Assessments and metrics for green chemistry

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Trends…

- Ecobuildings
- Green transportation
- Ecological agriculture
- Sustainable cities
- Green energy

- Green chemistry

Sustainable development

Sustainable development

- Society
- Economy
- Environment

Sustainable development

Sustain – strengthen or support physically or mentally

Sustainable development is the principle for meeting human development goals while at the same time sustaining the ability of natural systems to provide the natural resources and ecosystem services, upon which the economy and society depend.

•Society

Welfare state

- Economy
- Environment

- Society

- **Economy**

Industrial revolution

- Environment


Donald J. Trump
@realDonaldTrump
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The concept of global warming was created by and for the Chinese in order to make U.S. manufacturing non-competitive.
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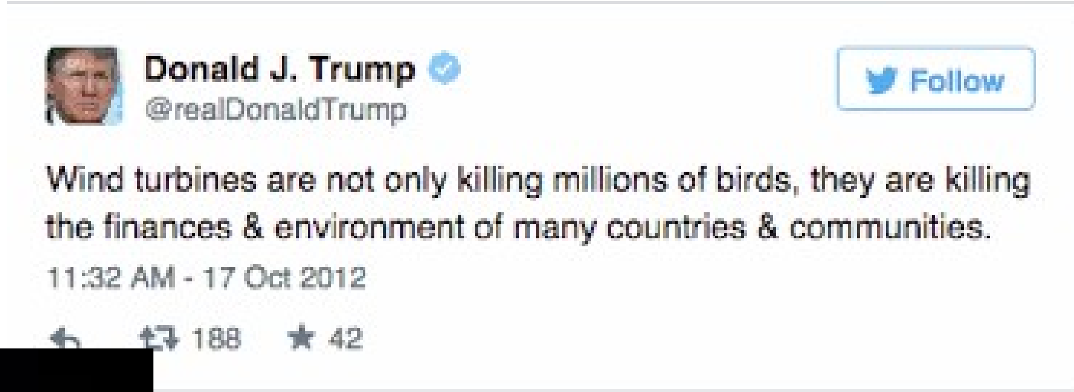
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Wind turbines are not only killing millions of birds, they are killing the finances & environment of many countries & communities.
11:32 AM - 17 Oct 2012
188
42

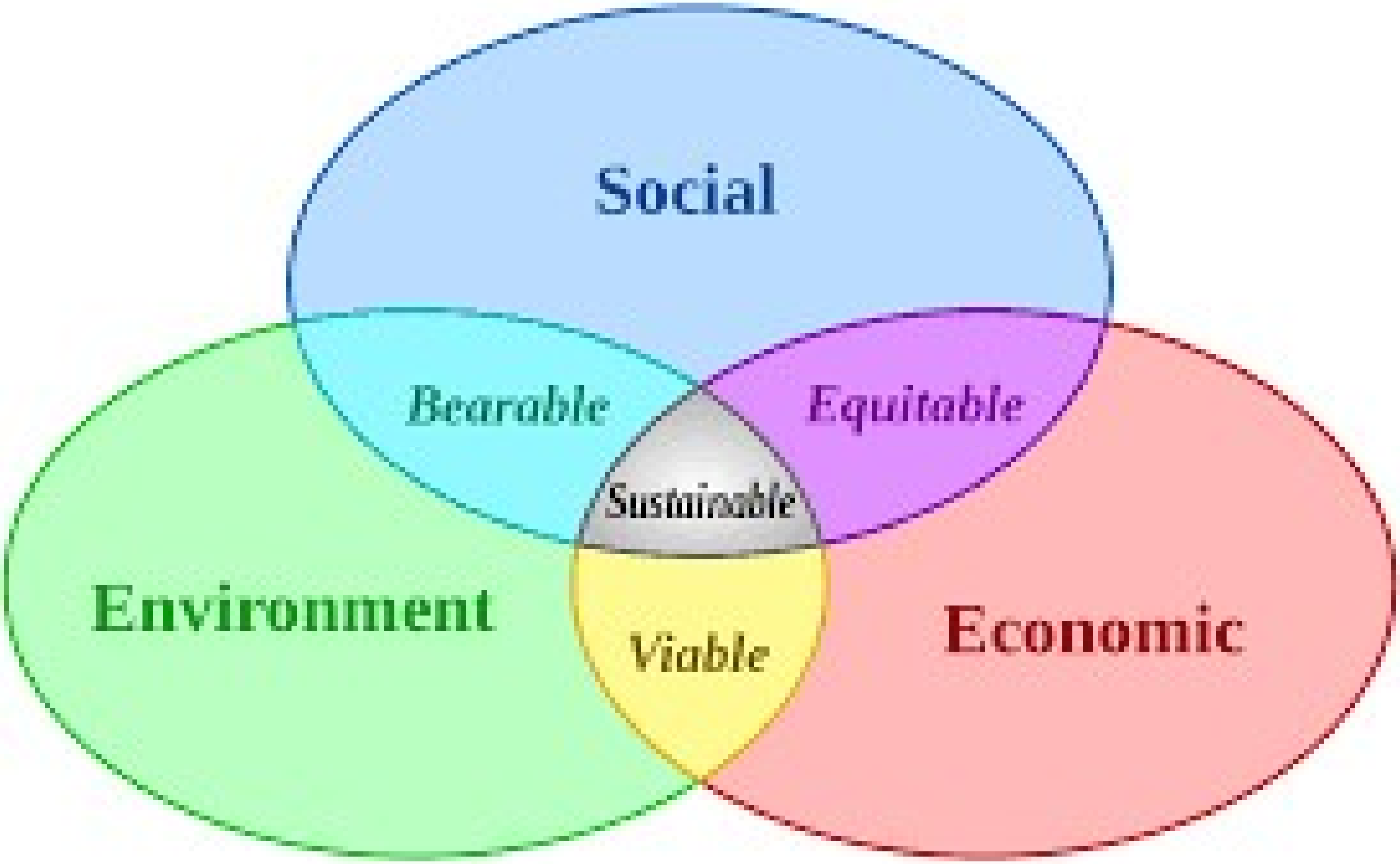

"WE'LL BE FINE WITH THE ENVIRONMENT. WE CAN LEAVE IT A LITTLE BIT."
imgflip.com

- Society
- Economy

•Environment

Ecofascism

- Sabotage actions
- Tree-sitting
- Limiting the global population
- Ban on using certain chemicals
- No technological development


Social
Bearable
Equitable
Sustainable
Environment
Viable
Economic

Sustainable development

- Genesis – The Club of Rome and „Limits of growth”

„Humankind cannot do with our planet whatever they want”

- Begining in year 1987.
- Brundtland Report– *„Our common future”*

„…sustainable development is possible, in which the needs of present generations can be fulfilled without decreasing chances of future generations to fulfill their needs.”

Sustainable development

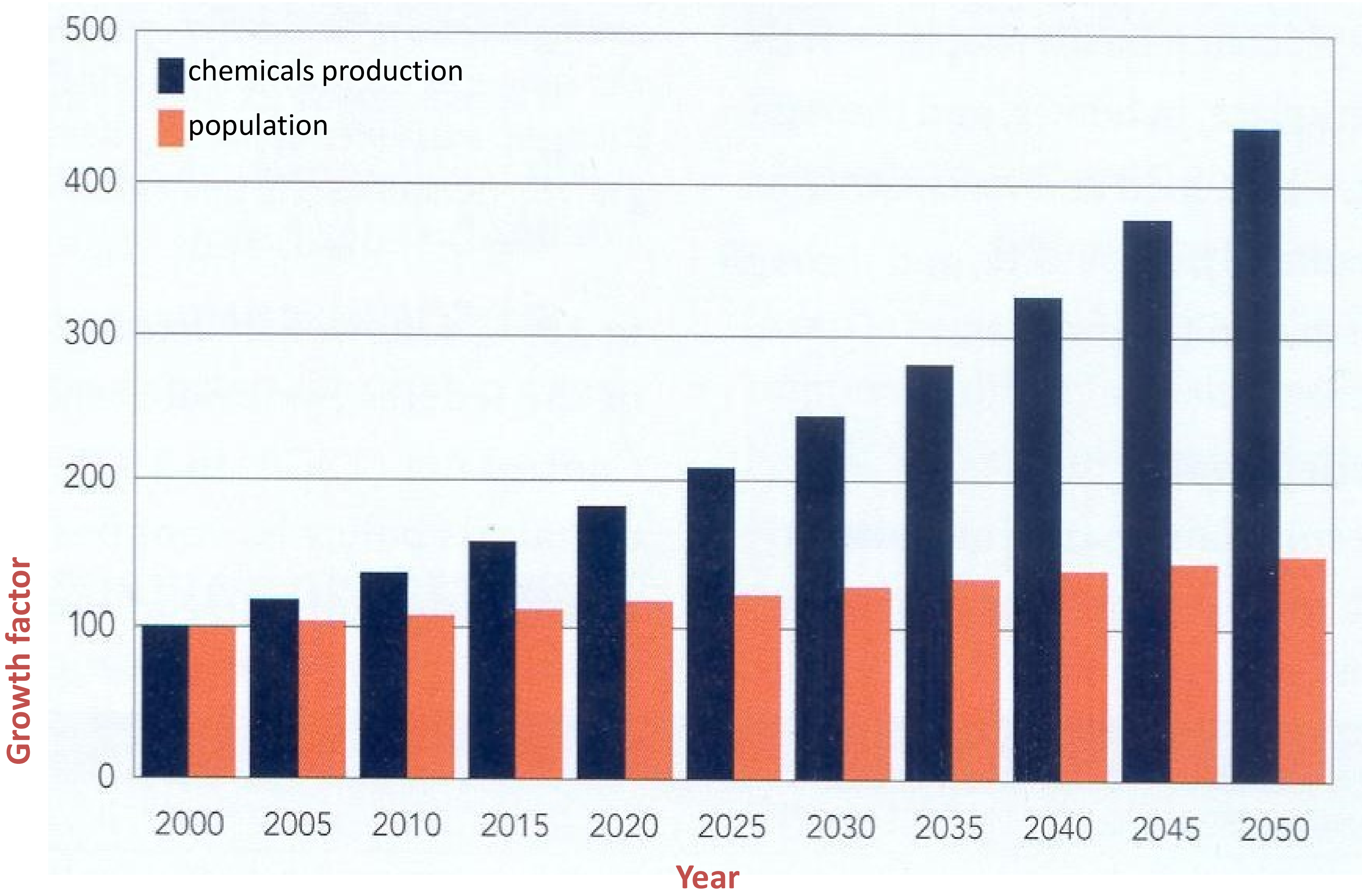
- Econimic growth increases social integrity – no social exclusion
- Economic growth considers the environment its ecosystems
- Growth prohibits overexploitation

Sustainable development

„We did not inherit Earth from our parents but we borrowed it from our children”

Think globally,

Act locally


chemicals production
population
Growth factor
500
400
300
200
100
0
2000
2005
2010
2015
2020
2025
2030
2035
2040
2045
2050
Year

GREEN CHEMISTRY

- Developed by Paul Anastas
- 1999 year
- Publication of 12 Principles of Green Chemistry

Definition

- Design of processes and products in a way to limit or eliminate hazardous substances.
- Considers entire product life cycle, from its design, production, application and disposal.

Risk = hazard x exposure

- Historical approach:

  Dilution is the best solution for pollution

- Green chemistry approach:

  An unce of prevention is worth a pound of cure

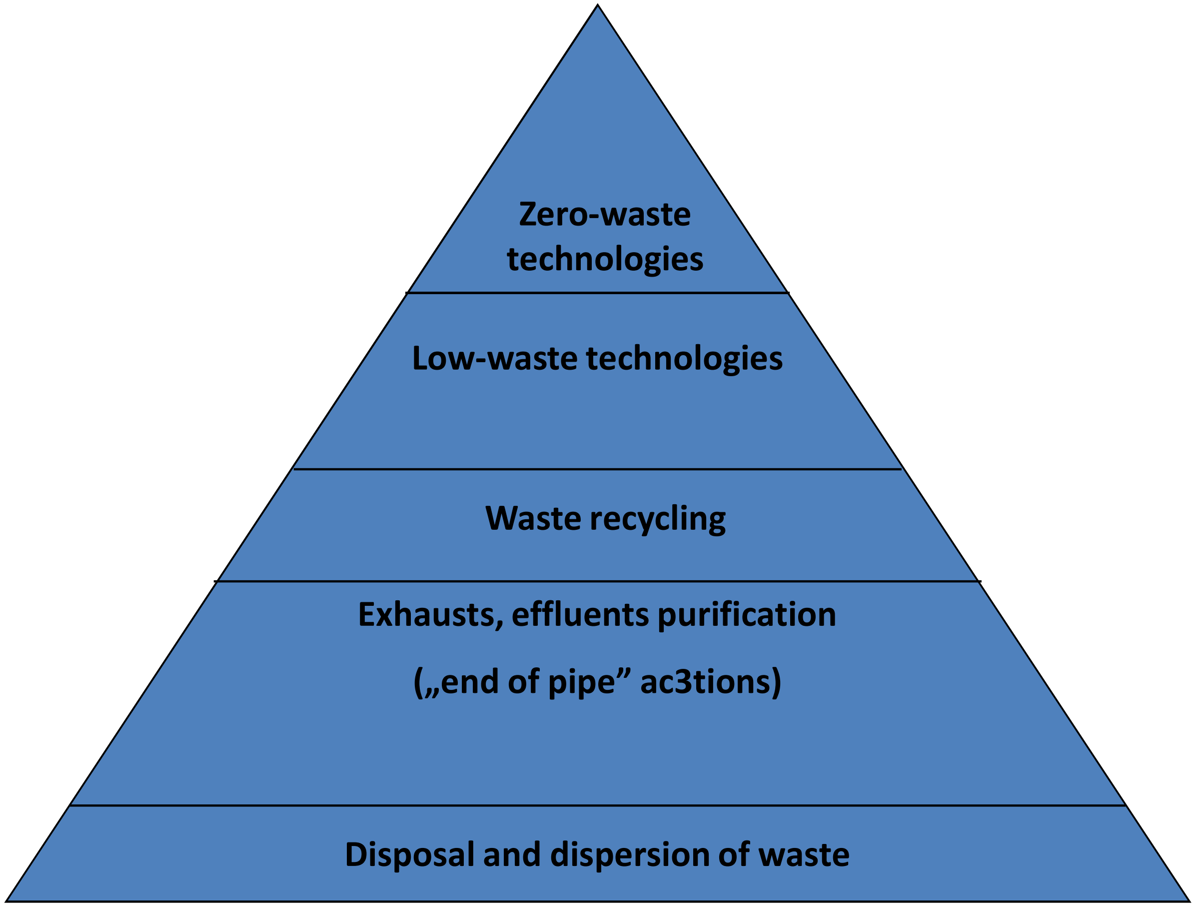
Green chemistry – synonims

- Environmentally friendly chemistry
- Proecological chemistry
- Clean chemistry

1. **Prevention**

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

Hierarchy in proecological actions in the manufacturing and production

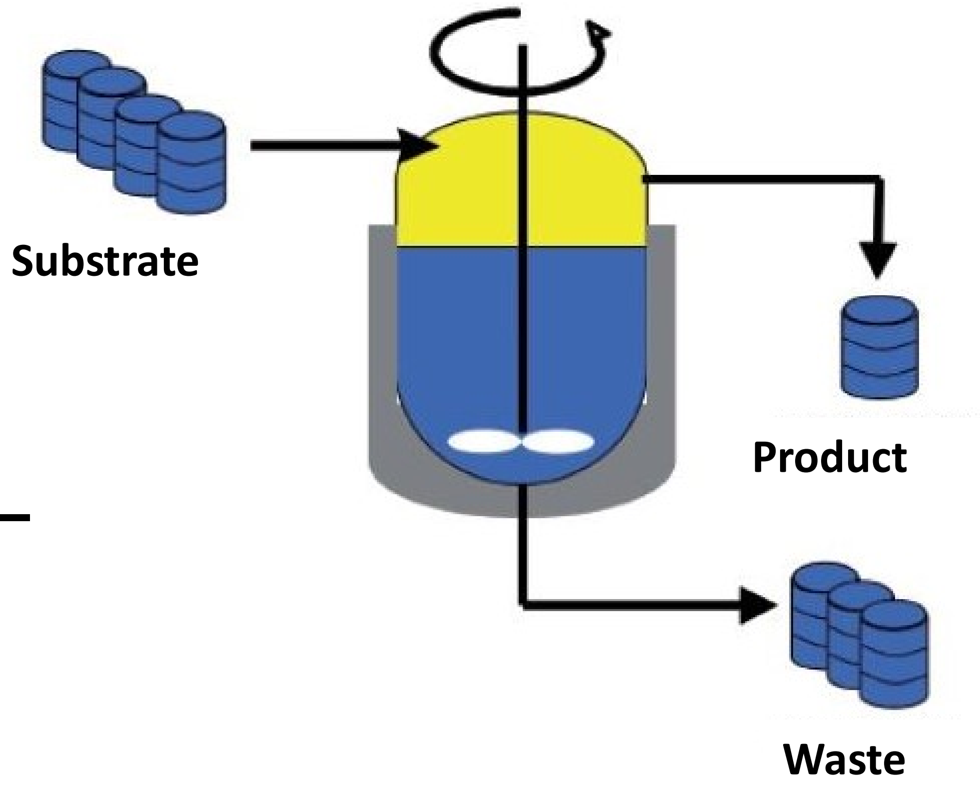


2. **Atom Economy**

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

E-factor (kg/ kg)

$$E = \frac{\textbf{Mass waste (kg)}}{\textbf{1 kg of product}}$$



R. A. Sheldon, *Chem. Ind.,***23***,* 903–906 (1992)

Waste in chemical production

Industry	Production scale (t)	E -factor (kg waste / kg product)
Petrochemistry	$10^6 – 10^8$	~ 0,1
Bulk chemistry	$10^4 – 10^6$	< 1 – 5
Fine chemistry	$10^2 – 10^4$	5 – 50
Pharmaceutical chemistry	$10 – 10^3$	25 – 100

R. A. Sheldon, *Green Chem.,* **9**, 1273-1283 (2007)

The drawback of e-factor is lack of characterization of produced waste and its influence on environment.

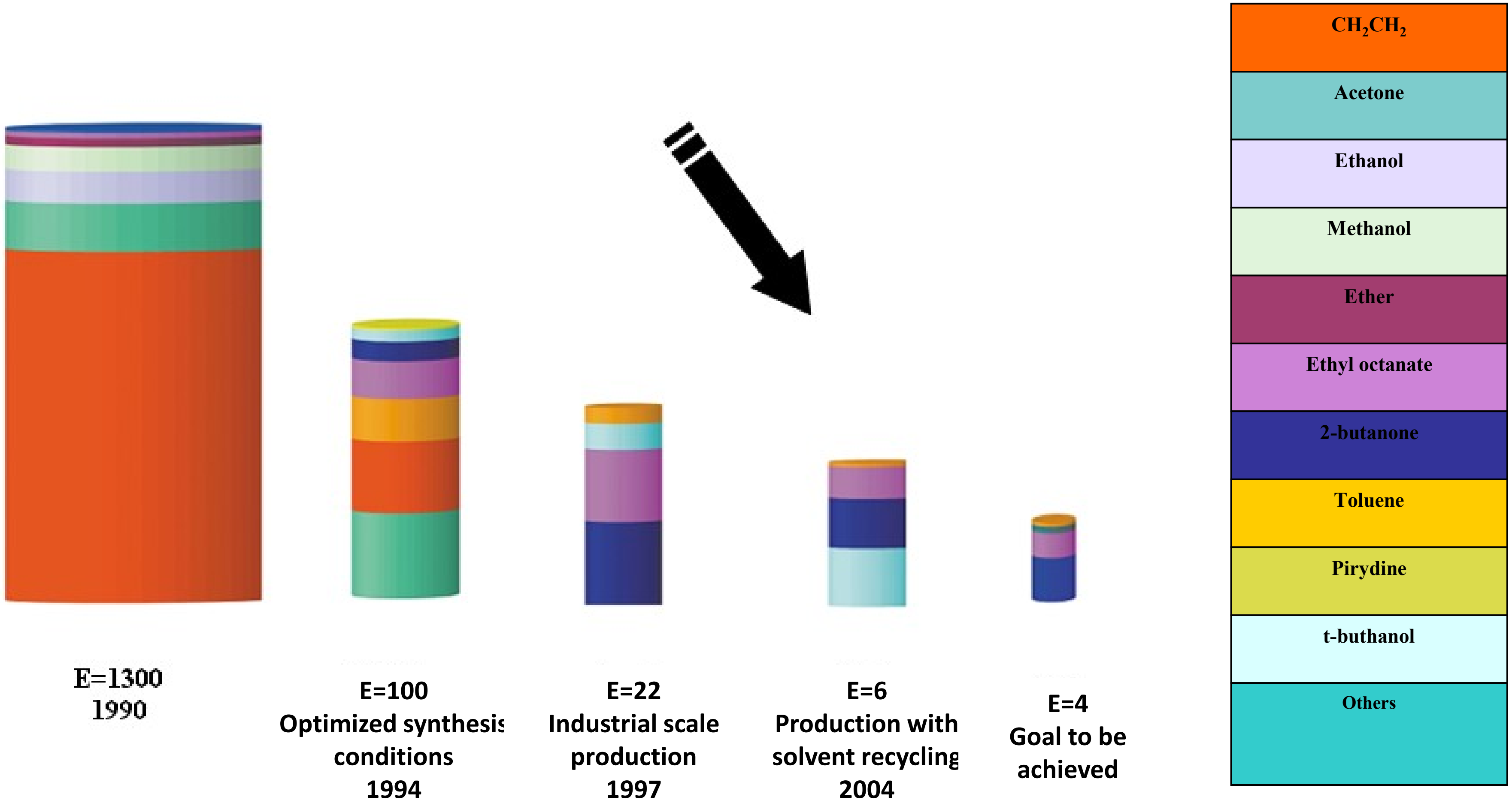
<u>Example:</u>

Environmentally friendly process of synthesis of SILDENAFIL CITRATE.

E= 6 kg waste/ kg product

P. J. Dunn, S. Galvin, K. Hettenbach, *Green Chem.*, **6**, 43-48 (2004)

Development of sildenafil citrate (VIAGRA ™) production



P. J. Dunn, S. Galvin, K. Hettenbach, *Green Chem.,* **6**, 43-48 (2004)

3. **Less Hazardous Chemical Syntheses**

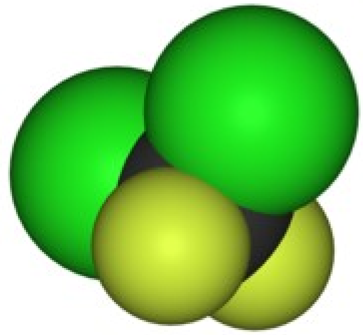
Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

i.e. synthesis with the help of microorganisms

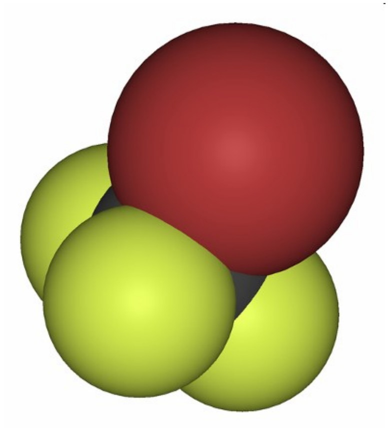
4. **Designing Safer Chemicals**
Chemical products should be designed to affect their desired function while minimizing their toxicity.

Freons used as:

- Solvents;
- Refridgerator working fluids;
- Gases in sprays;
- Anaesthesiological gases.



Freon-12 (Dichlorodifluoromethane; R-12)



Halon 1301 – bromotrifluoromethane – CBrF3)

OZONE DEPLETION POTENTIAL- ODP

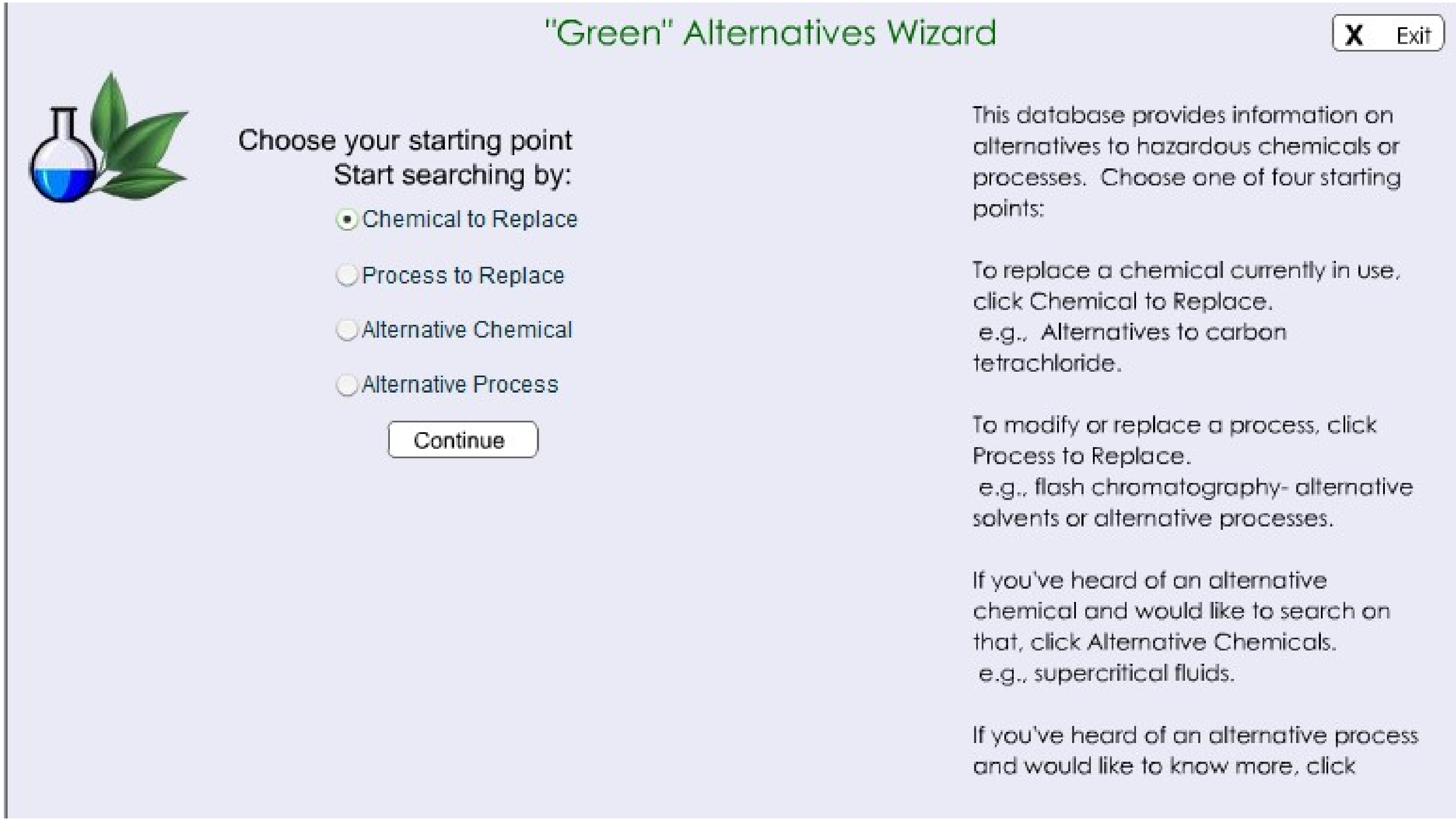
ODP depends:

-**Armospheric lifetime (mainly the number of H atoms)**

-**Reactivity towards ozone (mailny number of Br atoms)**

- Alternative pesticides:
  - Insecticides based on pheromones
  - SERENADE – antifungal agent in strawberry crops protection – stimulates the immunological responses in plants

Search for green alternatives for chemicals and processes – database „Green” Alternatives Wizard



http://ehs.mit.edu/greenchem/

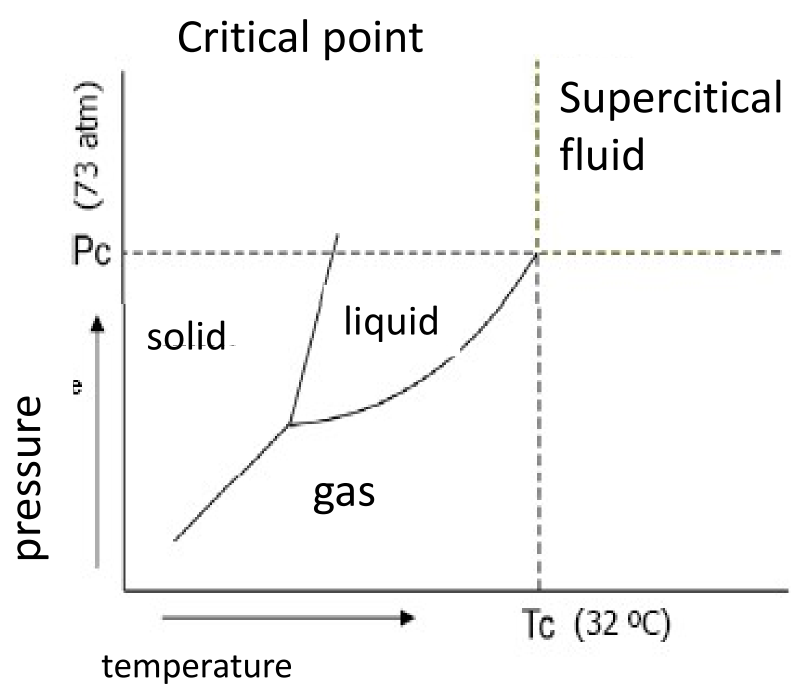
5. **Safer Solvents and Auxiliaries**

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

Undesirable features of organic solvents

- Volatile
- Toxic
- Carcinogenic
- Teratogenic
- Mutagenic
- Toxic towards aquatic organisms
- POCP – *photochemical ozone creation potential*
- They are environment of reaction, ONLY

Supercritical fluids



Phase diagram for single compound

Critical temperature

Maximum temperature in which gas can be changed to liquid while increasing pressure.

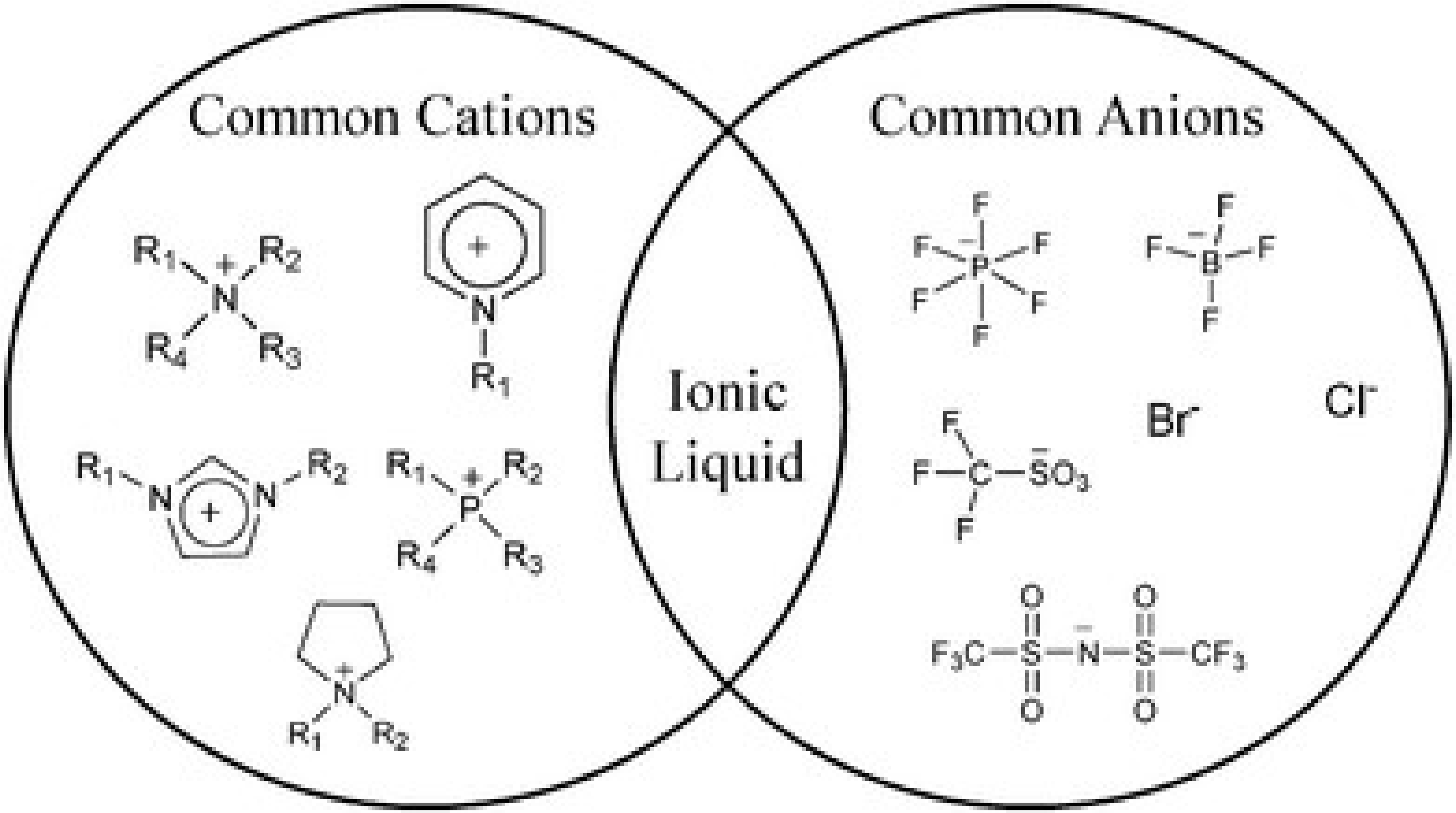
Critical pressure

Maximum pressure in which liquid can be changed to gas while increasing temperature.

Supercritical fluids – Why carbon dioxide is green solvent?

- Nontoxic
- Noncombustible
- Critical parameters are easily achievable
- Commercially available
- Relatively friendly for the environment

Ionic liquids



M.D. Joshi and J. L. Anderson RSC Adv., 2, 5470–5484 (2012)

Ionic liquids

Properties:

- Nonvolatile
- Dissolve organic and inorganic compounds
- Often nonmiscible with water
- Thermally stable (up to ~300 °C)
- Dissolve catalysts
- Their properties can be designed by proper selection of cation and anion

Applications:

- **Extraction**
- Reaction media
- Dissolving raw materials i.e. cellulose

Solventless techniques

Liquid solvents are not needed

Gain in popularity of these techniques

1.Environmental aspects:

✓Solvent waste are (very) toxic and can be emitted to environment.

2.Economic aspects:

✓High proce of high purity solvents

✓High recycling costs

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.

- Application of catalysts
- RT reactions
- Efficient energy delivery to the system
  - microwaves
  - ultrasounds
  - UV radiation

7. **Use of Renewable Feedstocks**
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Bio - substrates

- cellulose
- sea algae
- fruit waste
- mullosks shells
- rapeseeds
- wastes

LOCAL PRODUCT!!!

Biorafineries

- The main aim of biorefinery is separation of many valuable compounds produced by nature.
- These compounds are valuable products or are substrates for further reactions to obtain other compounds

Biorefineries

- Extraction of:
  - Pharmaceuticals
  - Insecticides
  - Fragnances
  - Dyes
  - Proteins
  - Enzimes
  - Carbohydrates

Perspectives on finding new compounds produced by nature

- Profitability of application of biosubstrates is criticized
- It depends on the distances substrates need to be transported
- Bioethanol – profitable???

8. **Reduce Derivatives**

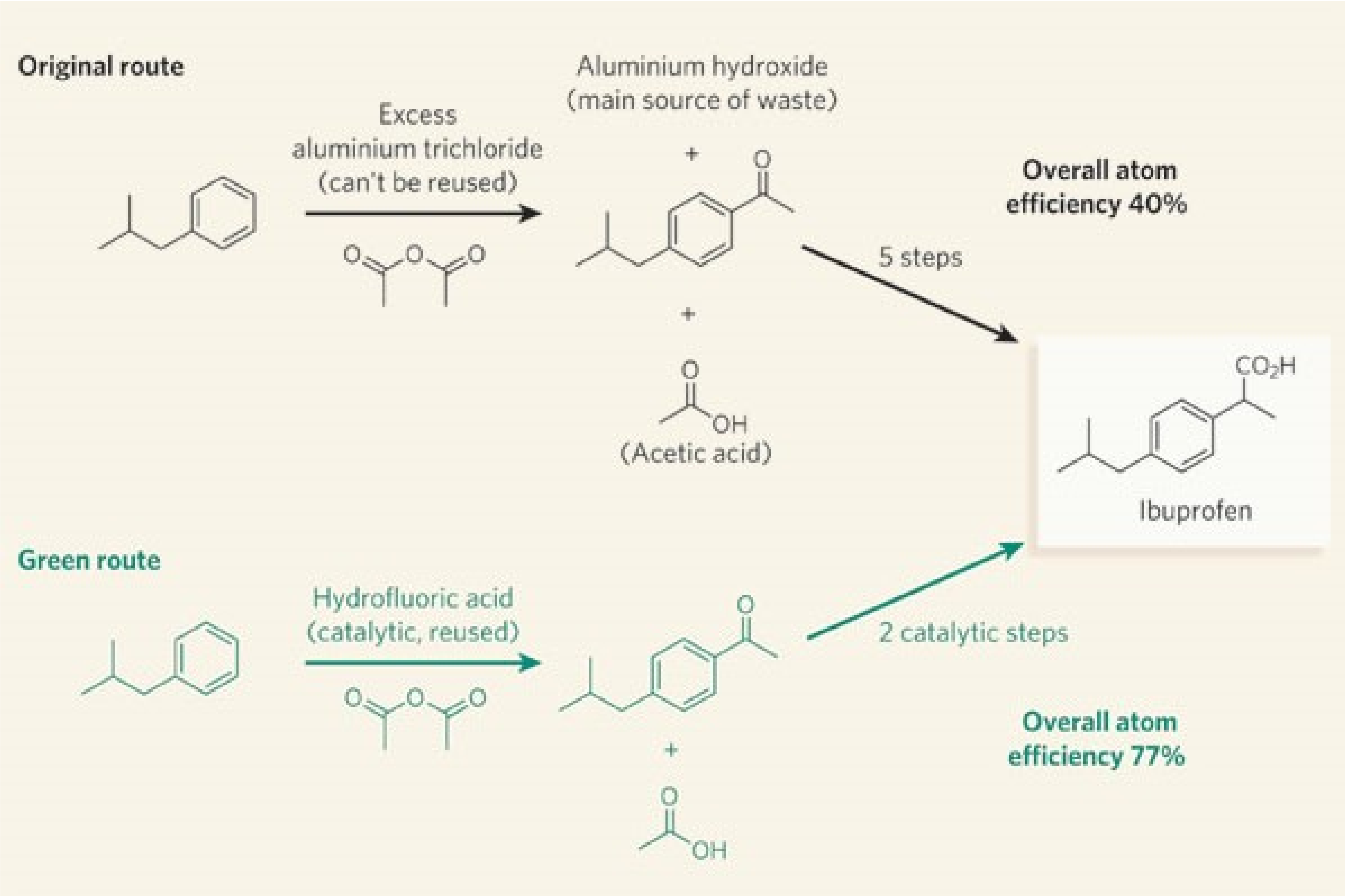
Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

- Avoiding of derivatization reactions
- Avoiding of protective goups application

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

- Metal catalysts
- Enzimes

- Only desired reactions take place
- Reactions in benign conditions


Original route
Excess
aluminium trichloride
(can't be reused)
Aluminium hydroxide
(main source of waste)
+
+
OH
(Acetic acid)
5 steps
Overall atom
efficiency 40%
CO_2H
Ibuprofen
Green route
Hydrofluoric acid
(catalytic, reused)
+
OH
2 catalytic steps
Overall atom
efficiency 77%

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.

- Polimers
  - Packages
  - Degradable products
- Pesticides

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.

- Application of sensors
  - Characterized by short response time
  - Sensitive
  - Working remotely

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.

Ecological catastrophes

- Seveso - 2,3,7,8 - TCDD
- Bophal - methyl isocyanate
- Enschede – fireworks factory explosion and fire
- Baia Mare –Dunai pollution with cyanides and HMs
- Chernobyl

How to measure greenness?

„You cannot manage things, you cannot measure"

Green Chemistry efectiveness measures

(Environmental quotient- EQ)

$$EQ = E \times Q \qquad [1]$$

Where: Q - ***Environmental Hazard Quotient***

The calue of Q is related to ecotoxicity of generated waste, i.e.:

- NaCl	***Q=1***
- HMs	***Q => <100;1000>***

(Environmental Assessment Tool for Organic Synthesis- EATOS [2])

[1] K. Hungerbuhler, *Ind. Eng. Chem. Res.,* **37**, 3395-3413 (1998)
[2] K. Hungerbuhler, *Ind. Eng. Chem. Res.,* **39**, 960-972 (2000)

Effective Mass Yield - EMY (%)

$$\frac{\textbf{Mass of reaction product} \times 100}{\textbf{Mass of toxic or environmentally problematic reagents}}$$

T. Hudlicky, D.A. Frey, L. Koroniak, C.D. Claeboe, L.E. Brammer, *Green Chem.,* **1**, 57-59 (1999)

Atom Economy – AE *OR* ***Atom Efficiency – AE***

Allows to calculate the fraction of substrates that make up final product

Examples:

1)

$$A + B \rightarrow C \Rightarrow AE = \left(\frac{\text{mass C}}{\text{mass A} + \text{mass B}} \right) \times 100\%$$

2)

$$\left. \begin{array}{l} A + B \rightarrow C \\ C + D \rightarrow E \\ E + F \rightarrow G \end{array} \right\} \Rightarrow AE = \left(\frac{\text{mass G}}{\text{mass A} + \text{mass B} + \text{mass D} + \text{mass F}} \right) \times 100\%$$

B.M. Trost, *Science*, **254**, 1471-1477 (1991)

Carbon Efficiency – CE

Allows to calculate the fraction of carbon from susbtrated that make up the final product

Example:

$$A + B \rightarrow C$$

$$\text{CE} = \frac{\textbf{Amount of carbon in product} \times \textbf{100\%}}{\textbf{Total amount of carbon in substrates}}$$

Stoichiometric Factor – SF

$$SF = 1 + \frac{\textbf{(AE) } \boldsymbol{\Sigma} \textbf{ mass of substrates excess}}{\textbf{Mass of product (assuming efficiency of 100\%)}}$$

J. Andraos, *Organic Process Res. Develop.*, **9**, 404-431 (2005)

Solvent and catalyst environmental impact parameter – f

$$f = \frac{\mathbf{\Sigma\ of\ masses\ of\ solvents\ and\ substrates + mass\ of\ catalysts}}{\mathbf{Mass\ of\ final\ product}}$$

J. Andraos, *Organic Process Res. Develop.*, **9**, 404-431 (2005)

Ecoscale

ECOSCALE: 100- penalty points

Comparison of chemical reactions and chemical syntheses

Scale:

0- <u>nonfavourable reactions</u>

100- <u>ideal reactions,</u>

Substrate A reacts with substrate B with 100% efficiency to form compound C in RT with minimal chemists exposure and environmental hazards.

Penalty points are given for any threat, hazard or low efficiency

K. Van Aken, L. Strekowski, L. Patiny, *Beilstein J. Org. Chem.,* **2**, 3-10 (2006)

Chemicals hazards

Globally Harmonized System of Classification and Labeling of Chemicals (GHS) –

Physical hazards

Health hazards

Environmental hazards

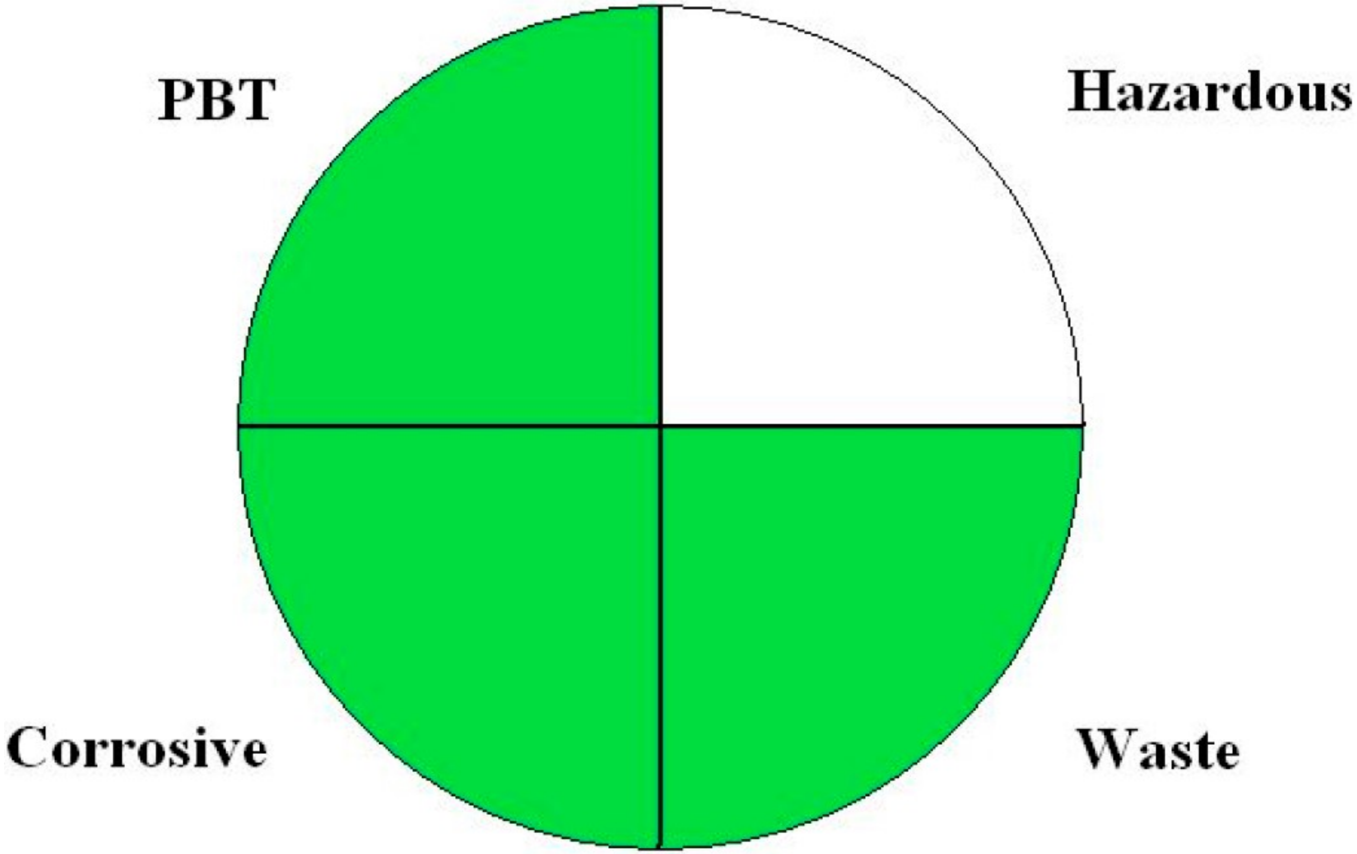
U. S. EPA National Environmental Methods Index-NEMI

PBT – any chemical is listed as peristent, bioacumulative or toxic

Hazardous – any chemical is listed as hazardous compound

Corrosive – pH is below 2 or above 12

Waste – the amount of waste produced is more than 50 g



Analytical Eco-scale

Eco-scale result = 100 – penalty points

Score:
100 – ideally **„green”**
>75 – **„ green”**
>50 – acceptably**„ green”**
<50 – not acceptably **„ green”**

Whole analytical procedure

Penalty points:
- amounts and hazards related to chemicals
- occupational exposure
- energy consumption
- waste generation

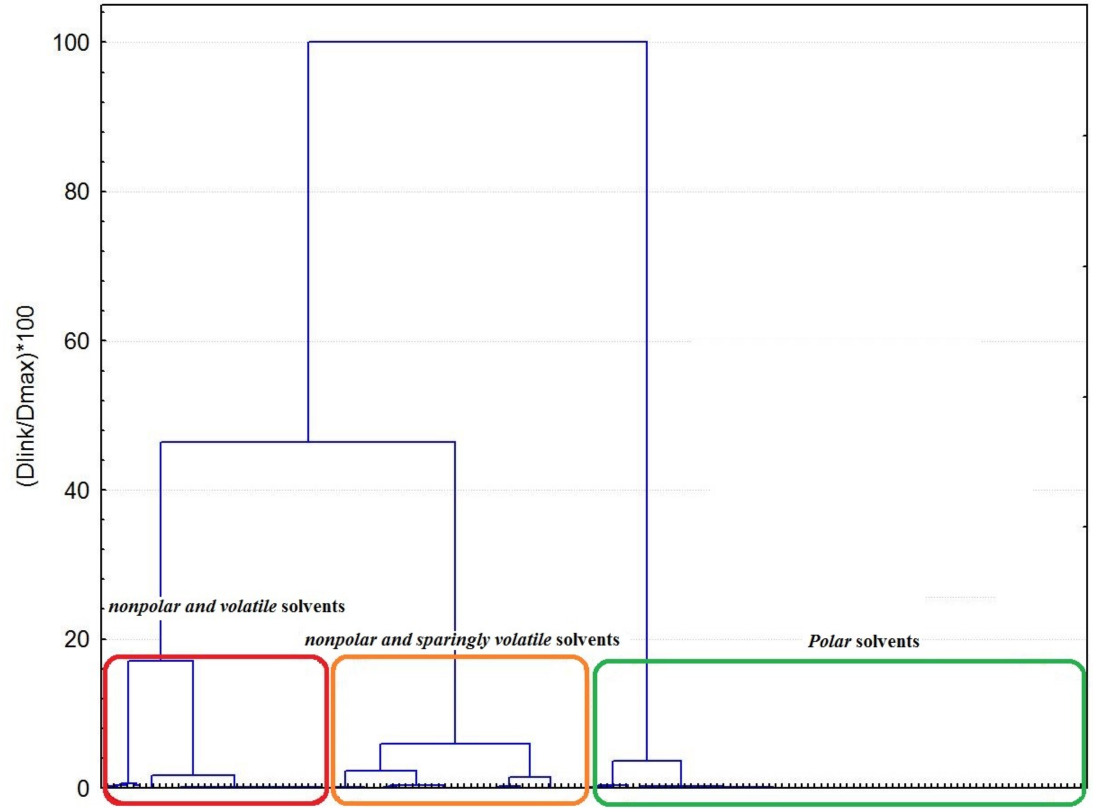
Trends in Analytical Chemistry, Vol. 37, 2012

Analytical Eco-Scale for assessing the greenness of analytical procedures

Agnieszka Gałuszka, Piotr Konieczka, Zdzisław M. Migaszewski, Jacek Namieśnik

SOLVENT SELECTION GUIDE

- Assessment of 151 solvents



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Cite this: *Green Chem.*, 2015, **17**, 4773

A solvent selection guide based on chemometrics and multicriteria decision analysis

Marek Tobiszewski,[a] Stefan Tsakovski,[b] Vasil Simeonov,[b] Jacek Namieśnik[a] and Francisco Pena-Pereira*[a,c]

SOLVENT SELECTION GUIDE

- Criteria for rankings:
  - Oral LD50
  - Inhalation LC50
  - IACR cancer class
  - Other specific effects
  - Fish LC50
  - Fish NOEL
  - BOD t1/2
  - Hydrolysis t1/2
  - Log BCF
  - Recycling by distillation
  - Feedstock renewability
  - Flash point
  - Flammability
  - Combustion products
  - POCP

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SOLVENT SELECTION GUIDE

- Availability of data
  - Rankings of solvents within confidence levels
  - High confidence – all criteria
  - Low confidence – only available criteria

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Solvent	High confidence ranking	Medium confidence ranking	Low confidence ranking	Very low confidence ranking
Water	0.849	0.849	0.778	0.668
Glycerol	0.451	0.379	0.499	0.659
Propanol	0.416	0.349	0.424	0.676
Ethanol	0.407	0.359	0.449	0.696
Methanol	0.382	0.305	0.350	0.546
Acetone	0.382	0.328	0.385	0.603
Acetic acid	0.381	0.332	0.393	0.634
Formic acid	0.375	0.329	0.385	0.622
Benzyl alcohol	0.372	0.329	0.378	0.590
Hexanoic acid	0.369	0.325	0.386	0.603
Butyl lactate	0.368	0.320	0.382	0.590
Butyric acid	0.368	0.320	0.381	0.604
Isobutyric acid	0.368	0.321	0.366	0.584
Furfural	0.367	0.315	0.370	0.595
Valeric acid	0.366	0.321	0.378	0.602
Isopropanol	0.364	0.306	0.355	0.539
Hexanol	0.364	0.317	0.358	0.562
Methyl formate	0.364	0.310	0.349	0.536
Ethyl lactate	0.361	0.312	0.367	0.535
Methyl acetate	0.361	0.314	0.358	0.544
Heptanol	0.360	0.317	0.358	0.530
Cyclohexanone	0.360	0.311	0.364	0.572
2-Heptanone	0.359	0.317	0.362	0.568
Tetrahydrofuran	0.359	0.315	0.374	0.589
2-Butanone	0.358	0.311	0.373	0.576
3-Pentanone	0.356	0.308	0.360	0.558
2-Hexanone	0.356	0.306	0.354	0.546

Green Chemistry

- Establishment of Institutes for green chemistry
- Cenferences
- Journals: *Clean Processes and Products, ChemSusChem, Green Chemistry, Current Green Chemistry.*

Thank you for your attention