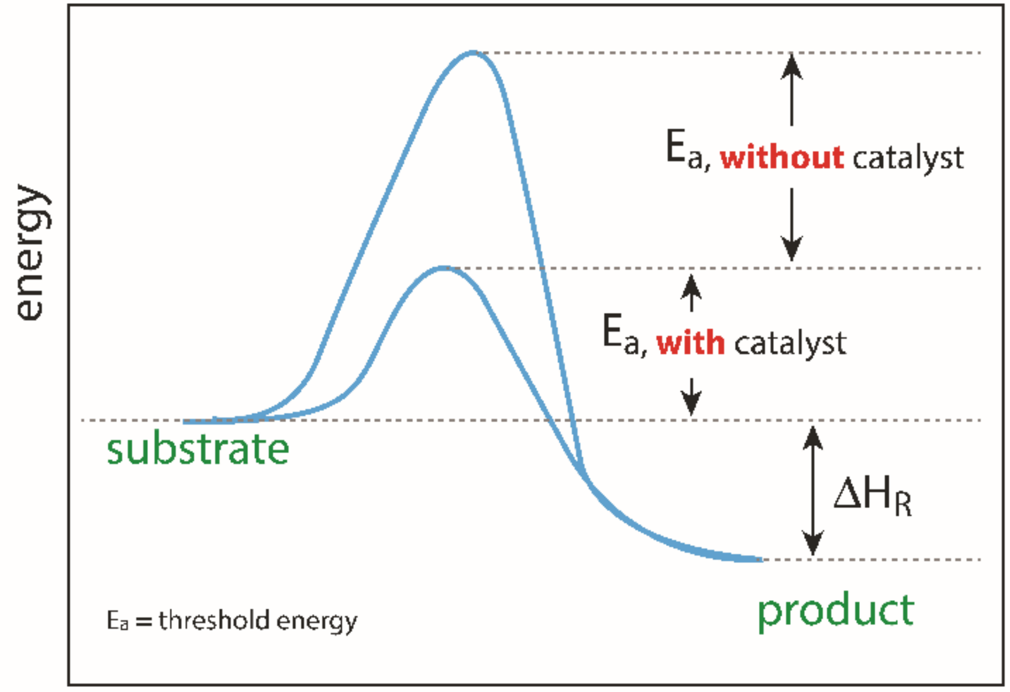


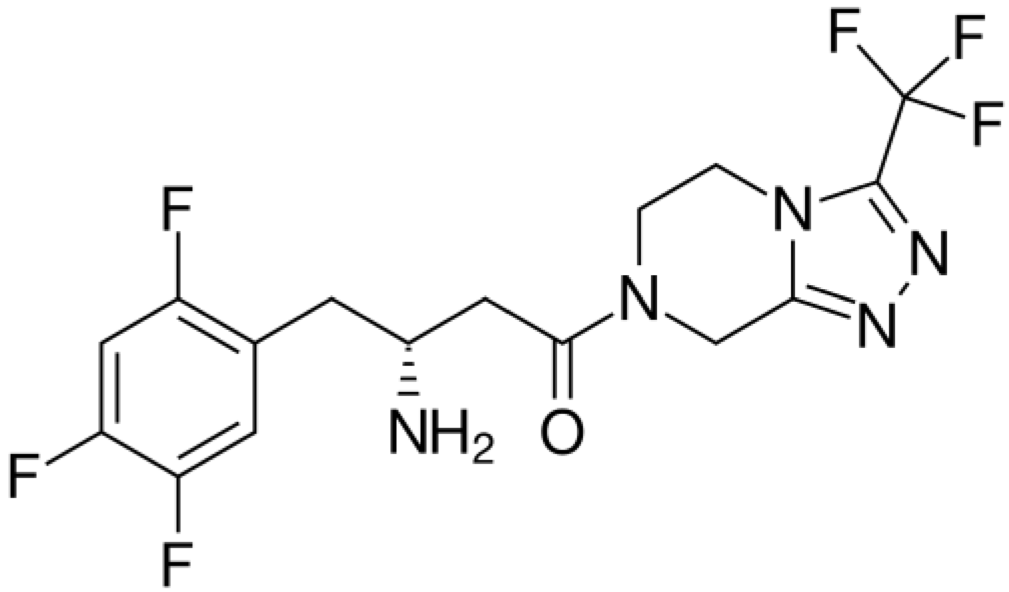
Image source: Adobe stock

Catalysis

Sitagliptin is Merck's top-selling diabetes drug.

Traditional synthesis used high pressure and a heavy metal – rhodium.

The new improved synthesis with enzymes allows for 99.95% selectivity to the desired product and eliminates all heavy metal wastes.



sitagliptin

https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-2010-greener-reaction-conditions-award

Image: Wikipedia, sitagliptin, Author: NEUROtiker

Enzymatic catalysis for plastic degradation

- With specific mutations a PETase properties were improved to degrade plastics. Bacterium in question: *Ideonella sakaiensis* 201-F6

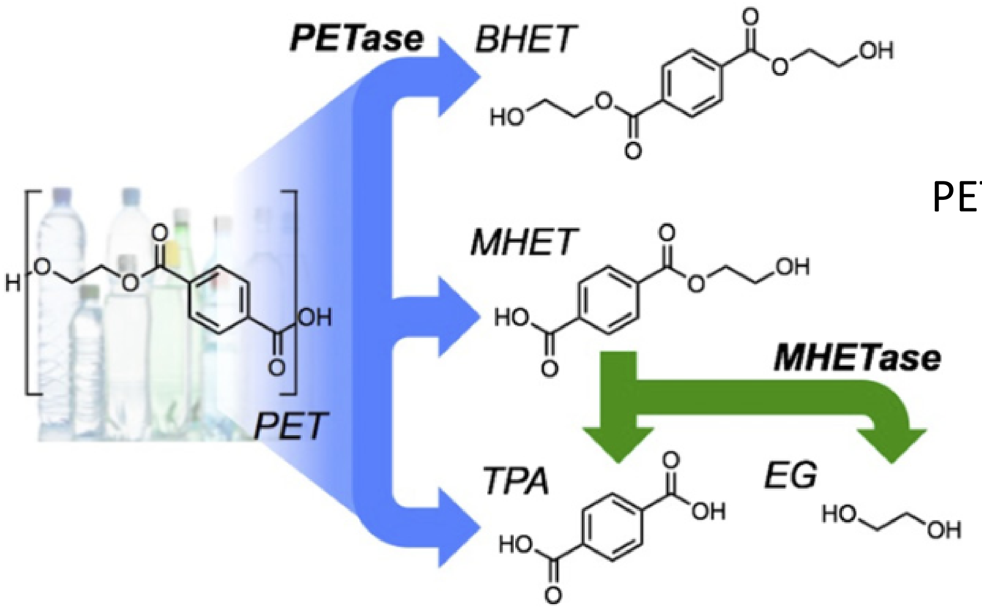
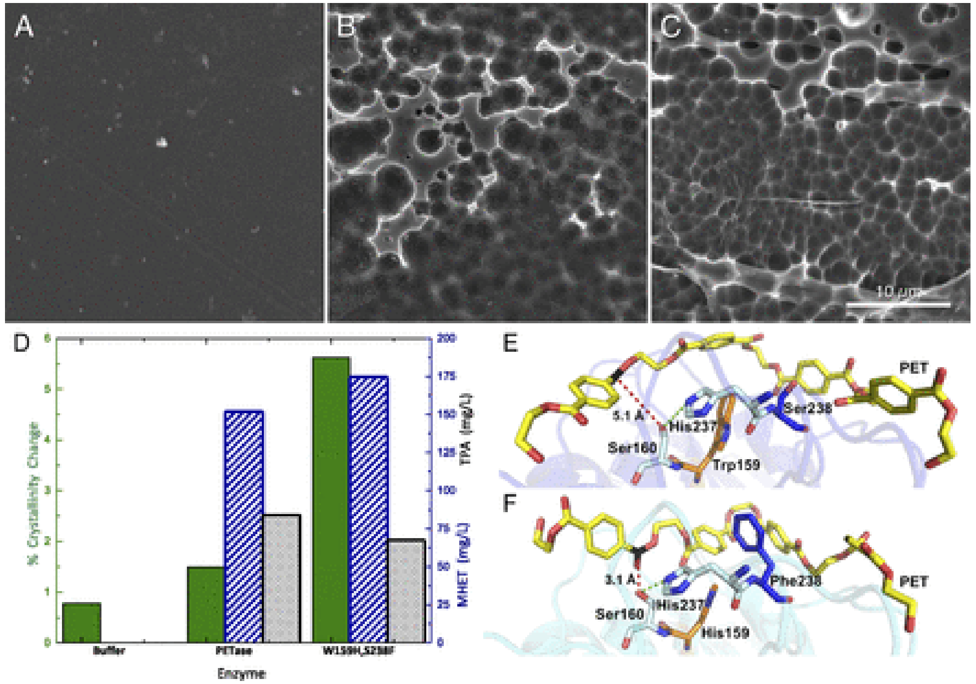


Fig. 1. PETase catalyzes the depolymerization of PET to bis(2-hydroxyethyl)-TPA (BHET), MHET, and TPA. MHETase converts MHET to TPA and EG.

A. No enzyme B. wild-type PETase C. mutant type PETase

PET films



Austin, H. P.; Allen, M. D.; Donohoe, B. S.; Rorrer, N. A.; Kearns, F. L.; Silveira, R. L.; Pollard, B. C.; Dominick, G.; Duman, R.; El Omari, K.; et al. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115* (19), E4350–E4357.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

Design for Degradation

Case study: Fire extinguishers

Conventional approaches:

- Chemical additives or alternatives to water for firefighting applications can have negative long-term environmental and health effects.
- Halon gases are destructive to the ozone layer.
- Aqueous film-forming foams release both toxic hydrofluoric acid and fluorocarbons when used.
- Fluorosurfactant compounds are resistant to microbial degradation, often leading to contamination of groundwater supplies and failure of wastewater treatment systems.

Image: Wikimedia Commons, Author: Caduser2003

Design for Degradation

Case study: Fire extinguishers

Alternative production:

- The development of a fire extinguishing foam that is nontoxic and highly biodegradable.
- PYROCOOL F.E.F. (Fire Extinguishing Foam) is an alternative formulation based on a biodegradable surfactant.
- PYROCOOL F.E.F. has a low application volume.
- Extinguishing an oil tanker fire estimated to take 10 days can be put out in 12.5 minutes.

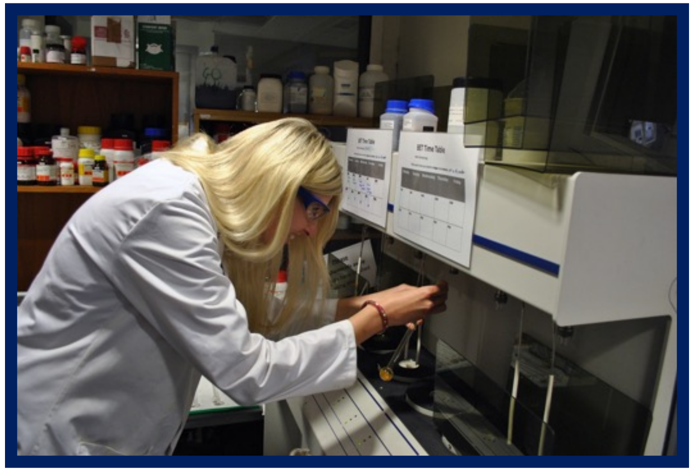
Image: Wikimedia Commons, Kyrgyz Republic firefighters, Author: Senior Airman Brett Clashman, U.S. Air Force

11. Real-time Analysis for Pollution Prevention

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

Real-time Analysis for Pollution Prevention

Real time analysis for a chemist is the process of "checking the progress of chemical reactions as it happens".



Knowing when your product is "done" can save a lot of waste, time, and energy.

Image sources: Flickr

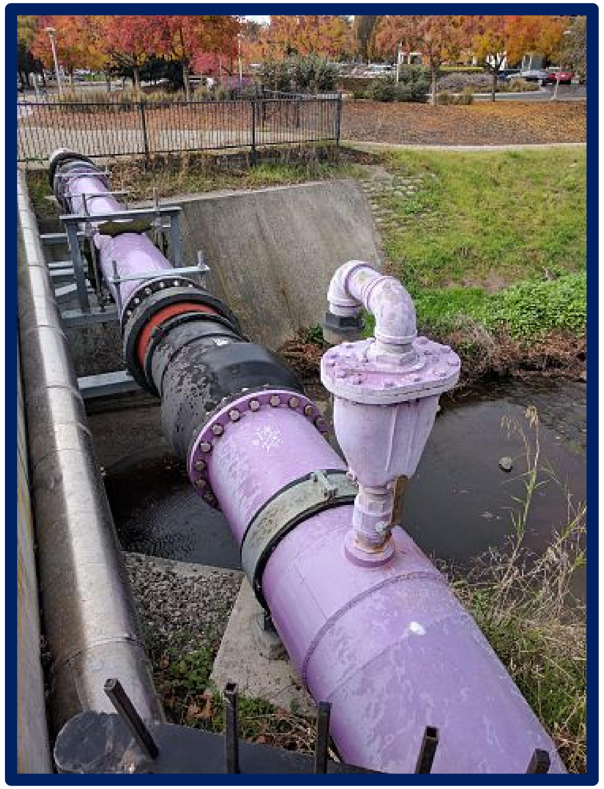
Real-time Analysis for Pollution Prevention

Case study: Real-time analysis in cooling systems

In 2008 Naclo Company won the EPA Greener Reaction Conditions Award for their innovative 3D TRASAR® Technology.

Alternative Cooling System with 3D TRASAR® Technology:

- The 3D TRASAR® System allows for the real-time monitoring of mineral scale buildup.
- This system can also utilize poor-quality water.
- 3D Scale Control prevents mineral scale formation to increase efficiency.
- 3D Bio-control performs a real-time check for planktonic and sessile bacteria. This reduces the amount of biocide used since biocides are then added only when necessary, rather than on a set schedule.
- The 3D TRASAR® System greatly reduces the amount of wastewater discharged from cooling systems.



https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-2008-greener-reaction-conditions-award

Image: Wikipedia, A lavender-colored nonpotable water pipeline in Mountain View, California, Author: Grendelkhan

12. Inherently Safer Chemistry for Accident Prevention

Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Inherently Safer Chemistry for Accident Prevention

Accidents can be avoided by minimizing hazards

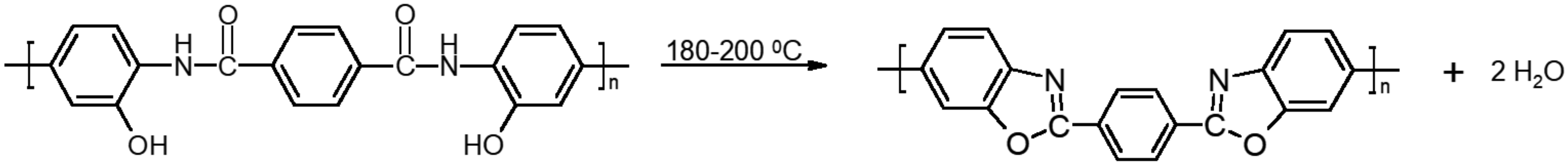
- Approaches to design safer chemistry can include the use of solids or low vapor pressure substances in place of volatile liquids.
- Other approaches include avoiding the use of molecular halogens in large quantities.
- Continuous flow processes can help to minimize chemical hazards.

Inherently Safer Chemistry for Accident Prevention

Case study: Designing safer polymers for use in airplanes

Polyhydroxyamide (PHA):

- Can be molded into seats, bins, and wall panels.
- It is synthesized under mild conditions.
- It decomposes into fire-resistant polybenzoxazole (PBO) and water upon heating.



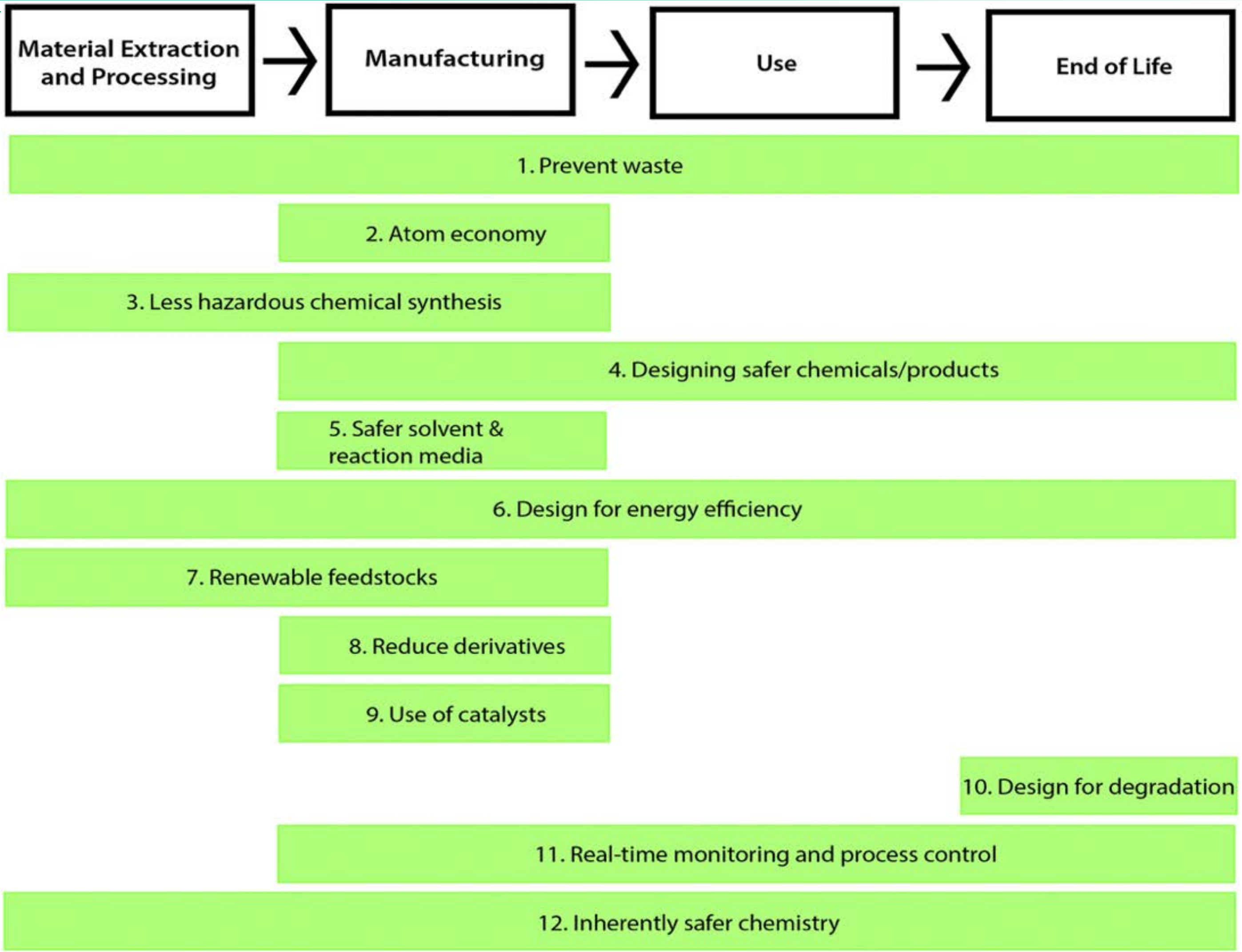
PHA

PBO

Westmoreland, UMass Amherst

Image Source: https://videohive.net/item/plane-interior-flying-in-the-clouds/9895121

Green Chemistry Principles and life-cycle



Chem. Soc. Rev., 2015, 44, 5758-5777

Time for Questions

Break

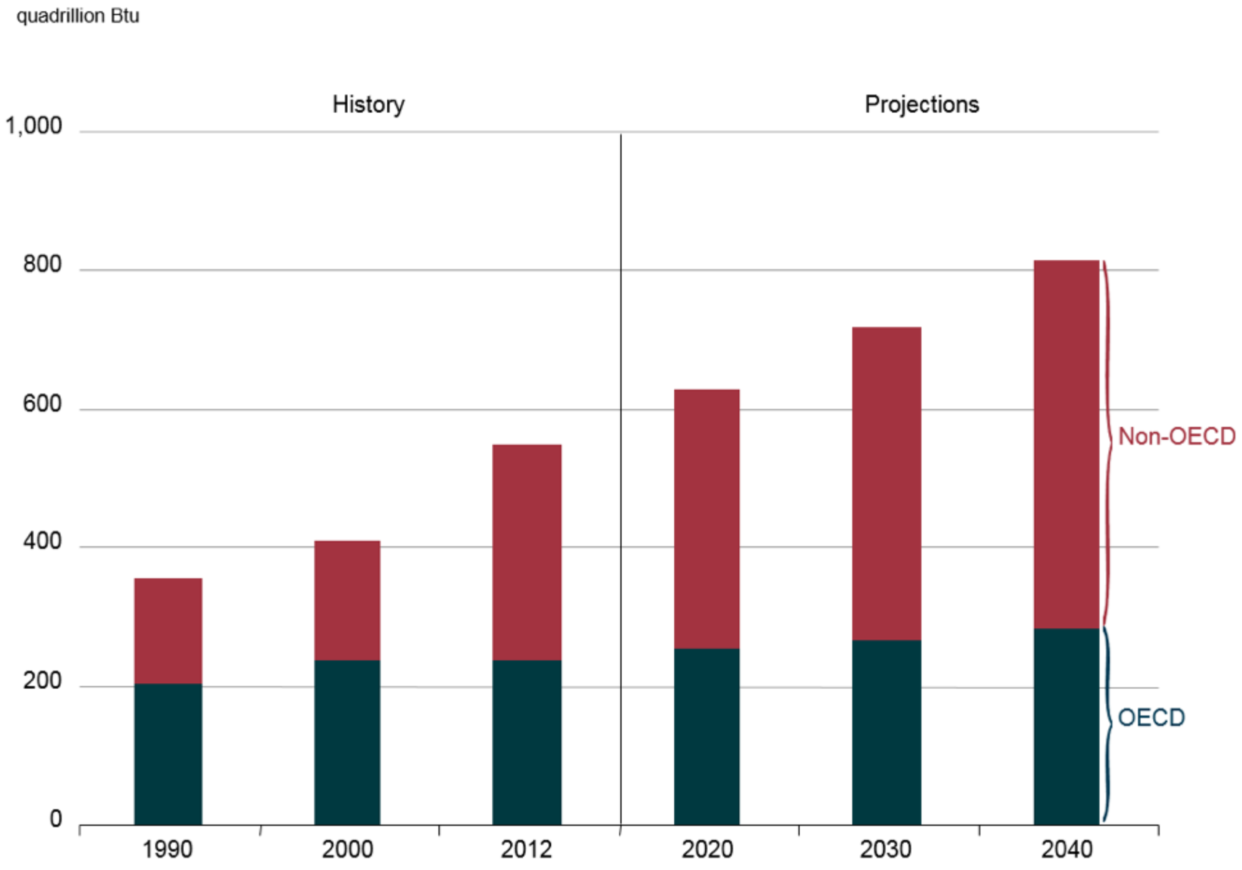
- We will be back shortly!

Session 3:
Areas of Green Chemistry

PRINCIPLE 7

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

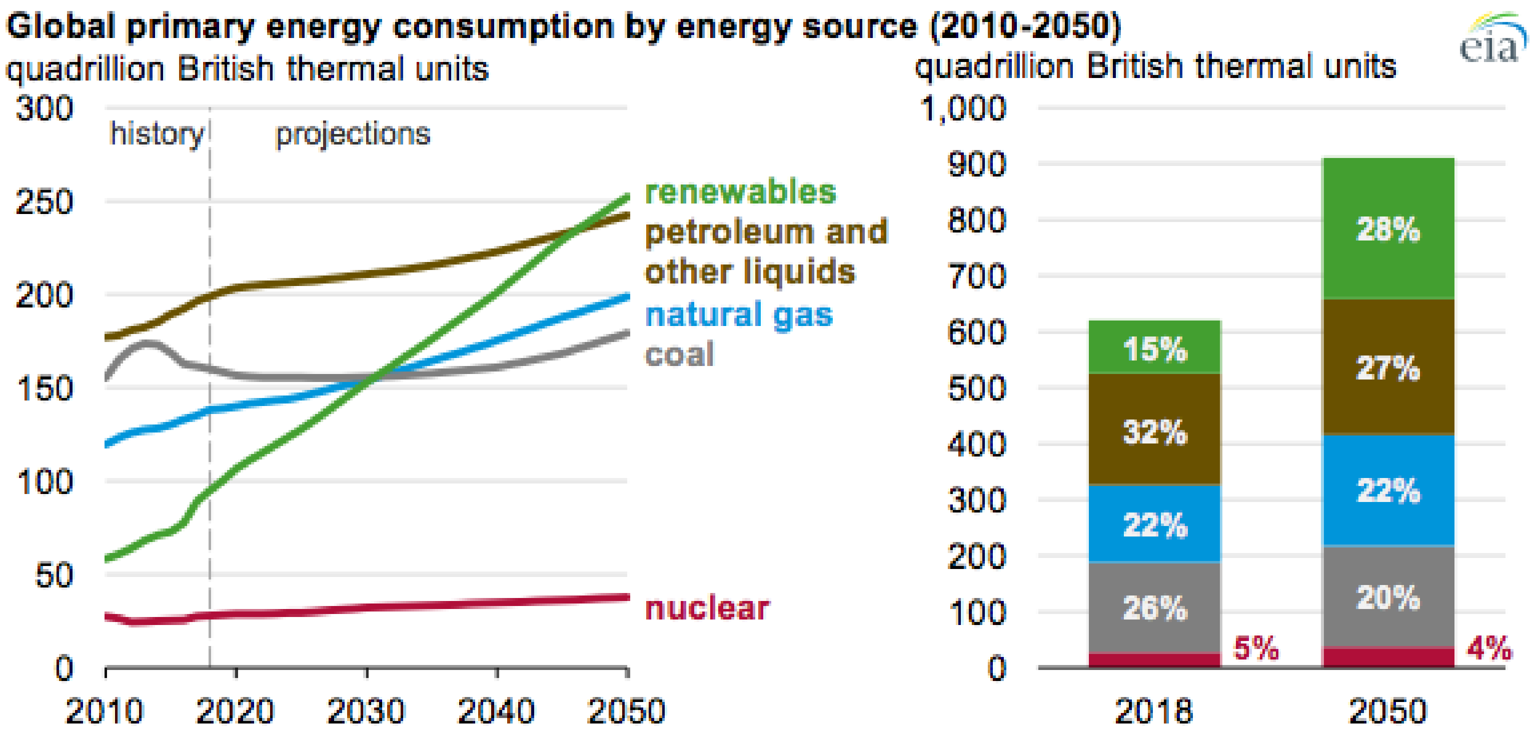
Energy Consumption: data and projections



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



With the rapid growth of electricity generation, renewables—including solar, wind, and hydroelectric power—are the fastest-growing energy source between 2018 and 2050, surpassing petroleum and other liquids to become the most used energy source in the Reference case.

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:

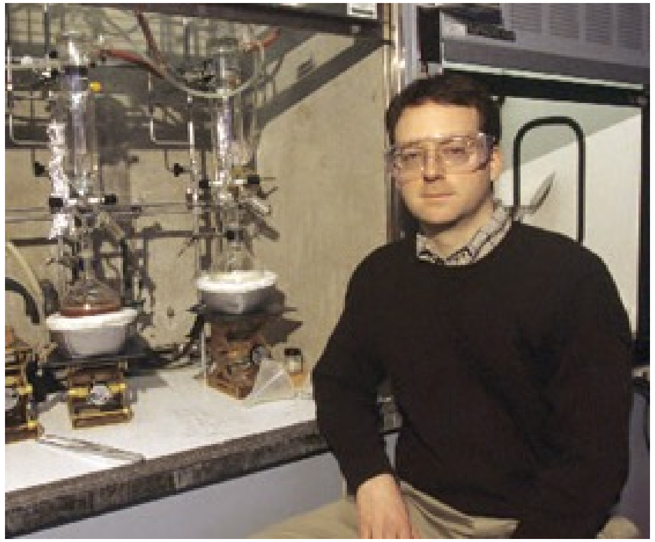
- How far do we push the analysis?

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

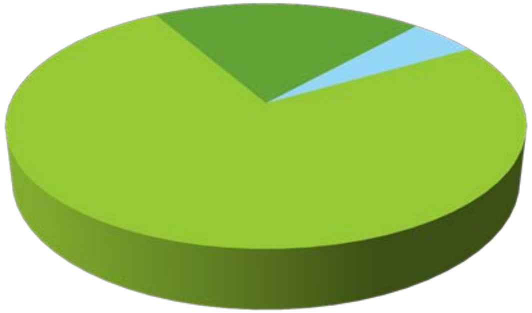


- Development of catalysts able to incorporate carbon monoxide and dioxide into polymers
- Utilize renewable sources of carbon monoxide and dioxide gases such as biomass (agricultural waste) and other low-cost sources such as coal or industrial waste
- High turnover numbers, frequencies, and selectivities
- 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)



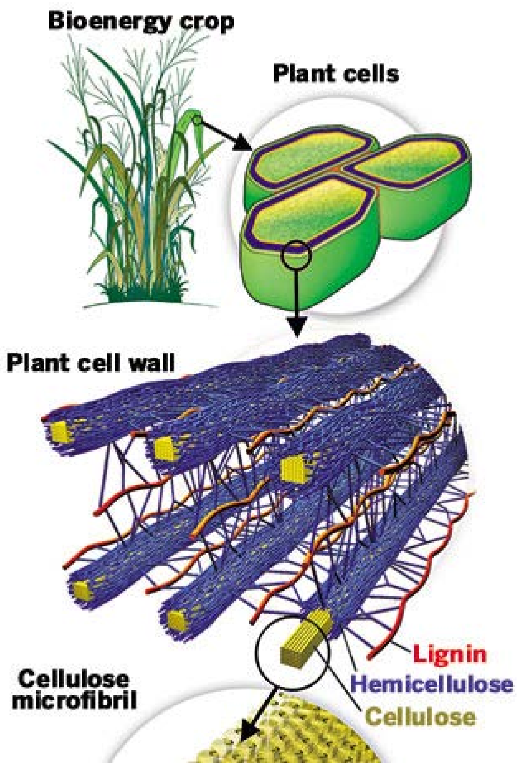
Carbohydrates | Lignin | Fats, proteins, terpenes, etc.

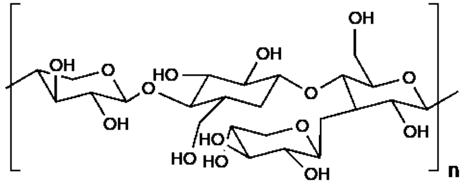
Carbohydrates: Building blocks for a diverse chemical platform.

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

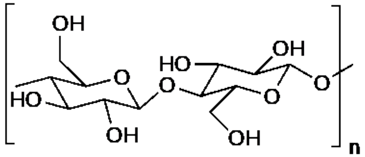
Fats, proteins, terpenes, etc.: Converted into polymers, lubricants, and detergents.

Lignocellulose Biomass



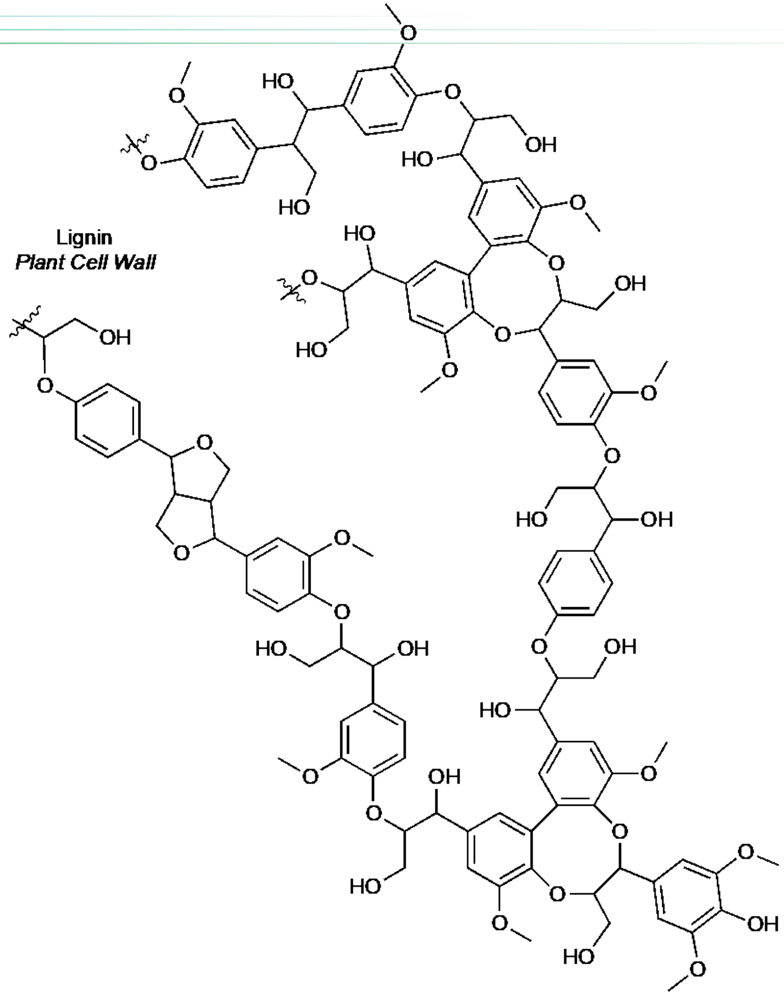


Hemicellulose
Plant Cell Wall



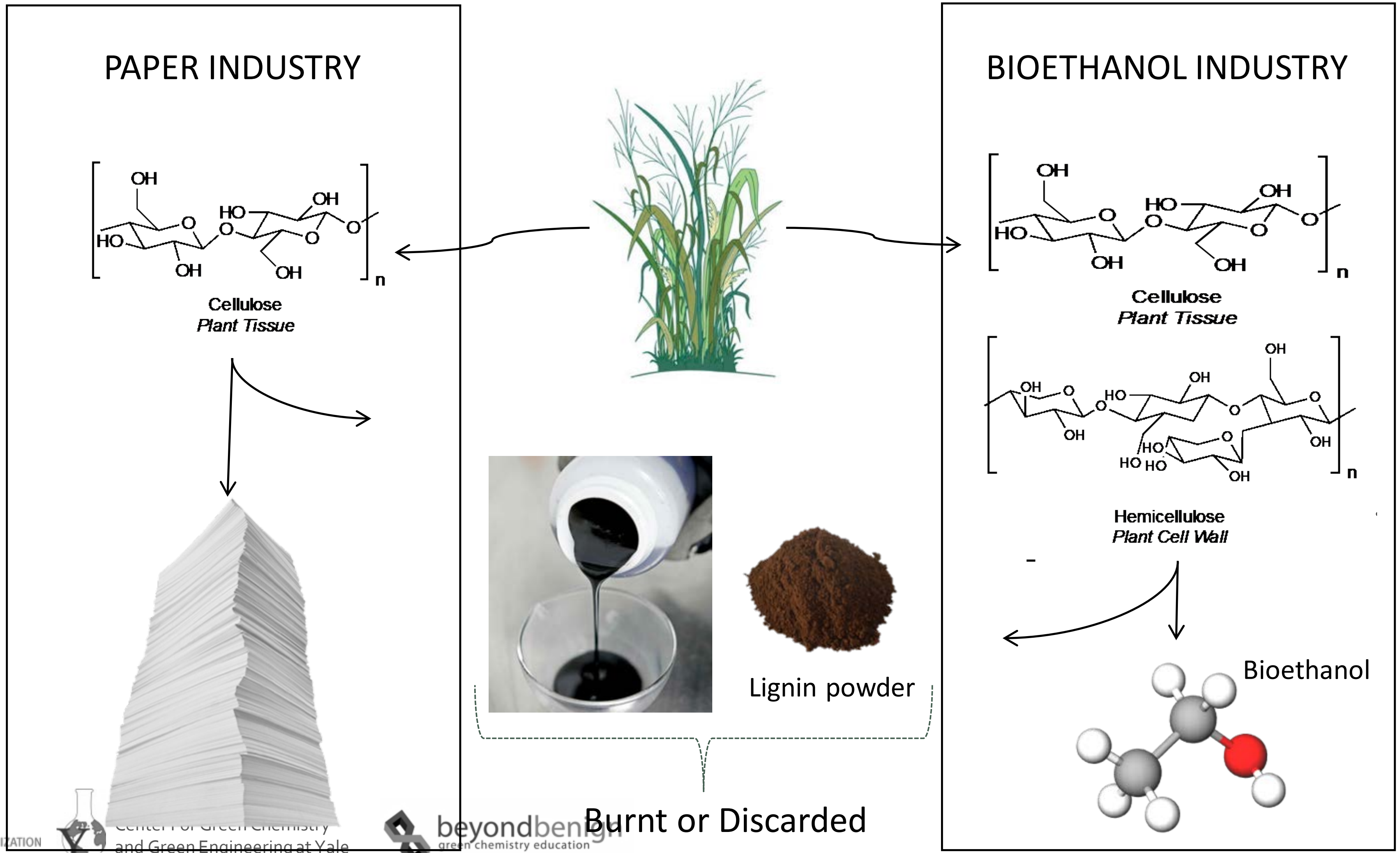
Cellulose
Plant Tissue

Lignin
Plant Cell Wall

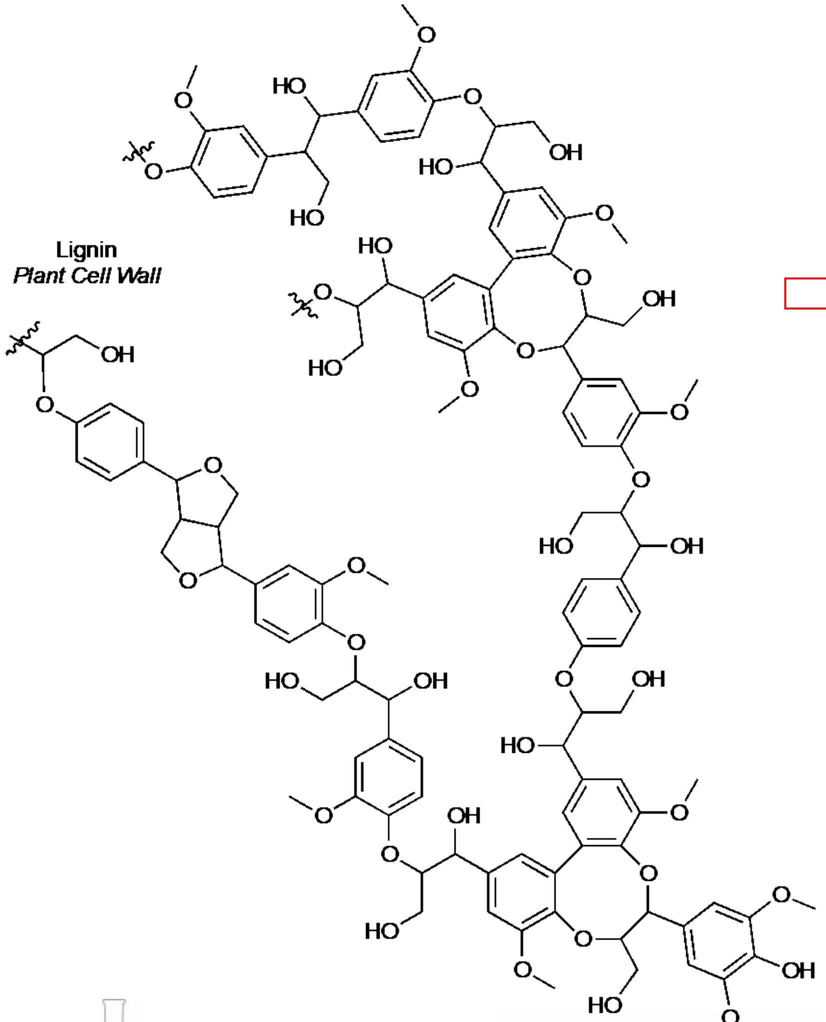


Lignocellulose is a complex polymer obtained from plant cell walls.

Main Industries for Lignocellulose

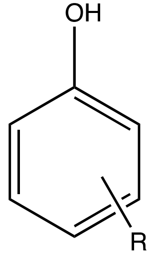


Lignin – Source of Renewable 'Drop-in' Platform Chemicals



A Need of New Technology:

Economical
Sustainable
Selective
Efficient

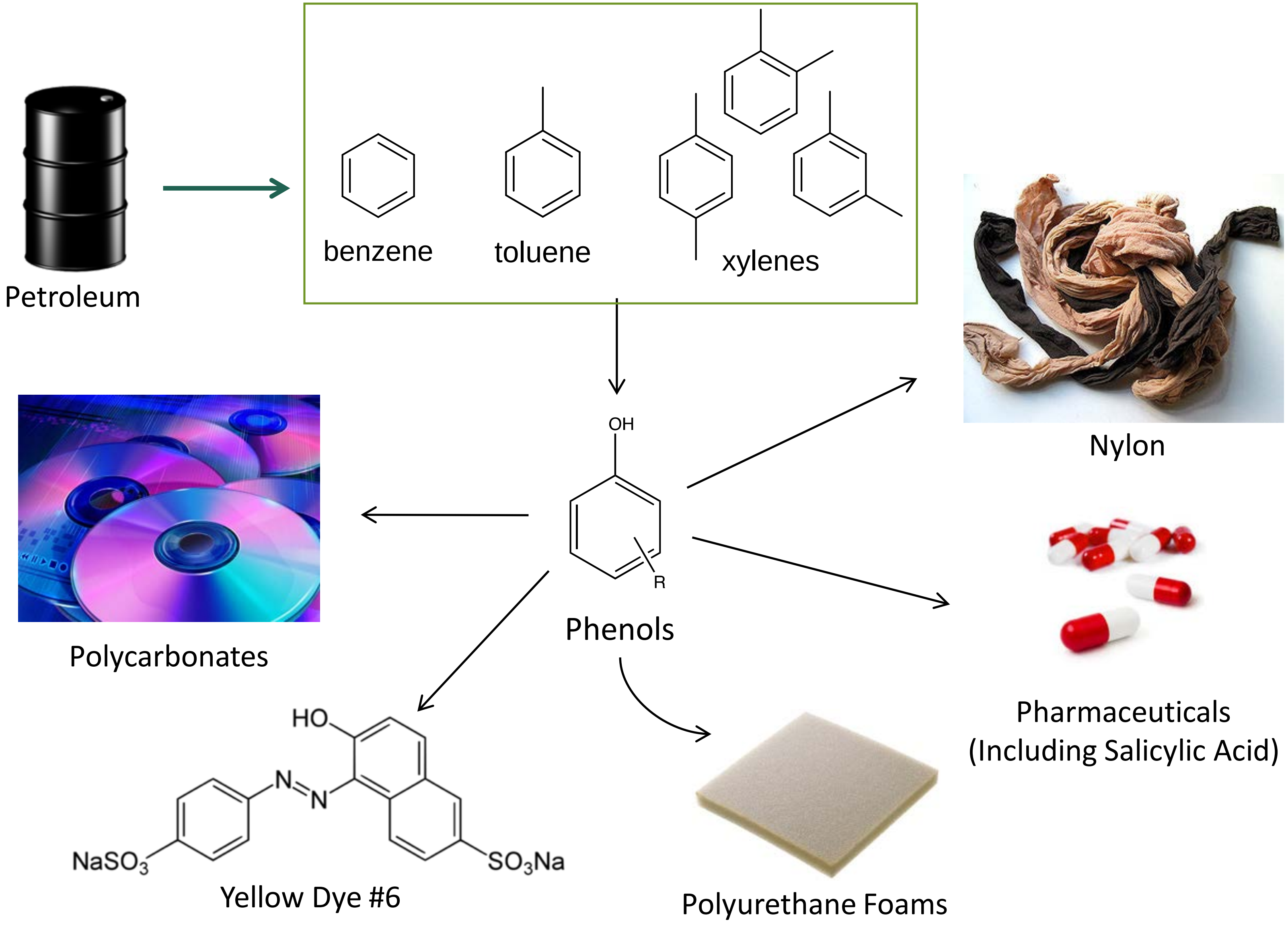


phenol

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
- Environmental reasons:
  - 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

Areas of Research in Green Chemistry

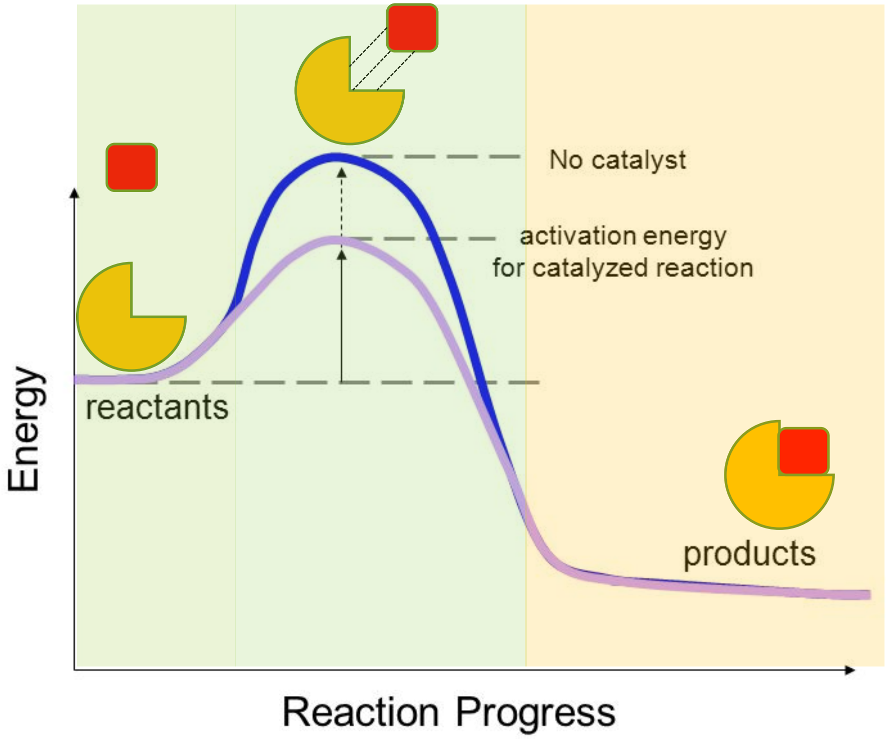
CATALYSIS

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.



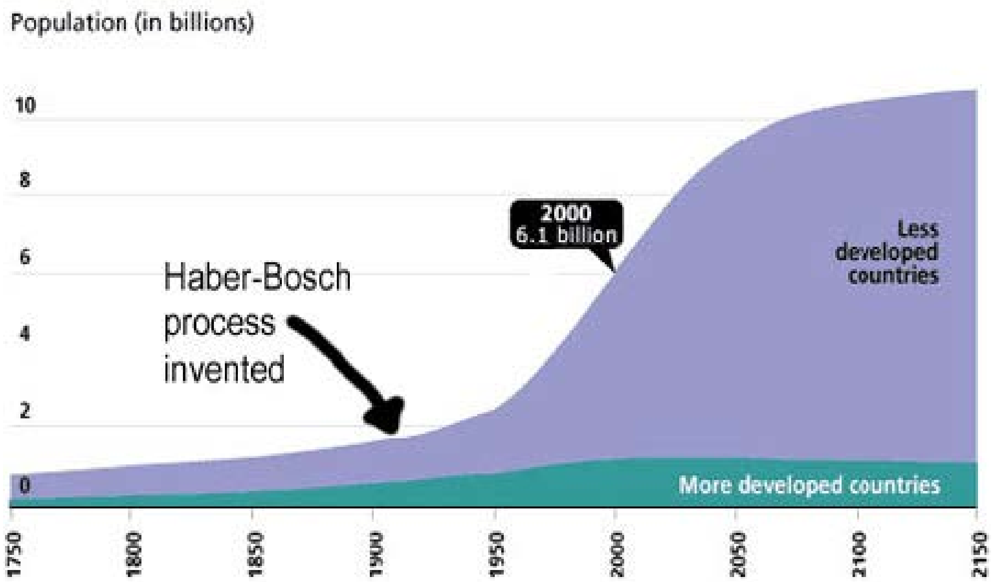
Advantages:

- 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.

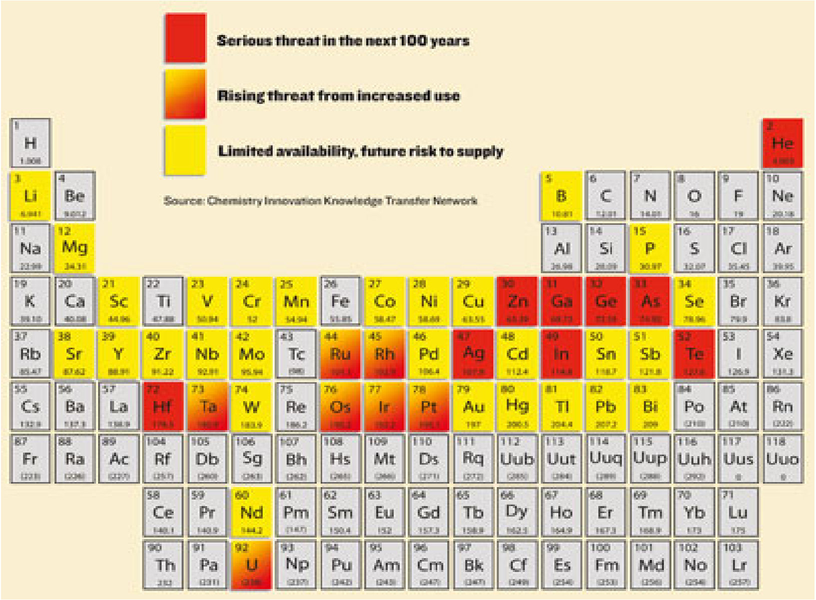
The reaction led to a global increase in human population.

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

Reduce Loading

- High Surface Area Support
- Atomic Layer deposition

Earth Abundant Alternative

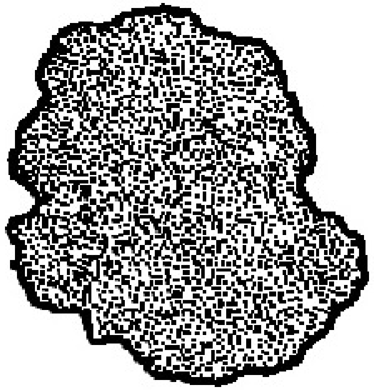
- Abundant metal
- Alloy - Synergistic Effect
- Adjust other parameters
  - Solvent
  - Surfactants

UNIDO UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Center For Green Chemistry and Green Engineering at Yale
beyondbenign green chemistry education

Increase Surface Area

High surface area porous support

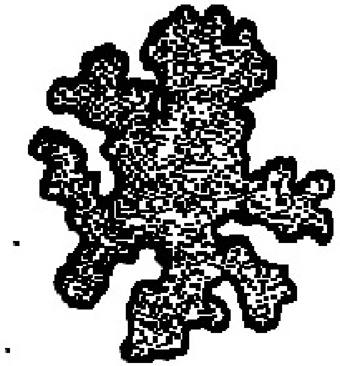
$<50\ cm^2\ g^{-1}$



Non-porous solid

Low specific surface area
Low specific pore volume

$50 – 4000\ cm^2\ g^{-1}$



Porous solid

High specific surface area
High specific pore volume

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.

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)

Traditional Solvents

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

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

GSK SSG-MC-02 September 2010

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

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

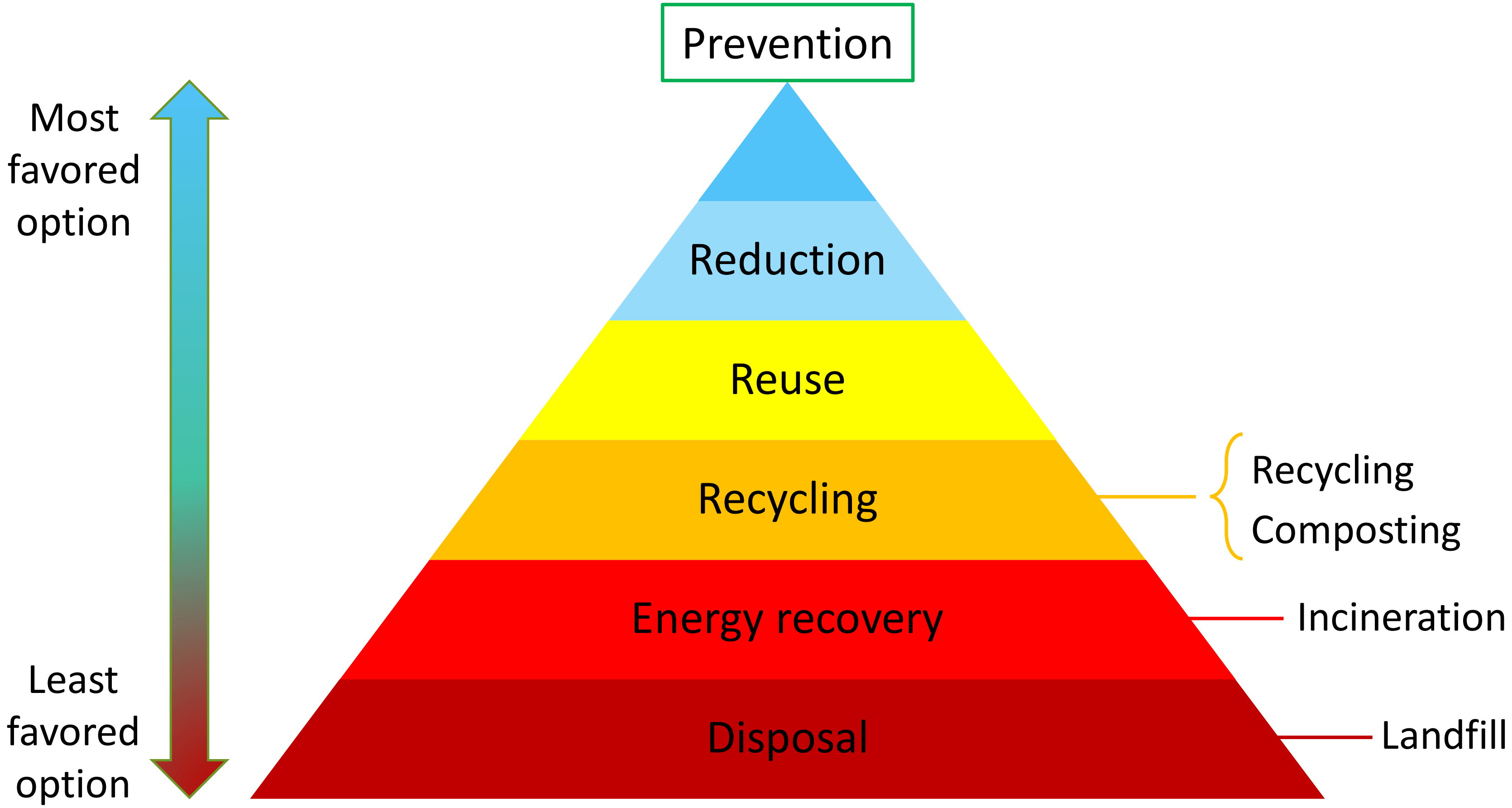
It is better to prevent waste than to treat or clean up waste after it is formed.

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



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Center For Green Chemistry and Green Engineering at Yale
beyondbenign green chemistry education

Prevent waste

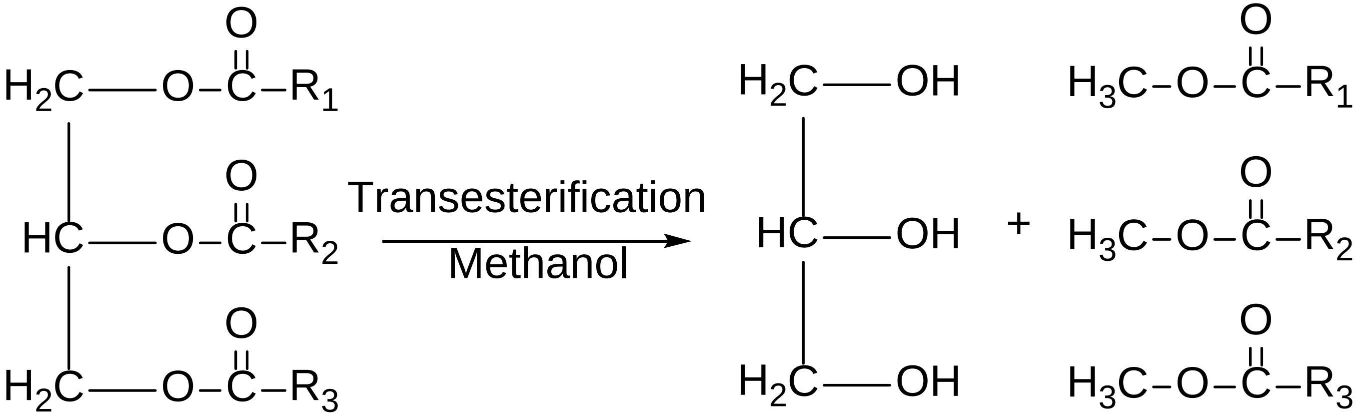
Design products which are biodegradable.

Use a waste as a feedstock for another process.

Example: Used oils as biofuel source

Biodiesel from virgin vegetable oil is considered first generation biofuel because it competes with food => Turning to waste can offer a solution: frying oil can be used instead.

Used frying oil



Triglyceride

Glycerol (Glycerin)

Long chain fatty acids

Current treatment:

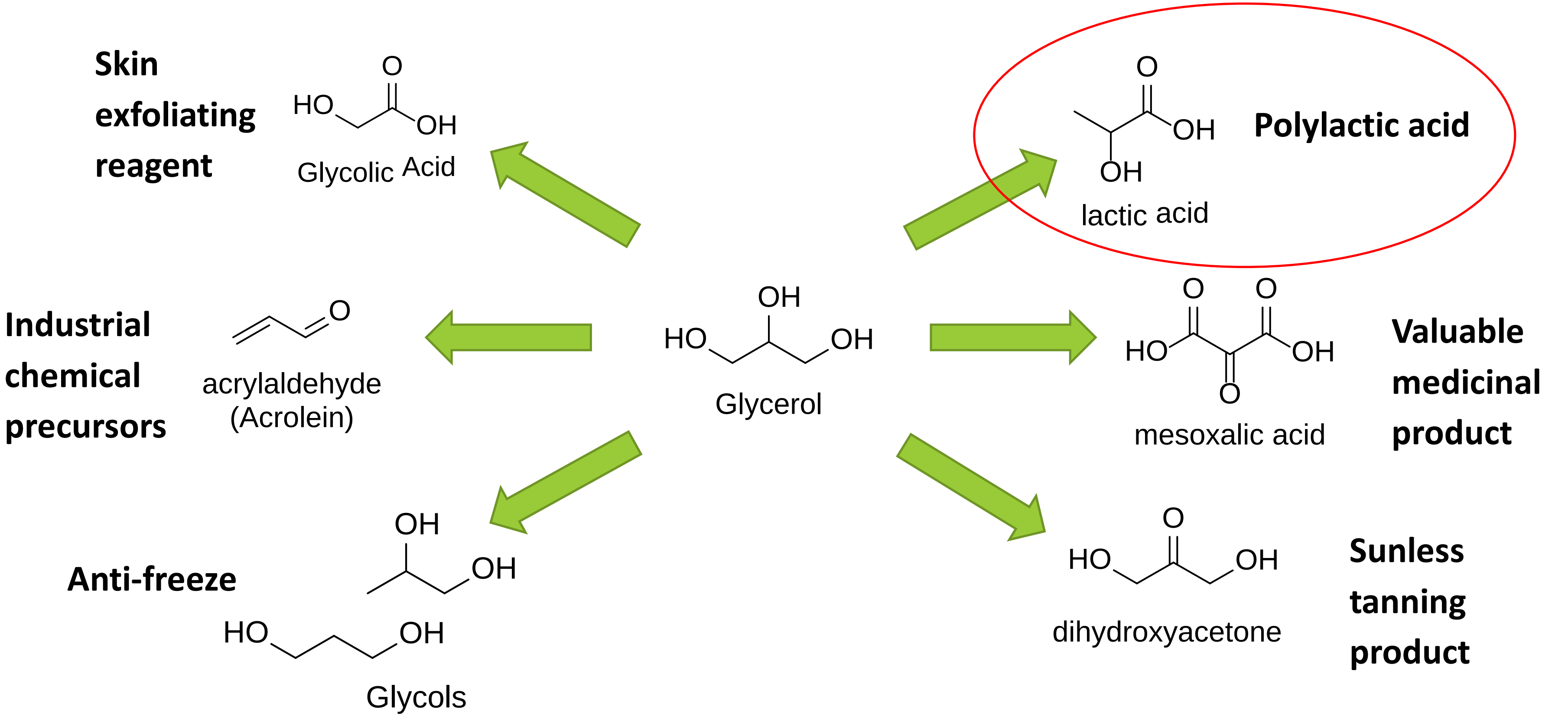
- Dispose / Combust as fuel.

"Waste"

Bio-diesel

Leung, D. Y. C., & Guo, Y. (2006). Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel processing technology*, *87*(10), 883-890.

Glycerol: a waste of biodiesel



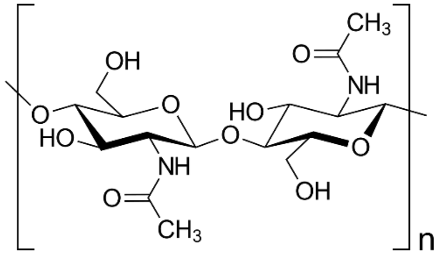
Example: Extracting chitin with an ionic liquid

GREEN CHEMISTRY CHALLENGE
A U.S. EPA Program

Robin Rogers and Mari Signum Mid-Atlantic, LLC, are commercializing a safe, environmentally friendly, low energy-demanding and overall less costly process to produce chitin from seafood waste. Chitin is used in a variety of applications, such as food processing, biodegradable plastics and biomedical applications. This zero-discharge process produces a very high-grade and pure chitin, making use of and monetizing this seafood processing waste.

Dr. Connelly (ACS), Robin Rogers, Julia Shamshina and John Keyes (awardees)

Ionic liquid



chitin

https://communities.acs.org/community/science/sustainability/green-chemistry-nexus-blog/blog/2018/10/18/american-chemical-society-announces-2018-green-chemistry-challenge-award-winners

Time for Questions

Resources

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- Erythropel, H. ; Zimmerman, J. ; deWinter, T. ; Petitjean, L. ; Melnikov, F. ; Lam, C. ; Lounsbury, A. ; Mellor, K. ; Jankovica, N. ; Tu, Q. ; Pincus, L. ; Falinski, M. ; Shi, W. ; Coish, P. ; Plata, D. ; Anastas, P. The Green ChemisTREE: 20 years after taking root with the 12 Principles, *Green Chemistry* **2018,** *20* (9), 1929-1961.

Special Thanks to:

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RECPnet

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