Green Chemistry

Chemistry (CY100N)
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Historical perspective

1960s → **1970s** → **1980s** →

In 1962, a book named '*Silent Spring*' was published by Rachel Carson about the devastating effect of certain chemicals on the local ecosystem.

The U.S. Environmental Protection Agency (EPA) was established.

The Organization for Economic Co-operation and Development (OECD) worked on minimizing environmental pollutions.

1990s → **2000s** → **Now and the Future**

Paul Anastas and John C. Warner co-authored the groundbreaking book, *Green Chemistry: Theory and Practice* in 1998.

The Nobel Prize in Chemistry was won for largely green chemistry research in 2001 and 2005.

Strict environmental regulations in place, public awareness for a sustainable future, Cleaner and safer chemical industries.

https://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/history-of-green-chemistry.html

Chemistry & Chemical Industry

Pros

- Food to clothes to home appliance to transportation to agriculture to medicines
- Mass production and better affordability
- Product movement across the countries
- Driving of force of any economy

Cons

- Rampant production and dumping of wastes
- Severe air, water, and soil pollution
- Health hazard to plants, animals, and humans

When things went south…

Example 1

Chlorofluorocarbons (CFCs) were developed for refrigeration and revolutionized the industry. However, when it was found to deplete the ozone layer, the damage was already severe.

It took decades to replace CFCs and repair the ozone hole.

Example 2

Dichlorodiphenyltrichloroethane (DDT) was used extensively to protect crops. It was considered a miracle pesticide, saving countless lives from typhoid and malaria.

By the time its negative consequences were known, it accumulated everywhere in the biosphere including the human body.

Green Chemistry/Sustainable Chemistry

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal.

Sustainable chemistry is a scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services. Sustainable chemistry encompasses the design, manufacture and use of efficient, effective, safe and more environmentally benign chemical products and processes.

Priorities for Pollution Prevention

- Green chemistry prevents pollution by source reduction at the molecular level and this philosophy applies to all disciplines of chemistry.

- It provides innovative scientific solutions to real-world environmental and health problems coming from chemical products and processes.

- It works towards cleaner and safer practices to lessen or eliminate hazard associated to existing products and processes.

Priority 1. Source reduction and prevention of chemical hazards

Priority 2. Treating chemicals to render them less hazardous before disposal

Priority 3. Disposing of untreated chemicals safely and only if other options are not feasible

https://www.epa.gov/greenchemistry/basics-green-chemistry

Principles of Green Chemistry

A mnemonic, **PRODUCTIVELY**, was developed which captures the essence of the **TWELVE (12)** principles of green chemistry.

P – Prevent wastes
R – Renewable materials
O - Omit derivatization steps
D – Degradable chemical products
U – Use of safe synthetic methods
C – Catalytic reagents
T – Temperature, pressure ambient
I – In-process monitoring
V – Very few auxiliary substances
E – E-factor, maximize feed in product
L – Low toxicity of chemical products
Y – Yes, it is safe

https://www.acs.org/content/acs/en/greenchemistry/principles/12-principles-of-green-chemistry.html

1. Prevention.

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

This is the most important principle of green chemistry and the other principles can be seen as guidelines in achieving this. Chemical syntheses and processes should be developed that reduce or eliminate waste generation at the source.

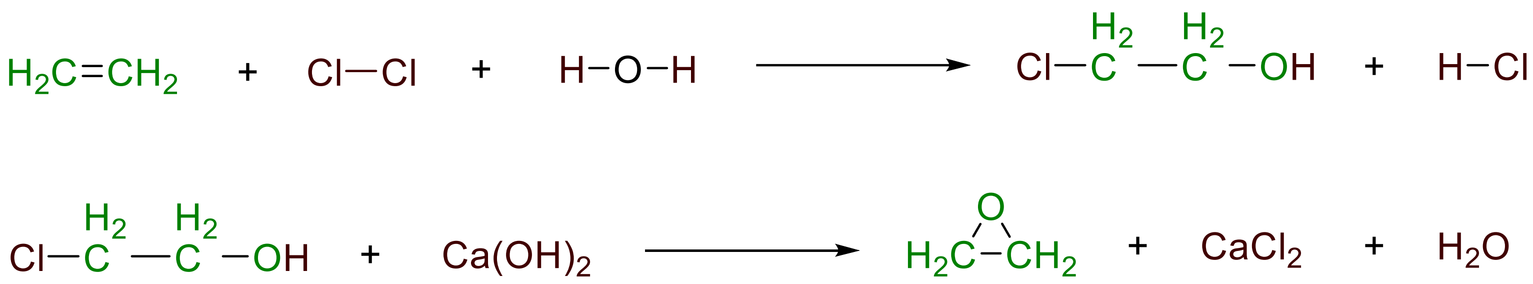
2. Atom economy.

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

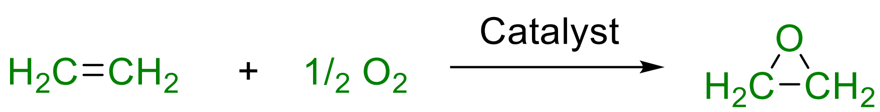
Atom economy, developed by Barry Trost, asks the question "what atoms of the reactants are incorporated into the final desired product(s) and what atoms are wasted?"
Traditionally, the efficiency of a reaction has been measured by calculating the percent yield. However, atom economy sheds more light on the efficiency of a reaction.

Synthesis of ethylene oxide

The chlorohydrin route



The catalytic route



Better atom economy, clean, no waste

3. Less hazardous chemicals 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.

Chemists use toxic substances all the time because reactive chemicals afford reactions that are kinetically and thermodynamically favorable. Unless and until replacement chemicals along with new synthetic protocols are developed, inherently toxic materials will continue to be used. Utmost care should be taken on the materials added to the reaction flask along with the reagents and evaluate their roles and effects on the chemical transformation. For example, the tragedy of Bhopal happened due to the accidental leakage of methyl isocyanate, a highly toxic chemical.

4. Design safer chemicals.

Chemical products should be designed to effect their desired function while minimizing their toxicity.

Reactive chemicals used by chemists to manufacture products are also likely to react with unintended biological targets, human and ecological, resulting in unwanted adverse effects. Minimizing toxicity, while simultaneously maintaining function and efficacy, may be one of the most challenging aspects of designing safer products and processes. Achieving this goal requires an understanding of not only chemistry but also of the principles of toxicology and environmental science.

5. Safer solvents and auxiliaries.

The use of the auxiliary substances – solvents, separation agents, and others – should be made unnecessary wherever possible and innocuous when used.

Solvents account for a significant proportion of mass and energy consumption in a standard batch chemical operation. Solvents are also the major contributors to the overall toxicity profile, health and environmental hazards associated with a process. The objective is to choose solvents that make sense chemically, reduce the energy requirements, have the least toxicity, have the fewest life cycle environmental impacts and don't have major safety impacts. An example for the successful use of safer solvent is the decaffeination of coffee using super critical CO_2 *instead of chlorinated hydrocarbon solvents.*

6. Design for energy efficiency.

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

Energy is a crucial issue for the 21st century. Discussions about energy requirements in chemical processes should be more elaborate than simply proposing to run reactions at ambient temperature and pressure. The attention that energy gets from chemists is mostly devoted to heating, cooling, separations, electrochemistry, and pumping. Reactions themselves are rarely where a majority of energy is used; most is used in solvent removal, or to isolate the desired product, or to remove impurities. For the design of new molecules, a detailed and extended consideration of how energy will be used is required.

7. Use renewable feedstocks.

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

The concept of making all our future fuels, chemicals and materials from renewable feedstocks is an interesting concept which at first glance seems impracticable. Fossil fuels for carbon-based chemicals and materials are being rapidly depleted in a predictable manner with the expected rise of global populations and expanding energy intensive economies. Plant biomass can be a viable carbon-based feedstock for fuels and chemicals. It is estimated that about 40 billion tons of biomass, about 25% of the annual production, would be required to completely generate a bio-based economy. The technical challenge is to develop low energy, non-toxic pathways to convert the biomass to useful chemicals in an environment-friendly manner.

8. Reduced derivatives.

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

One of the key principles of green chemistry is to reduce the use of derivatives and protecting groups in the synthesis of target molecules. One of the best ways of doing this is the use of enzymes. Enzymes are so specific that they can often react with one site of the molecule and leave the rest of the molecule alone and hence protecting groups are often not required. A great example of the use of enzymes to avoid protecting groups and clean up processes is the industrial synthesis of semi-synthetic antibiotics such as ampicillin and amoxicillin.

9. Catalysis.

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

A primary goal of green chemistry is the minimization or elimination of waste in the manufacture of chemicals and allied products. Reduction of a ketone into secondary alcohol using $NaBH_4$ has an atom economy of 81% while reduction by hydrogenation is 100% atom economic and no waste is produced. Unfortunately, hydrogen reacts with ketones only in presence of a catalyst such as palladium-on-charcoal. A catalyst is a substance that changes the velocity of a reaction without itself being consumed in the process. Catalyst lowers the activation energy of the reaction and therefore decreases the energy demand of the process. In principle, it can be used in small amounts and be recycled indefinitely. Catalysis has been widely applied in the pharmaceutical and fine chemical industries, with the goal of minimizing the enormous amounts of waste generated by the use of stoichiometric reagents.

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.

A green chemistry objective is to design out molecular features responsible for hazardous characteristics and risk. Principle 10 guides the design of products that degrade after their commercial function in order to reduce risk or the probability of harm occurring. Degradation can eliminate significant exposure, thereby minimizing risk regardless of the hazard of the chemical involved. Biodegradation, hydrolysis, and photolysis can be designed into chemical products. An understanding of the mechanisms of degradation and persistence are required to design in chemical features that promote degradation and eliminate features that promote persistence.

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 feedback is essential in proper functioning chemical processes. In addition to laboratory analyses, analysis can also be performed in-line, on-line, or at-line in a chemical plant, a subdiscipline known as process analytical chemistry. Such analysis can detect changes in process temperature or pH prior to a reaction going out of control, poisoning of catalysts can be determined, and other deleterious events can be detected before a major incident occurs.

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.

Safety can be defined as the control of recognized hazards to achieve an acceptable level of risk. It may be the most overlooked of the twelve principles, yet it is the logical outcome of many of the other principles. In fact it is practically impossible to achieve the goals of Principle 12 without the implementation of at least one of the others. Green Chemistry's primary focus is clearly to make the environment safer. Materials and processes that are safer for the environment also are likely to be safer for the general public. The manufacturing or laboratory worker is often the first in-line person to benefit from hazard reductions.

Green Metrics

Green chemistry metrics measure aspects of a chemical process relating to the principles of green chemistry. These metrics serve to quantify the efficiency or environmental performance of chemical processes, and allow changes in performance to be measured. The motivation for using metrics is the expectation that quantifying technical and environmental improvements can make the benefits of new technologies more tangible, perceptible, or understandable.

Most of the modern “green” processes fall into the area of fine chemicals rather than bulk organic chemicals. Nonetheless, they have had an impact on bulk chemical processing in terms of emissions, heat conservation, and catalyst development.

Atom Economy

The atom efficiency or atom economy concept is an extremely useful tool for rapid evaluation of the amounts of waste that will be generated by alternative processes. It is calculated by dividing the molecular weight of the product by the sum total of the molecular weights of all reagents used in the reaction.

Atom Economy = (MW of the PRODUCT / MW of ALL REAGENTS used) × 100%

E Factor

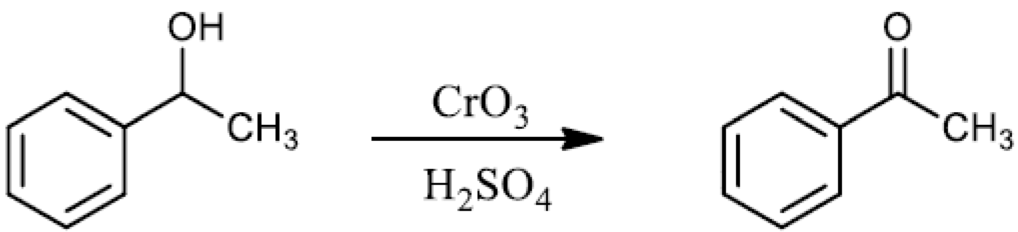
The E-factor concept has played a major role in focusing the attention of the chemical industry world-wide, particularly the pharmaceutical industry, on the problem of waste generation in chemicals manufacture. It provides the impetus for developing cleaner and more sustainable processes. A higher E factor means more waste and, consequently, greater negative environmental impact. The E-factor increases significantly from oil refining (0.1) to bulk chemicals (1) to fine chemicals (5) to pharmaceuticals (25). It can be easily calculated from a knowledge of the number of tons of raw materials purchased and the number of tons of product sold, for a particular product or a production site or even a whole company.

E-factor = Kg of WASTES produced / Kg of PRODUCT obtained

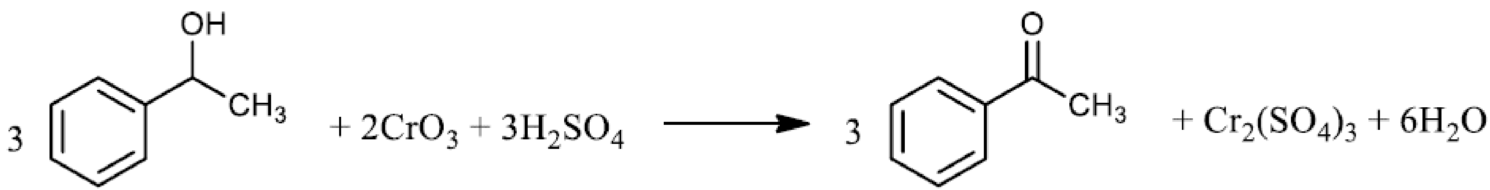
http://www.sheldon.nl/roger/efactor.html

Calculation of Atom Economy & E-factor:

Calculate the Atom economy and E-factor of the following oxidation reaction using the Jones reagent.



Step 1. Balance the chemical equation.



Step 2. Calculate the MW of product(s) and reagents.

Product: MW of $PhCOCH_3$ = 120.
Reagents: MW of $PhCH(OH)CH_3$ = 122; MW of CrO_3 = 100;
MW of H_2SO_4 = 98

Step 3. Calculate Atom Economy using the formula

Atom economy of the above process = (3×120) [(3×122)+(2×100)+(3×98)] × 100 = 42%

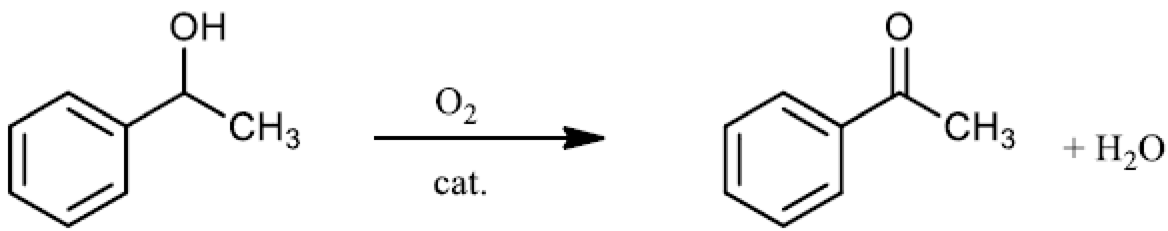
For the calculation of E-factor, calculate the MW of the wastes i.e. $Cr_2(SO_4)_3$ and H_2O.

MW of $Cr_2(SO_4)_3$ = 392; MW of H_2O = 18.

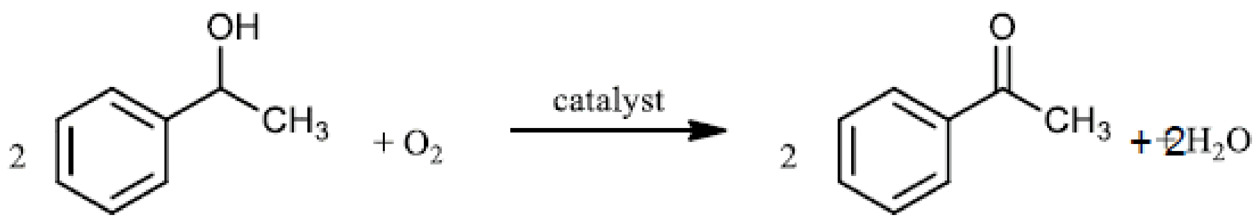
For 3 moles of $PhCOCH_3$, one mole of $Cr_2(SO_4)_3$ and 6 moles of H_2O is produced.

Thus E-factor for the above process = [392+(6×18)] (3×120) = 1.38

Calculate the Atom economy of the following reaction



Step 1.



Step 2.

Product: MW of $PhCOCH_3$ = 120.
Reagents: MW of O_2 = 32.

Step 3.

Atom Economy of the catalytic oxidation process = $\frac{(2\times120)}{[(2\times122)+32]}\times 100 = 87\%$

E-factor of the process = $\frac{(2\times18)}{(2\times120)} = 0.15$