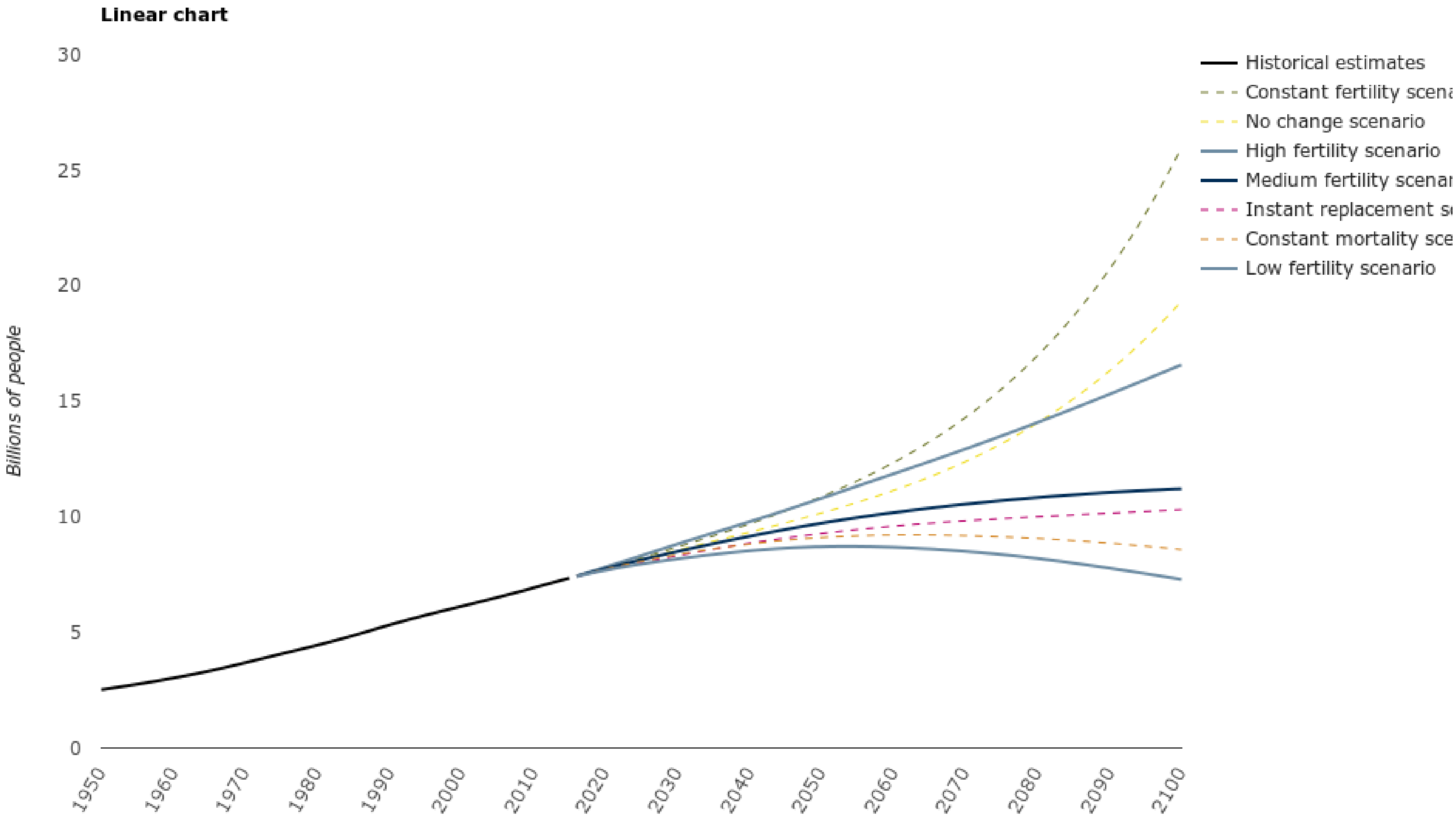
Environmentally benign chemical processes (EBChemP)

Green chemistry metrics

Erika Vági, Edit Székely

BME, Department of Chemical and Environmental Process Engineering

Population growth



The effect of growing population

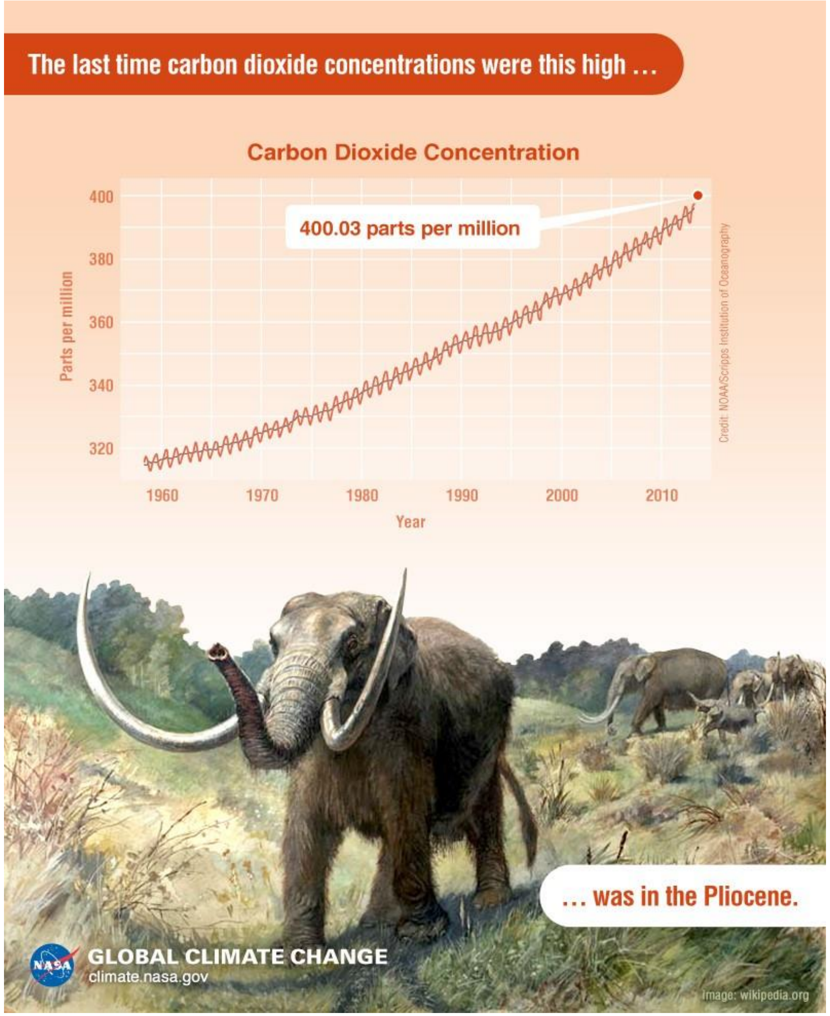
- Humans need more and more
  - Water
  - Food
  - Energy
  - And all the others (mobile phones, washing materials, cars, etc..)

→ Consume more energy, fuel based chemicals, land, basics

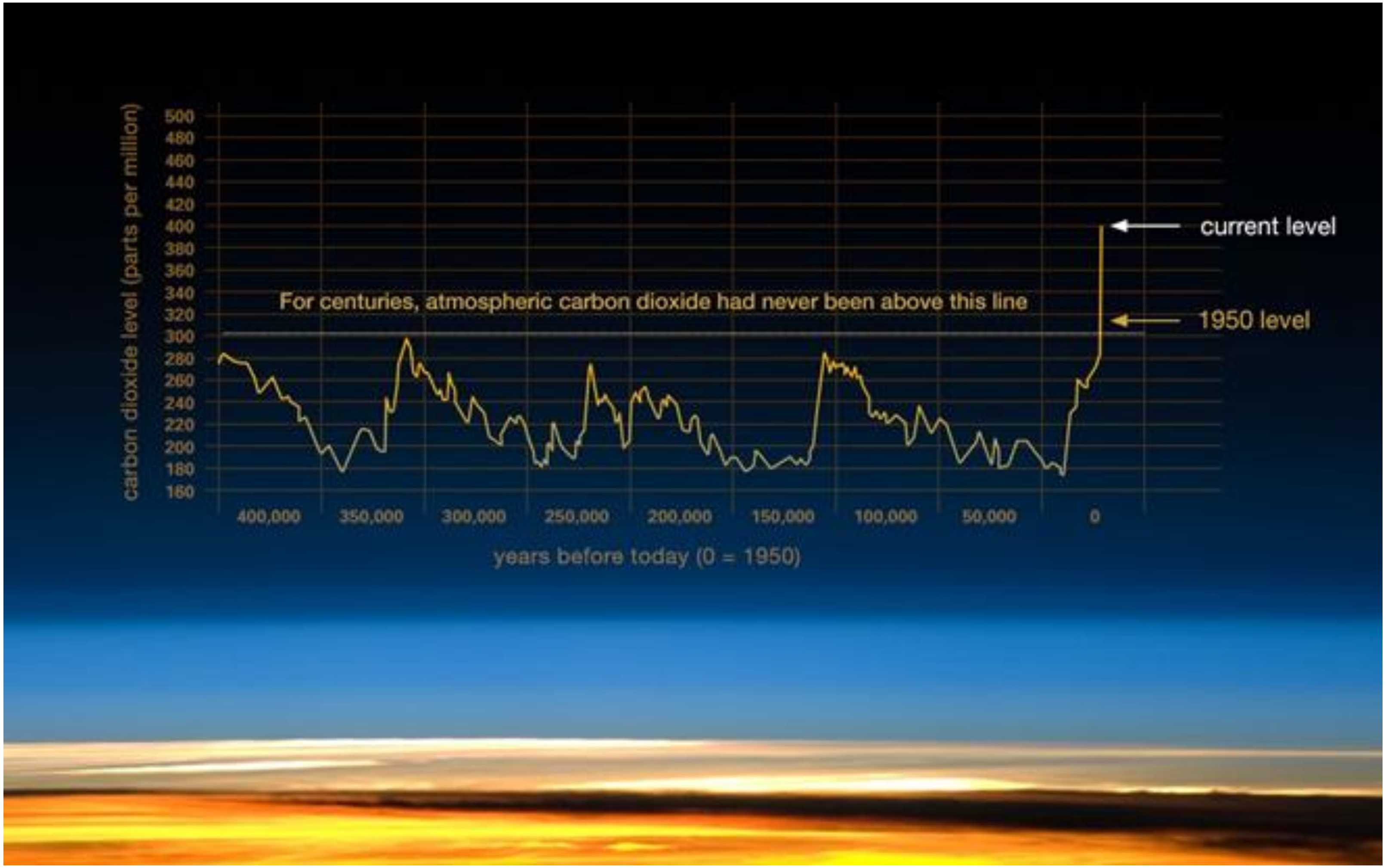
→ ? Impact on Globe?

Possible impacts:

- Increasing temperature (global warming);
- Increasing sea levels;
- Drastic climate changes;
- Decreasing drinking water;
- Running out of fuels (gases and oil)
- Increase in CO_2 concentration in atmosphere



Measuring of CO_2-level



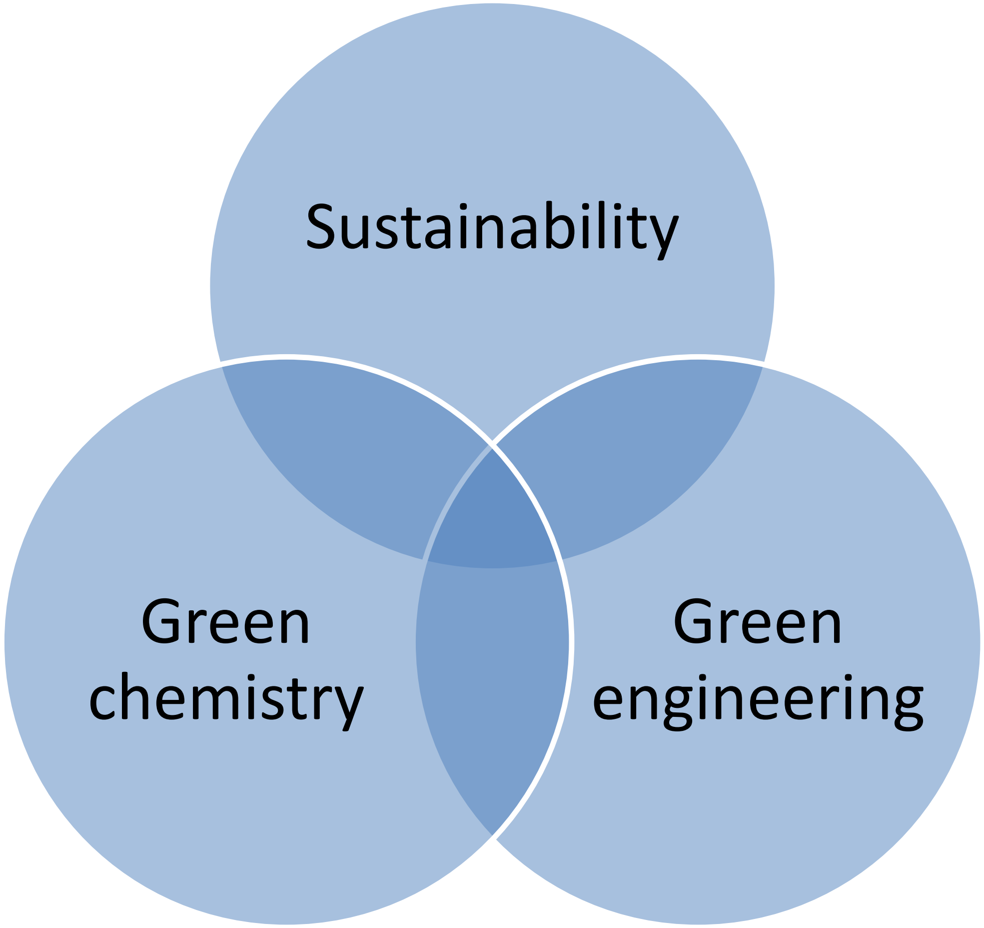
In 1995 - 315 ppm, in Jan 2019 it was 410.73 ppm.

UN- emerging environmental concerns

- Antimicrobial resistance;
- Nanomaterials;
- Marine protected areas;
- Sand and dust storms,
- Solar solutions;
- Environmental dis-placement.

UNEP (2017). Frontiers 2017 Emerging Issues of Environmental Concern. United Nations Environment Programme, Nairobi

Green….



- Sustainability
  - Ecosystems
  - Human health
- Green engineering
  - Lifecycle
  - Systems
  - Metrics
- Green chemistry
  - Reactions, catalysts
  - Solvents
  - Thermodynamics
  - Toxicology

Sustainable development

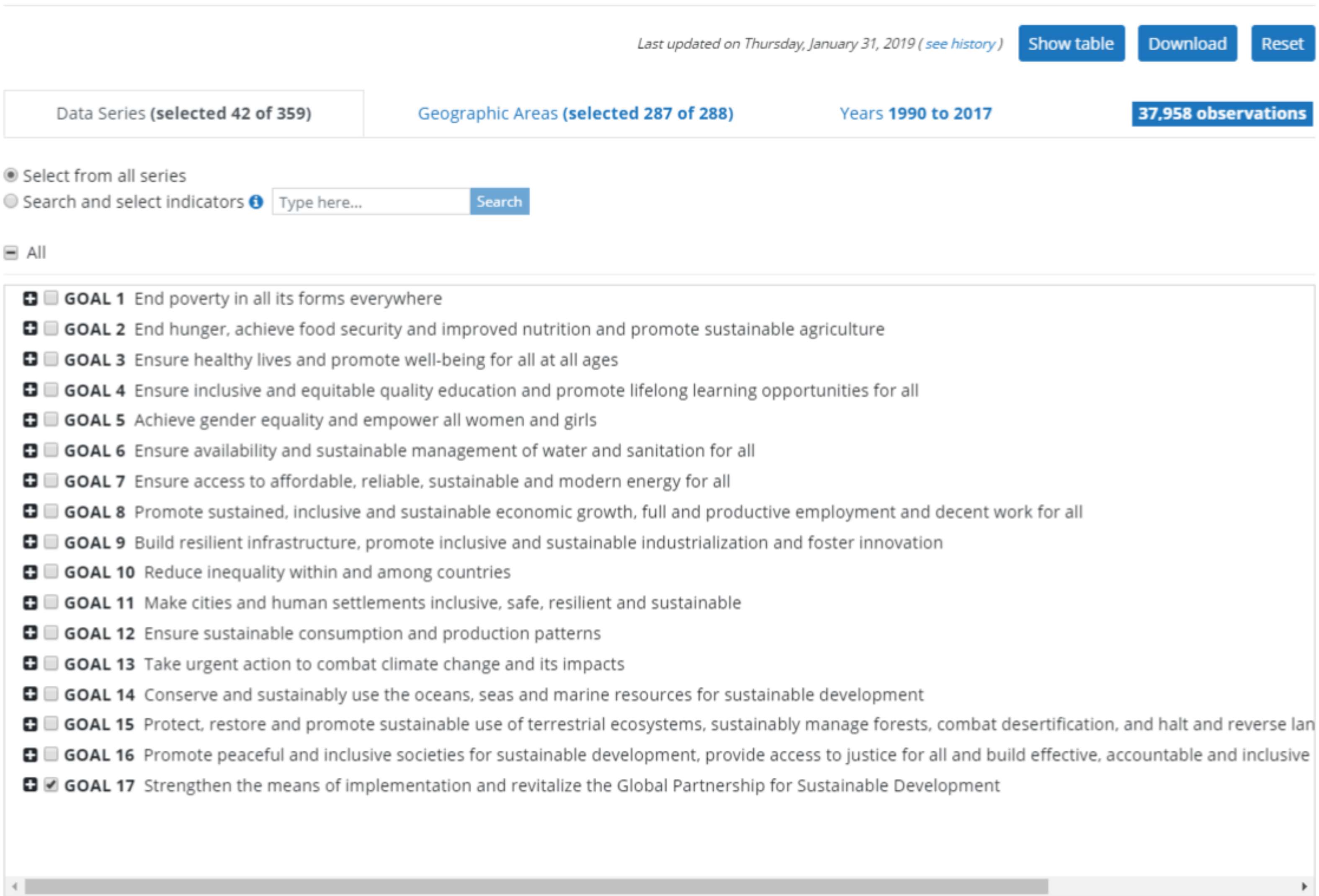
- "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs".
- It contains two key concepts:
  - the concept of "needs", in particular the essential needs of the world's poor, to which overriding priority should be given; and
  - the idea of limitations imposed by the state of technology and social organization on the environment's ability to meet present and **future needs**."

The Report of the Brundtland Commission, Our Common Future, 1987.

„sustainable development for all”

#Envision2030: 17 goals to transform the world for persons with disabilities, 2015.

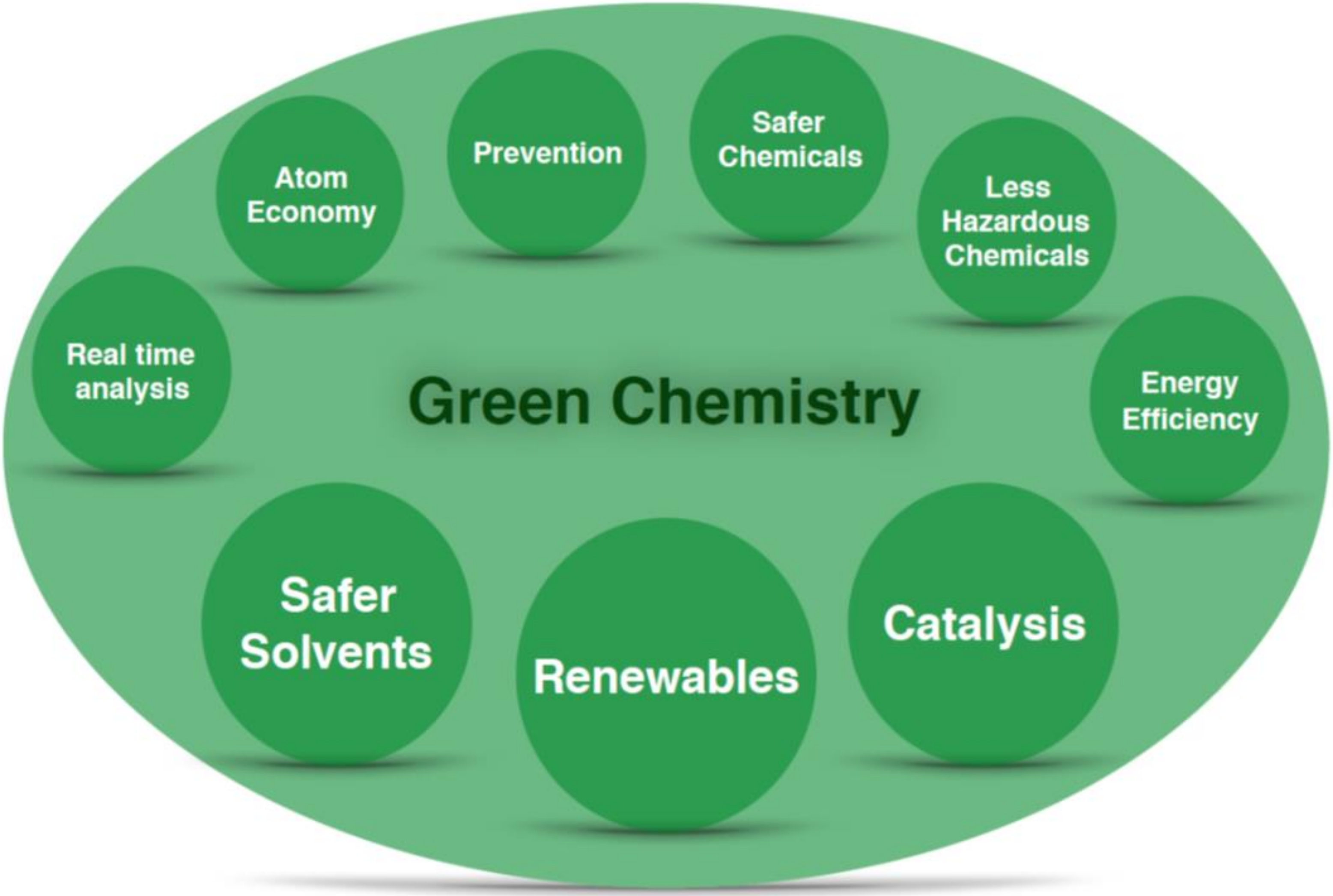
Within 17 goals, 169 SDG targets are defined and 232 indicators are tracked.



https://unstats.un.org/sdgs/indicators/database/

Sustainability is our ultimate common goal and green chemistry is the means of achieving it.

Green chemistry



Anastas, P. T.; Warner, J. C.; Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30.

Green chemistry – 12 principles (EPA)

1. **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy**
   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
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.
4. **Designing Safer Chemicals**
   Chemical products should be designed to effect their desired function while minimizing their toxicity.
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.

Green chemistry – 12 principles

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.
7. **Use of Renewable Feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
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.
9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Green chemistry – 12 principles

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.
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.
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.

Anastas, P. T.; Warner, J. C.; Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30.

Challenge of Green Chemistry

- A central goal of Green Chemistry is not only to ensure that **energy efficiency** is ingrained from the molecular level and through our products, processes, and systems, but also to ensure that the **nature of that energy is sustainable** to both humans and the biosphere.
- Decrease the use of solvents, apply new solvents (water, $scCO_2$, ionic-liquids) and recycling
- Discover and develop new chemical reactions or processes with high yields (95 - 99%).

Horvath T. I. and P. T. Anastas - Chem. Rev. 2007, 107, 6, 2169-2173

Green engineering (EPA)

Green Engineering is the design, commercialization and use of processes and products that are *feasible* and *economical* while:

- Reducing the generation of pollution at the source.
- Minimizing the risk to human health and to the environment.

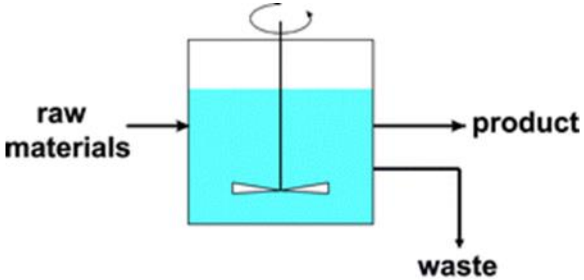
12 Principles of Green Engineering

The Twelve Principles of Green Engineering [1]

Principle 1 – Designers need to strive to ensure that all material and energy inputs and outputs are as inherently non-hazardous as possible.
Principle 2 – It is better to prevent waste than to treat or clean up waste after it is formed.
Principle 3 – Separation and purification operations should be a component of the design framework.
Principle 4 – System components should be designed to maximize mass, energy and temporal efficiency.
Principle 5 – System components should be output pulled rather than input pushed through the use of energy and materials.
Principle 6 – Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse or beneficial disposition.
Principle 7 – Targeted durability, not immortality, should be a design goal.
Principle 8 – Design for unnecessary capacity or capability should be considered a design flaw. This includes engineering "one size fits all" solutions.
Principle 9 – Multi-component products should strive for material unification to promote disassembly and value retention – (minimize material diversity).
Principle 10 – Design of processes and systems must include integration of interconnectivity with available energy and materials flows.
Principle 11 – Performance metrics include designing for performance in commercial "after-life".
Principle 12 – Design should be based on renewable and readily available inputs throughout the life-cycle.

Anastas P. T., Zimmerman J. B. Chapter 2 in Sustainability Science and Engineering, 2006.

Quantification of environmental impacts



$$E = \frac{\text{kg waste}}{\text{kg product}}$$

- „To measure is to know” by Lord Kelvin
- „Atom economy” by B. M. Trost in 1991.
- „Atom efficiency” and „E(nvironmental)-factor” defined by R. A. Sheldon in 1992.

R. A. Sheldon – Green Chem, 2007, 9, 1273-1283.

Atom efficiency

$$AE = \frac{\sum M_{\text{product}}}{\sum \mathrm{M}_{\text{reagent}}}$$

Where M is molecular mass

Stoichiometric factor

$$SF = 1 + \frac{\sum m_{\text{reagent, in excess}}}{\sum \mathrm{m}_{\text{reagent, stoichiometric}}} =$$

$$= 1 + \frac{AE \cdot \sum m_{\text{reagent, in excess}}}{\sum \mathrm{m}_{\text{product, theoretical}}}$$

Where m is mass

Mass recovery parameter

$$MRP = \frac{1}{1 + \frac{X \cdot AE \cdot (c + s + \omega)}{SF \cdot m_{\text{product}}}}$$

Where X is the conversion (limiting compound)
m is mass
c is the mass of the reused catalyst
s is the mass of the reused solvent
ω is the mass of any reused other material

Reaction mass efficiency

$$RME = X \cdot AE \, \frac{1}{SF} \cdot MRP = \frac{1}{1+E}$$

E(nvironmental) factor (Sheldon)

$$E = \frac{\sum m_{\mathrm{waste}}}{\sum m_{\mathrm{product}}}$$

Lapkin A., Constable D.; Green Chemistry Metrics, Wiley, 2008.

E-factor

- Higher the E-factor – means more wastes → greater the environmental impact.
- But no data on the quality of wastes!
- Put it simply:

$$\frac{\text{Kg of raw material IN} - \text{kg of desired product}}{\text{kg of desired product OUT}}$$

Typical values of E factors

Industry	E-factor	Annual Production tonnes	Total Waste tpa	No of transform-ations	Years of develop-ment
Oil Refining	*ca*. 0.1	10^6 - 10^8	10 million	Separations	100+
Bulk Chemicals	<1 to 5	10^4 - 10^6	5 million	1-2	10 – 50
Fine Chemicals	5 to >50	10^2 - 10^4	0.5 million	3-4	4 - 7
Pharmaceuticals	25 to >100	10 – 10^3	0.1 million	6+	3 - 5

Due to downstream from bulk to fine chemicals, no catalysts used, batch production.

An example

Stoichiometric:

$$3\ PhCH(OH)CH_3 + 2\ CrO_3 + 3\ H_2SO_4 \longrightarrow$$

$$3\ PhCOCH_3 + Cr_2(SO_4)_3 + 6\ H_2O$$

Atom efficiency = 360 / 860 = 42% E_{theor} = ca. 1.5

Catalytic:

$$PhCH(OH)CH_3 + 0.5\ O_2 \xrightarrow{\text{Catalyst}} PhCOCH_3 + H_2O$$

Atom efficiency = 120/138 = 87% E_{theor} = ca. 0.1(0)

Byproduct: H_2O

R. A. Sheldon – Green Chem, 2007, 9, 1273-1283.

EQ factor = environmental quotient

$$EQ = \frac{\sum (m_{\text{waste,i}} \cdot Q_i)}{\sum m_{\text{product, j}}}$$

Where Q is the unfriendliness quotient

Q is 0 for water, 1 for NaCl, cromate salts >100
A list, upon agreement.
Depends on:
• physical properties (corrosivity, exposion risk, flammability, pH etc.)
• toxicological properties (letality, carcinogenity, mutagenity, acut and chronic toxicity etc.)

Advantages - disadvantages

- Simple
- Based on mass-balanced
- Adopted world-widely
- Comparison
- Give a better „big picture" view of a plan
- Need for process development

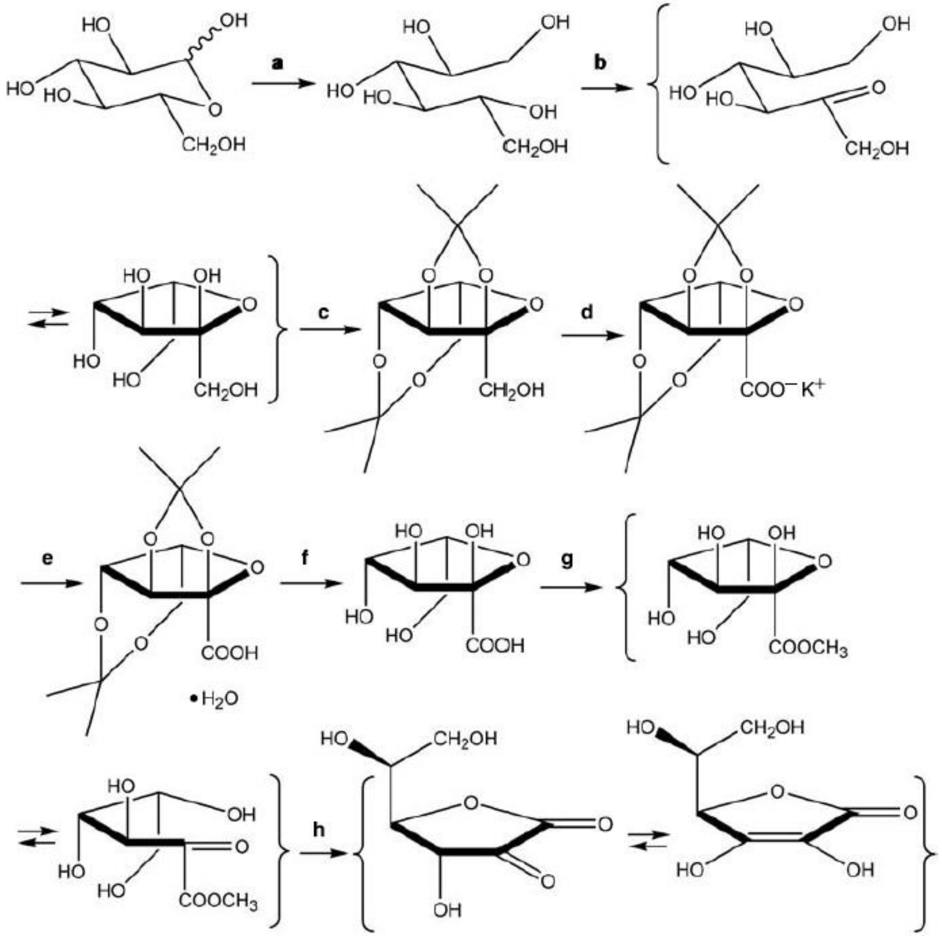
- nature of waste?
- Effect of waste on environment?

Example – Ascorbic acid synthesis

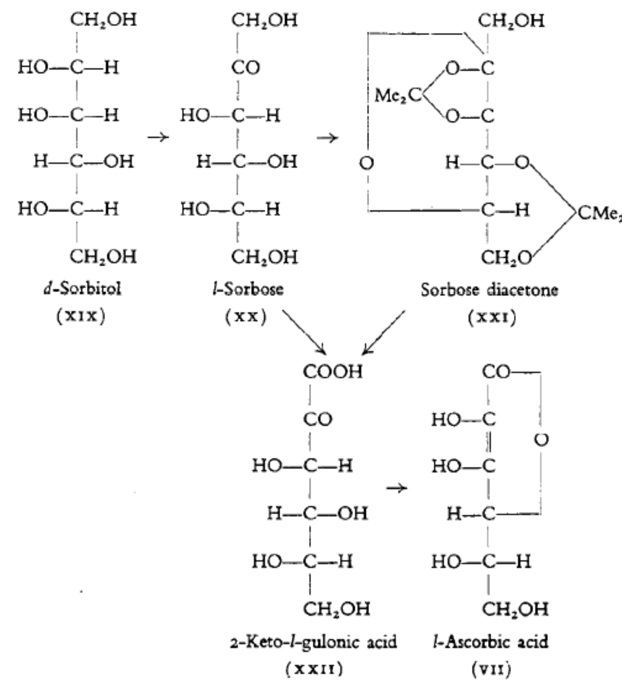
	N	M	I	δ	β	μ	% AE	% (εT)	% RME
Reichstein (1934)	8	8	12	0.377	0.749	+25.1	23.1	11.2	5.7
Haworth (1933)	12	12	27	0.412	0.895	+42.1	5.1	0.3	0.06

N – number of reaction stages
M – Number of reaction steps
I – Number of reactants input structures
δ - degree of convergence relative to single step MCR
β – asymmetry parameter
μ - first molecular weight moment
% AE – atom economy
% (εT) – reaction yield
% RME – reaction mass efficiency

Lapkin A., Constable D.; Green Chemistry Metrics, Wiley, 2008.



Scheme 4.11 Reichstein ascorbic acid (vitamin C) synthesis plan (1934). (a) H_2/Pd-C (cat.) (100%); (b) 1/2O_2, *Acetobacter suboxidans* (60%); (c) 2$(CH_3)_2CO$, H_2SO_4 (cat.) (34.5%); (d) 4/3$KMnO_4$ (91%); (e) H_2O, HCl (90%); (f) 2H_2O, H_2SO_4 (cat.) (82%); (g) 1/2$(CH_3O)_2SO_2$, (84%); (h) Na, CH_3OH, then HCl (96%).



The firm of Hoffmann–La Roche developed an industrial-scale preparation, on the basis of which over 60,000 tons of L-ascorbic acid are to this day produced annually from glucose.

Haworth's synthesis plan from sorbitol

Intensity factors for evaluation of processes (relative values for 1 kg product)

- Mass
  - Reagent
  - Solvent
  - Waste
- Energy
  - Consumed
  - Life cycle energy
  - Solvent recovery
- Waste
  - Reduce VOCs
  - Avoid bio-accumulating materials

$$\text{Mass Intensity} = \frac{\text{Total mass into the process (kg)}}{\text{Mass of product (kg)}}$$

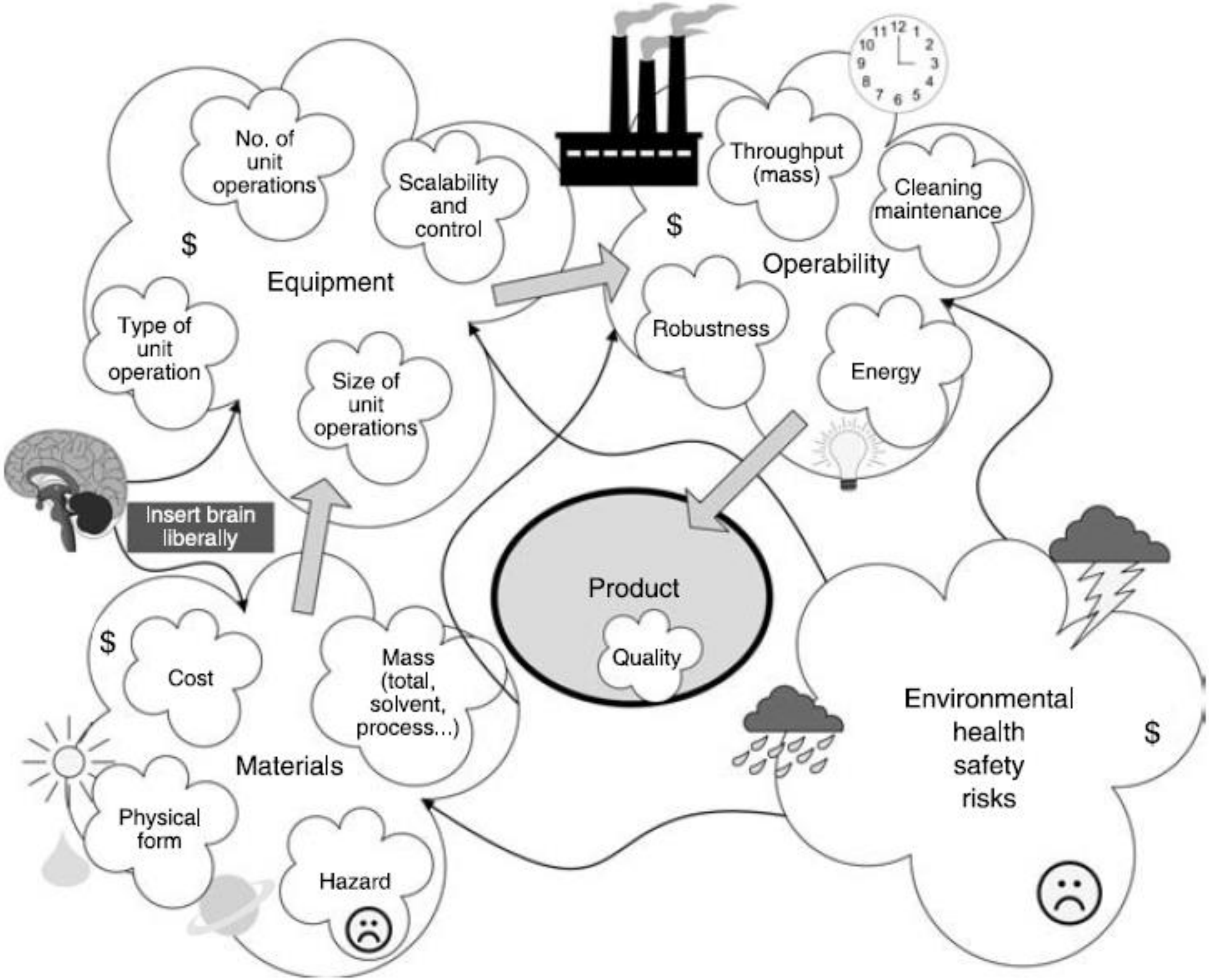
$$\text{Solvent Intensity} = \frac{\text{Total solvent input without water}}{\text{Total mass input}}$$

$$\text{Waste Intensity} = \frac{\text{Total waste produced}}{\text{Total mass input}}$$

- CO_2 equivalent
- Ethanol equivalent
- Bioethanol equivalent
- Energy equivalent

„Equivalents" in details

- **CO_2 equivalent**
  - A metric measure used to compare the emissions from various greenhouse gases on the basis of their global-warming potential (GWP), by converting amounts of other gases to the equivalent amount of carbon dioxide with the same global warming potential.
- **Ethanol equivalent**
  - Mass of EtOH needed to deliver the equivalent amount of energy from a given feedstock using energy equivalency or produce the equivalent amount of mass of carbon-based chemical using molar equivalency.
- **Bioethanol equivalent**
  - Mass of EtOH needed to deliver the equivalent amount of energy from a given biological feedstock using energy equivalency.
- **Energy equivalent**
  - Amount of energy is required to produce a certain product.



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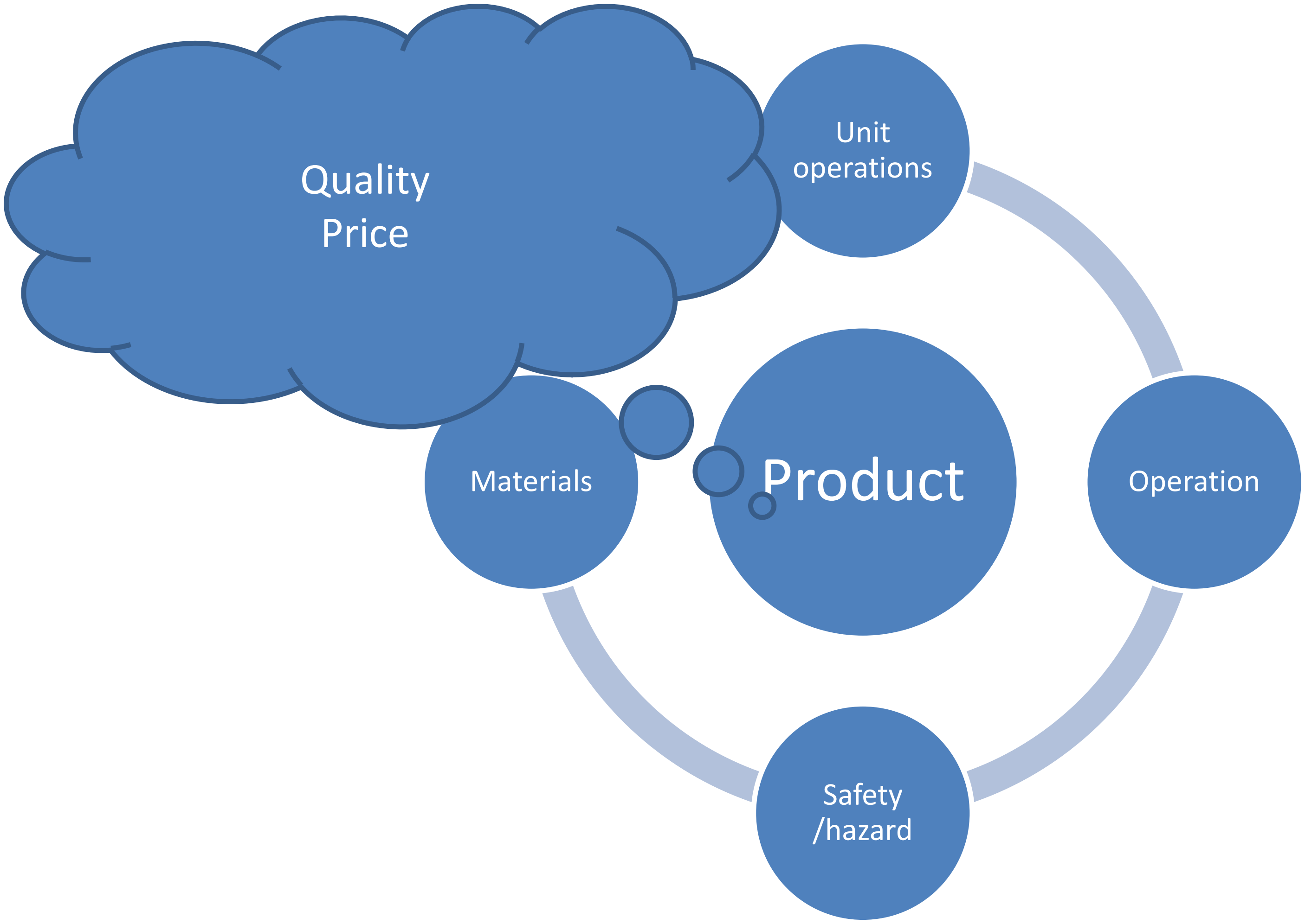
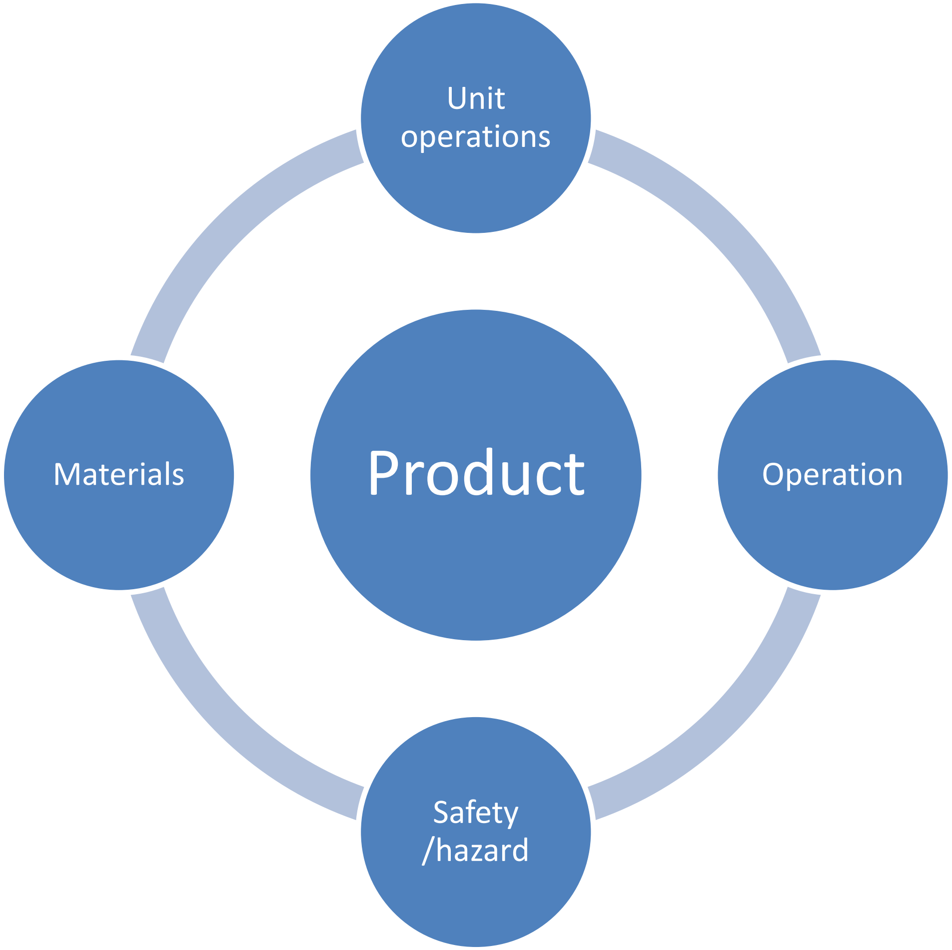
When you have to design a process…

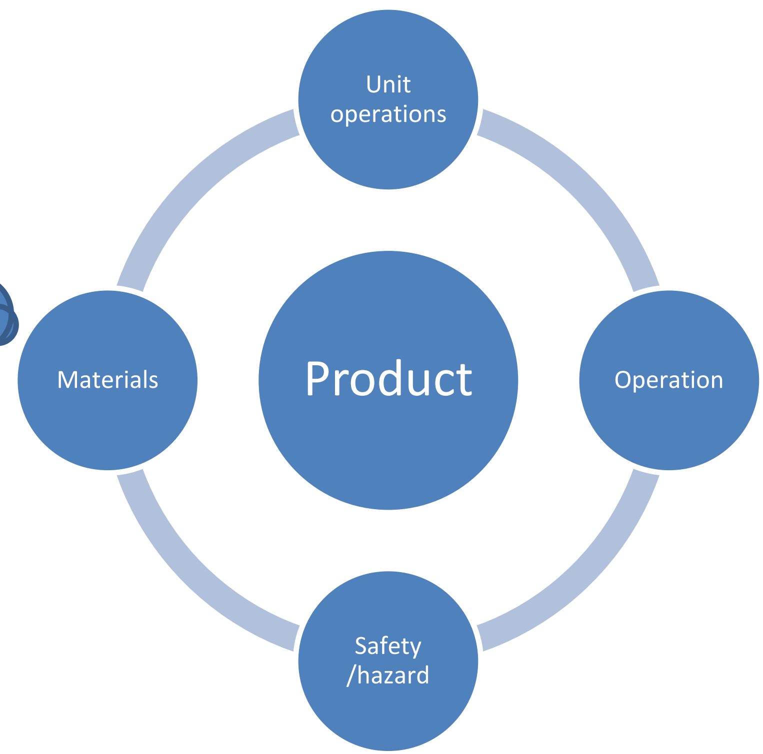


When you have to design a process…



When you have to design a process…

Chemical and physical properties,
Price vs. mass needed,
Availablity,



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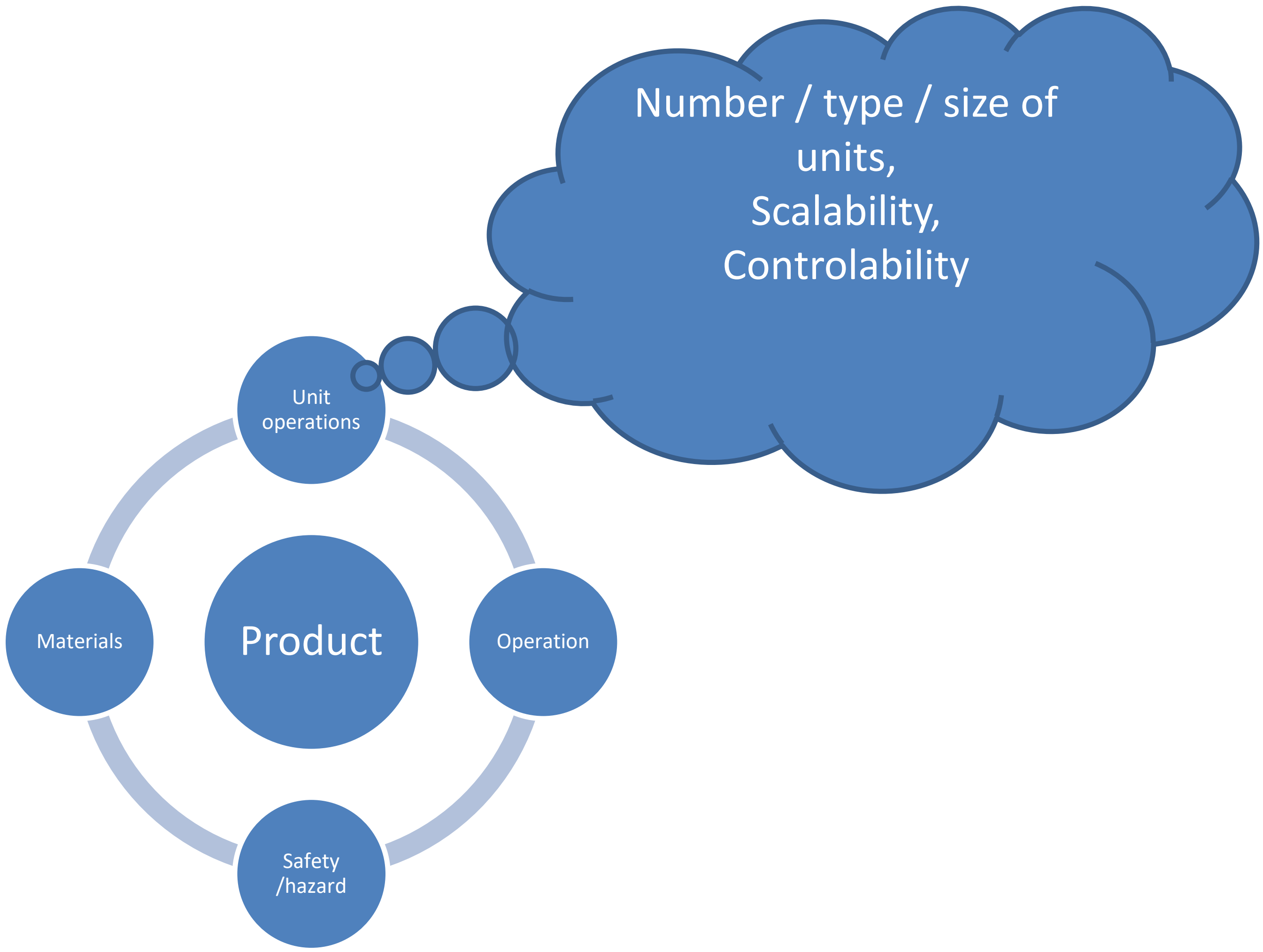

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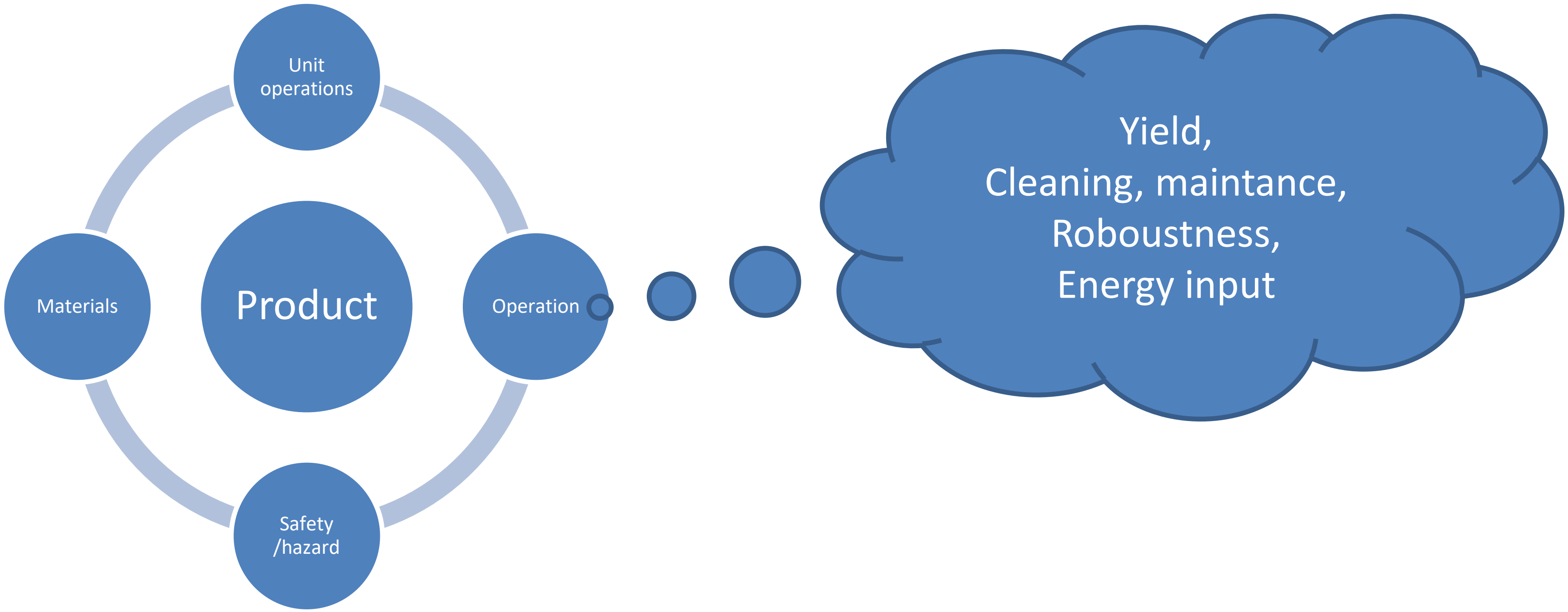
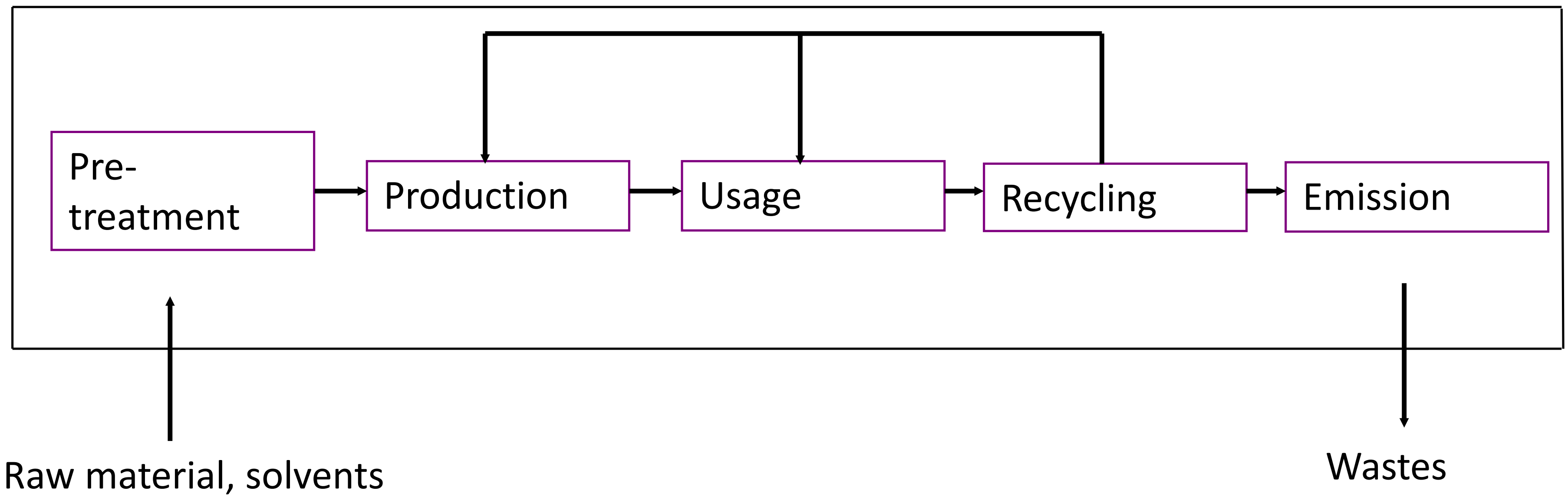


When you have to design a process…

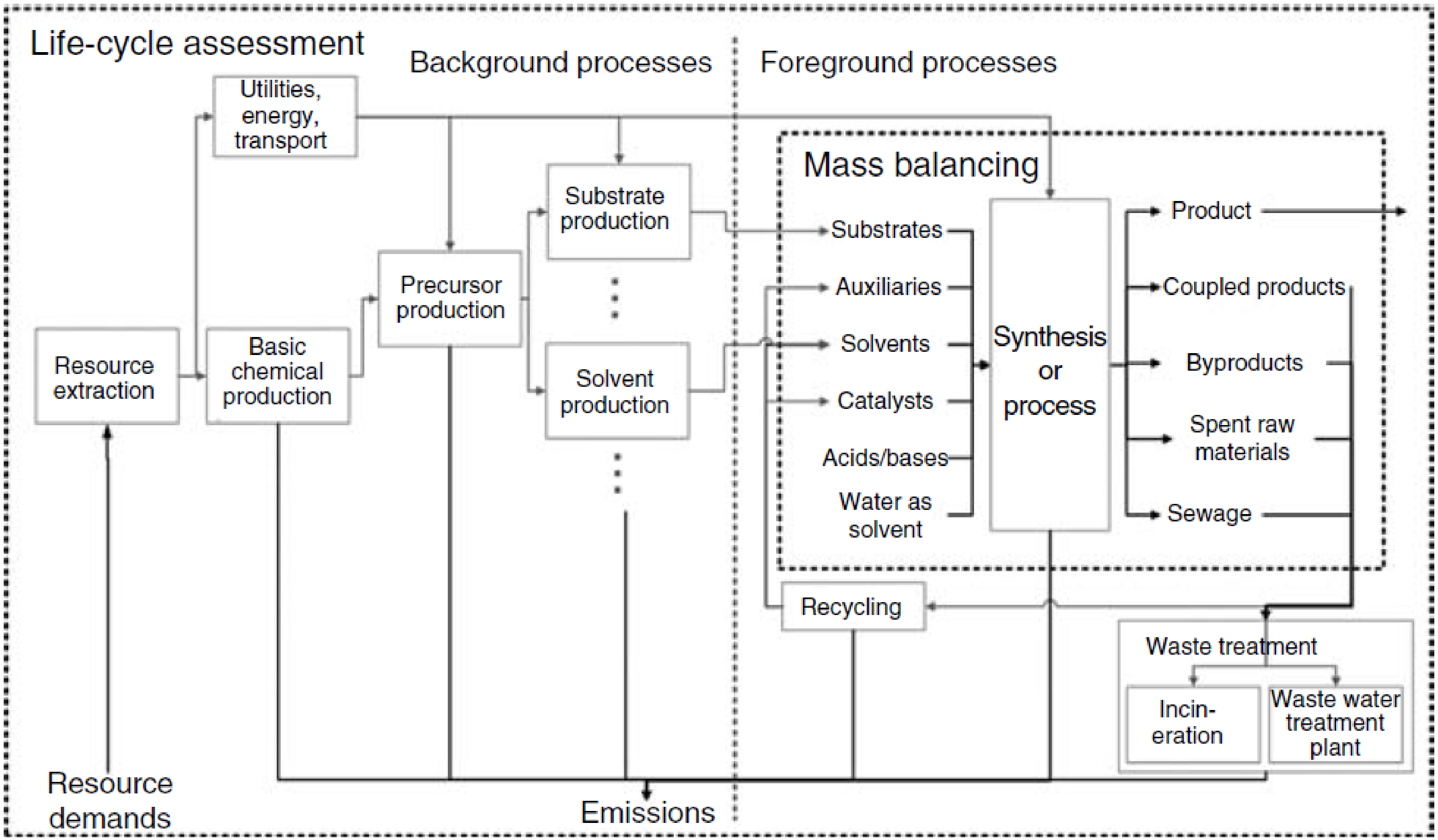
Life Cycle Analysis (LCA)

- LCA methodology is standardised by International Standard Organisation (ISO 14040:2006 and ISO 14044:2006).
- Defined as „compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle”.

Application of LCA



Mass balancing and LCA



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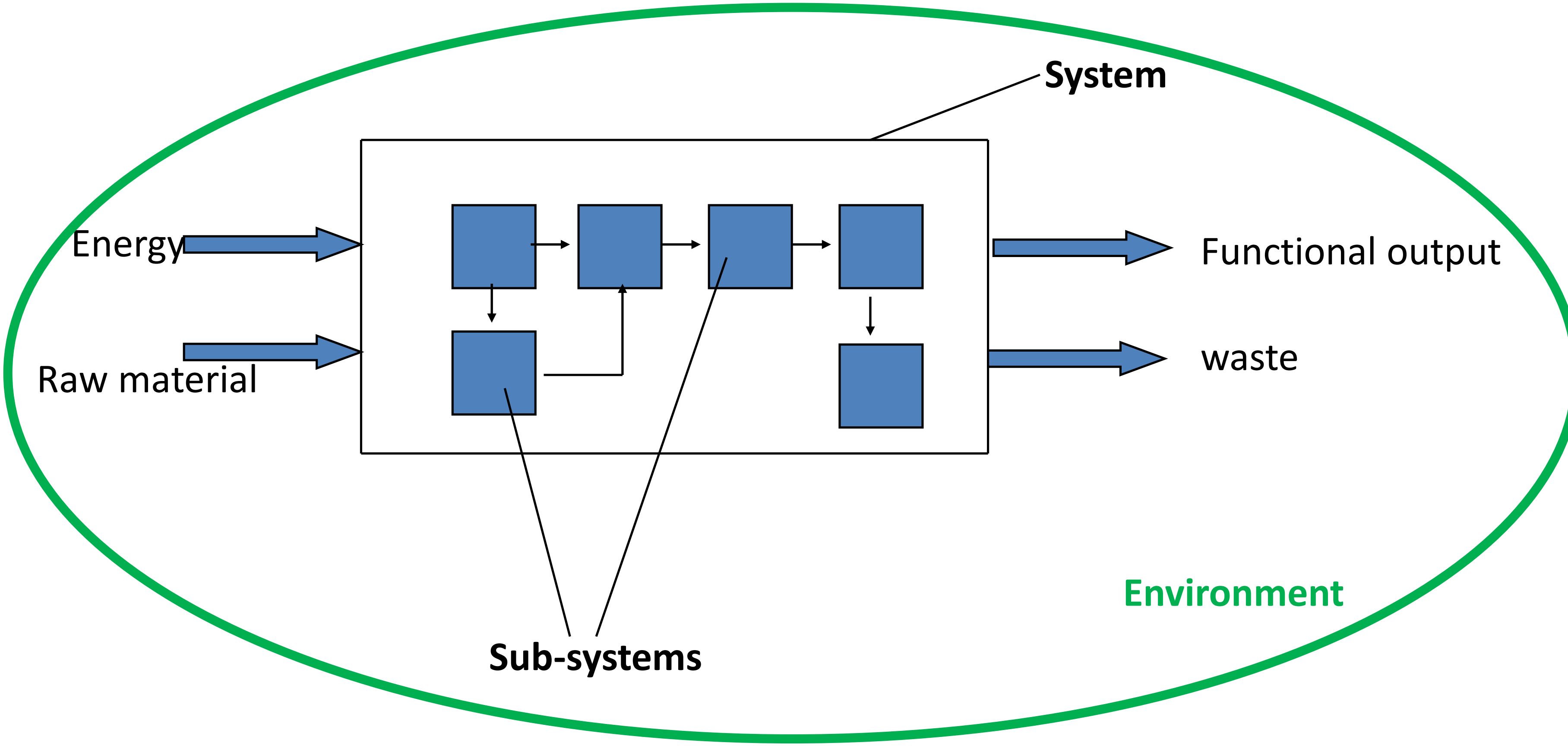
LCA control

1) Definition of results and goals (ISO 14041);
2) Examine the plan/ process (ISO 14041);
3) Map the environmental loading (ISO 14042);
4) Report (ISO 14043).

1. Definition of goals – always from an environmental view point
2. Map and qualify the environmental impacts within a border of a system.



3. Mapping environmental loading

- Characterization;
- Environmental loading can be for example:
  - Global warming;
  - Ozone degradation effects;
  - Acidification;
  - Eutrophication;
  - Photochemical oxidative loading;
  - Water and/ or human poisoning.
- Normalising;
- Solutions → 4. LCA Report