Green Economy - Through Green Chemistry

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References
Contribution of Chemistry to Society
Pharmaceutical Drugs to Treat Ailments: Aspirin®

Acetyl Salicylic Acid (A.S.A.
90% yield) is synthesized from Salicylic Acid and Acetic anhydride.

Cumene undergoes the Hock process to form Phenol.

Cumene + Benzene + Propylene go through catalytic processes.

Phenol reacts with NaOH to form Phenol NaO.

Salicylic Acid undergoes the Kolbe-Schmitt reaction to form Acetic anhydride.

Acetic anhydride reacts with H2SO4 to form Acetaldehyde.

Acetaldehyde reacts with O2 to form Ethene.

Ethene undergoes thermal cracking to form Ethene + 0.5 O2.

Phenol NaO reacts with PdCl2 / CuCl2 to form FOSSIL FUELS: LPG, Coal, Petroleum, etc.

FOSSIL FUELS: LPG, Coal, Petroleum, etc. undergoes thermal cracking to form Ethene + 0.5 O2.

Phenol NaO undergoes liquid phase 50EC, 3-4 bar to form Acetaldehyde.

Acetic anhydride undergoes liquid phase 50EC, 3-4 bar to form Acetaldehyde.

H2SO4 liquid phase T & P > STP to form Phenol.

Kellogg/Monsanto liquid phase T & P > STP to form Phenol.

Shawinigan (Canada) liquid phase 50EC, 3-4 bar to form Acetaldehyde.

Wacker-Hoechst Process liquid phase 50EC, 3-4 bar to form Acetaldehyde.
The Cars we use - Organic Chemistry of the Automobile

- Epichlorohydrin
  - Epoxy resin
    - Bisphenol A or Brominated Bisphenol A
      - Structural adhesives
      - Structural sealants
      - Primer paints
      - Electrical insulation
      - Fiber reinforced plastic composites

- Bisphenol A or Brominated Bisphenol A
- Allyl chloride
- Propylene
- Epichlorohydrin
- Epoxy resin
- BTX
- Ethylene
- Vinyl chloride monomer
- Vinyl
- Vinyl chloride monomer
- Cl₂
- Cl₂
- BTX
- Ethylene
- Vinyl
- Vinyl chloride monomer
- Cl₂
- CO₂
- Phosgene
- Cl₂
- Polyurethanes
- Polysocyanates
- Cl₂
- Polyisocyanates

- Tires
- Rubber hoses
- Foam for seats
- Caulks & sealants
- Bumpers & fenders

- Dashboards
- Electrical insulation
- Vinyl tops
- Floor mats
- Upholstery
- Modular window frame units
- Body side moldings
- Molded armrests
- Exterior & interior trim

- Tires
- Rubber hoses
- Foam for seats
- Caulks & sealants
- Bumpers & fenders
World chemicals sales in 2010 are valued at €2,353 billion.

The Chemical industry is a significant contributor to world economy.
Throughout history, chemists have discovered some revolutionary molecules and synthetic pathways that bring new products and technologies to society.

Production techniques have often neglected the impact of these materials and processes on the environment.

This has resulted in harmful effect on the biotic as well as abiotic environment.
Unintended Negative Impact of Chemistry
Toxic Chemicals in the Environment

SO₂  NOₓ  Heavy metals (Hg, Pb etc.)

H₂SO₄  NH₃  NO₃  Hg  Pb

Toxic substances
The industrial disaster of 1984 in Bhopal, India, was caused by the release of 40 tons of methyl isocyanate gas by a Union Carbide pesticide plant, resulting from a series of worker errors and safety issues that had not been properly addressed.
Plastics Polluting the Environment

It takes more than a 1000 years for plastics to degrade!!
Ukrain presidential candidate poisoned

Dioxin poison caused the mysterious illness of Ukrainian presidential candidate Viktor Yushchenko. He first fell ill in September and recent tests showed dioxin levels 1,000 times above normal.


Toxic effects
Severe exposure – Chloracne is a skin disease with acne-like lesions of the face and upper body and may take two to three years to heal. Cancer and liver damage is an increased risk.
Low levels – Exposure over long periods might result in reproductive, developmental, hormonal and immunological damage.

Dioxin is a by-product from waste incineration, chemical and pesticide manufacturing and pulp and paper bleaching.

SOURCE: Environmental Protection Agency
“.. the soil they walk on, the water they drink and the food they eat is contaminated by lead ....”
This is not sustainable, leading to a new thinking/revolution called Green Chemistry.
Green chemistry (a term coined in 1991) is defined as “the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products”

Green Chemistry is Based on Twelve (12) Principles.
Green chemistry applies fundamental chemical principles to produce chemical products that are inherently less toxic, either to humans or to the ecosystem, than currently existing chemical products.

It is applied to any of the various elements of the chemical product life cycle, from manufacture, to use, and ultimately to disposal.

Thus, green chemistry may be applied to the production of a particular chemical to minimize the hazard associated with its use, or it may focus on the manufacture of the chemical to minimize the environmental consequences of the by-products or the synthesis, or it may equally well look into the development of more environmentally friendly alternatives to a specific chemical. Regardless, green chemistry seeks to reduce the hazard associated with chemical species.
The Twelve (12) Principles of Green Chemistry

1. Prevention

2. Atom Economy
3. Less Hazardous Chemical Syntheses

4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries

6. Design for Energy Efficiency
7. Use of Renewable Feedstock

8. Reduce Derivatives
9. Catalysis
10. Design for Degradation

11. Real-time analysis for Pollution Prevention

12. Inherently Safer Chemistry for Accident Prevention
1. Prevention

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

• Prevention starts by avoiding the use or generation of hazardous substances. If hazardous materials are not produced, then treatment and disposal are not required.

• Moreover, extraordinary safety measures needed for the manufacture of hazardous materials are not required, making the green product less costly to produce and easier to use.

Prevent rather than treat
Replacing Ozone Depleting CFCs

Ozone depleting ChloroFluoroCarbons (CFCs) or flammable hydrocarbons had been used as a blowing agent in the production of polystyrene foam.

Dow Chemical discovered that supercritical carbon dioxide, which is neither ozone-depleting nor flammable, could be used as an effective blowing agent, and, because the carbon dioxide they use is sourced from other industries where it as a waste product, its impact on the human-induced greenhouse effect is negligible.
2. Atom Economy

\[ \text{A + B} \rightarrow \text{P + Waste} \]

- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Atom economy is a measure of how much of the reactants are actually incorporated into the products.
- Atom economy is an essential tool in measuring how much waste is being produced.

\[
\text{Atom economy} = \frac{\text{MW}_{\text{Desired product}}}{\sum \text{MW}_{\text{Reactants}}} \times 100\%
\]

Maximize use of materials – atom economy
Epoxidation of Styrene

\[
\text{Molecular Weight} \quad 104.15 \quad 172.56 \quad 120.15 \quad \text{Waste}
\]

\[
\text{Atom economy} = \frac{\text{MW}_{\text{Desired product}}}{\sum \text{MW}_{\text{Reactants}}} \times 100% = \frac{120.15}{104.15+172.56} = 43.4\%
\]

Assuming 100% yield, the atom economy of the reaction is 43.4 % and 66.6% of the product is waste. An alternative method that avoids the production of waste should be designed.
3. Less Hazardous Chemical Syntheses

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

• The use of hazardous chemicals is linked to risk of harm. Risk can be written as the product of exposure and hazard.

\[ \text{Risk} = \text{Exposure} \times \text{Hazard} \]

Avoid hazardous materials (reagents, starting materials and solvents) and products or by-products
Synthesis of Polycarbonates

◆ Disadvantages

- Phosgene is highly toxic, corrosive
- Requires large amount of CH₂Cl₂
- Polycarbonate contaminated with Cl impurities

◆ Advantages

- Polycarbonate synthesized without phosgene
- Solid state process, eliminates use of CH₂Cl₂
- Higher-quality polycarbonates
4. Designing Safer Chemicals

- Chemical products should be designed to achieve their desired function while minimizing their toxicity.
- Many chemicals are multifunctional, with a specific portion of the molecule providing the desired function while another portion of the molecule might impart some undesirable toxicity characteristics.
- Careful analysis of a selected chemical can elicit which elements of the molecule provide the desired and undesired functions.
- By redesigning the molecule, the functionality related to the toxic effect can then be avoided, minimized, or totally suppressed, while the functionality providing the desired activity is retained.
Replacement of Environmentally Unfriendly Firefighting Foam with Environmentally Benign Foam

Fluorinated surfactants are critical components of firefighting foams. But the surfactants come with significant health and environmental concerns because they are persistent, bioaccumulative, and toxic.

Solberg Co., a leading global maker of the foams, addressed the issue by designing a halogen-free foaming liquid concentrates in which halogenated materials are replaced by an environmentally benign blend of biobased surfactants and complex carbohydrates. The foams are biodegradable, completely falling apart after six weeks.
5. Safer Solvents and Auxiliaries

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

• Whenever possible, reactions should be developed with the environmental impacts of the solvent in mind, and benign solvents such as supercritical CO$_2$ or water, immobilized solvents, or solventless systems should be considered.
In the first commercial synthesis of Viagra by Pfizer, 31 L of solvents per kg of product were used. The newer microwave-mediated synthesis requires only 10 L of solvents per kg of product for the production of Viagra.
6. Design for Energy Efficiency

• Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized.

• Synthetic methods that are conducted at ambient temperature and atmospheric pressure consume less energy than those that are done at high temperature and pressure.

• Use of greener source of energy should be encouraged.
Sources of Energy

Non-renewable
Fossil fuels
Crude oil
Natural gas
Coal, etc

Renewable
Biomass
Organic waste
Oil and Fats
Carbohydrates, Proteins
Sewage, etc
Biodiesel from Oils and Fats (triglyceride)

The calorific value of triglycerides is about 9 Kcal/g comparable to 11 Kcal/g of fossil fuels.

The high viscosity of triglycerides does not allow them to be used as it is, however, it can be transesterified with methanol in the presence of a base to yield the less viscous biodiesel which can be used as a renewable source of energy.

A biodegradable and environmental energy you can grow !!!
7. Use of Renewable Feedstock

- A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- Depleting or nonrenewable fossil resources are subject to the criterion of time and cannot be replenished nearly as rapidly as they are consumed.
- Renewable feedstock are biological and plant-based starting materials that can be replaced through their natural processes.
- The reuse and recycle of metals and other nonrenewable natural resources must also be considered as an opportunity to minimize the consumption of these depleting materials.
Use of glycerol as renewable feedstock for the chemical industry

\[
\text{CH}_2\text{O} - \text{C} - \text{R}_1 \\
\text{CH-O-} - \text{C} - \text{R}_2 \\
\text{H}_2\text{C-} - \text{O-} - \text{C} - \text{R}_3
\]

+ 3 MeOH \xrightarrow{\text{KOH}}

\[
\text{Me-O-} - \text{C} - \text{R}_1 \\
\text{Me-O-} - \text{C} - \text{R}_2 \\
\text{Me-O-} - \text{C} - \text{R}_3
\]

\[
\text{CH}_2\text{O-} - \text{H} \\
\text{CH-O-} - \text{H} \\
\text{H}_2\text{C-} - \text{O-} - \text{H}
\]

Triglyceride  Methanol  Biodiesel

Atom economy  85 - 90 %

10 - 15 % Waste
Current uses of glycerol

In 2001, $97 \times 10^6$ lb of glycerol were consumed for the production of skin care products (suntan lotions, cleansing wipes and cloths, creams, other cosmetics and toiletries), hair care (moisturizers and conditioners), soaps (Neutrogena, designer soaps), toothpastes and mouthwashes, etc.

If biodiesel became a significant product of the oleochemical industry, capture of even a relatively small portion of the current nonrenewable diesel market would result in a large increase in the amount of glycerol available for the marketplace.

The most broad based opportunity for the effective consumption of glycerol will arise from its use as a primary chemical building block (feedstock).
Once it is recognized that a ready source of low cost glycerol is available from the biodiesel unit operation, glycerol could be positioned within the biorefinery as a primary renewable building block analogous to those of the petrochemical industry (methane, ethylene, BTX, etc.).

As the price of glycerol drops and its availability rises, glycerol ceases to become an “additive” for a fragmented list of small volume products, and assumes a position as the starting point for the production of fewer, but much larger volume materials.

When the cost of a chemical drops, its range of industrial utility broadens, and the ability to absorb the cost of additional chemical transformations increases.
Glycerol would transition from its current state as an advanced intermediate or chemical end-product to utility as a starting material for a family of compounds.

Epichlorohydrin is a chemical intermediate used in the manufacture of epoxy resins, elastomers, water treatment chemicals, polyols, pharmaceutical products, etc.

1,2-Propanediol is used in the pharmaceutical manufacturing as a solvent and vehicle especially for drugs unstable or insoluble in water. It may also be used as a stabilizing agent, plasticizer and as a preservative.
8. Reduce Derivatives

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

Protection of the carbonyl group

\[
\text{Ethylene glycol} + \text{p-TsOH} \rightarrow \text{Benzene} + \text{H}_2\text{O}
\]

Alkylation of alkyne

\[
\text{NaNH}_2 + \text{H}_3\text{C}\text{CH}_2\text{Cl} \rightarrow \text{HCl}
\]

Deprotection of the carbonyl group
• Catalytic reagents are superior to stoichiometric reagents.
• Catalysts increase the rates of chemical reactions but are not consumed in the reactions. As such, a catalyst may decrease the temperature at which a reaction can be performed economically, thus saving energy costs.
10. Design for Degradation

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

• Some chemicals such as plastics made from petroleum intermediates or pesticides persist in the environment.
Materials Designed to be Biodegradable

Plastics made from Polyhydroxyalkanoates synthesized by bacteria

Made from starch like maize
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.

• The monitoring of a chemical process is beneficial for several reasons: the formation of toxic by-products can be detected early on and parameters can be adjusted to reduce or eliminate formation of these substances.
12. Inherently Safer Chemistry for Accident Prevention

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

• Toxicity, explosivity, and flammability must be part of the design of chemical products and processes.

• Pollution prevention relies on accident prevention to minimize the likelihood of chemicals leaking into the environment. However, if one uses inherently safe materials, then even in the event of a leak, there is minimal hazard.
Example: Green Synthesis of the Pain Killer Ibuprofen

The Boots’ synthesis (1960)

- Six steps
- 40% atom economy, which implies 60% of the materials used is wasted,
- The only ‘catalyst’ in the Boots’ synthesis (AlCl₃) is not a true catalyst. In the process it is changed into a hydrated form that has to be disposed of – usually in landfill sites.

The green synthesis is cheaper as well as more environment friendly.

The BHC synthesis (1993)

- Three steps,
- 77% atom economy,
- All the three steps in the green synthesis use catalyst (HF, Raney nickel and palladium) that are recovered and re-used.
Green chemistry is not just a way to protect the environment by preventing pollution before its creation; it is also a way to increase efficiency and reduce costs of production, an opportunity for businesses to lighten their environmental burdens and make money.
Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.

Reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.

Diagram:

Reactant → Reagents, Energy → Solvent → Product + By-products
Green Chemistry is about...

Reducing

Waste
Materials
Hazard
Risk
Energy
Cost

.... vital for green economy, embrace it.