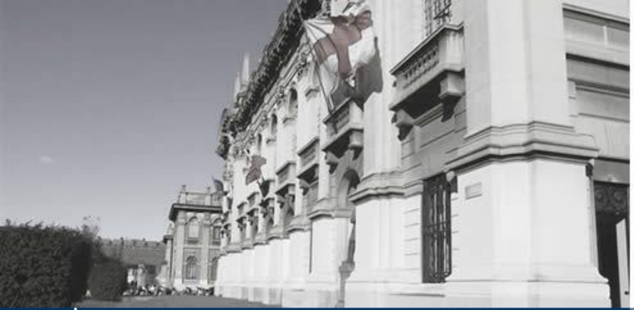


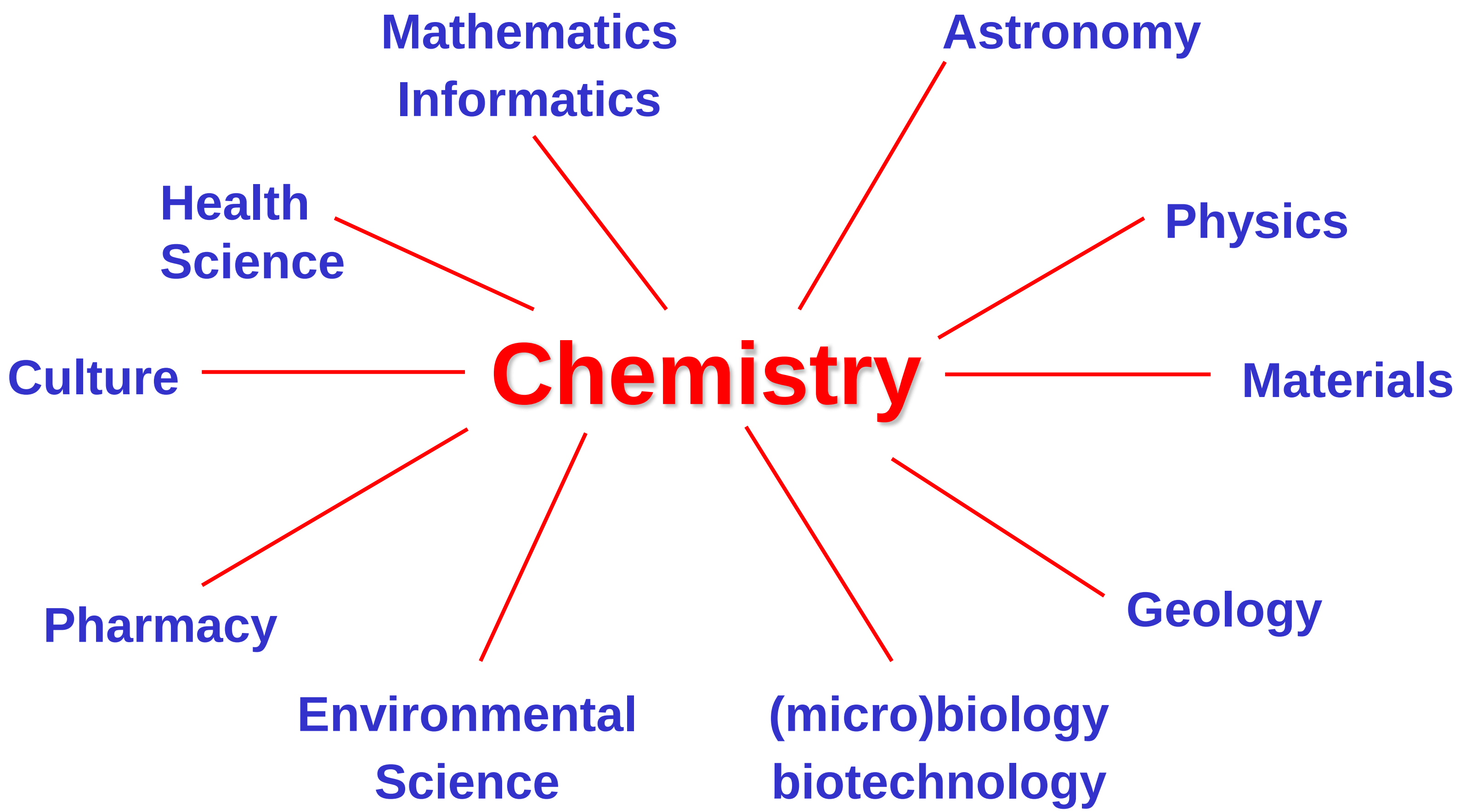
School of Industrial and Information Engineering
Course 096125 (095857)
Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

The Principles of Green Chemistry / Engineering for Sustainability.

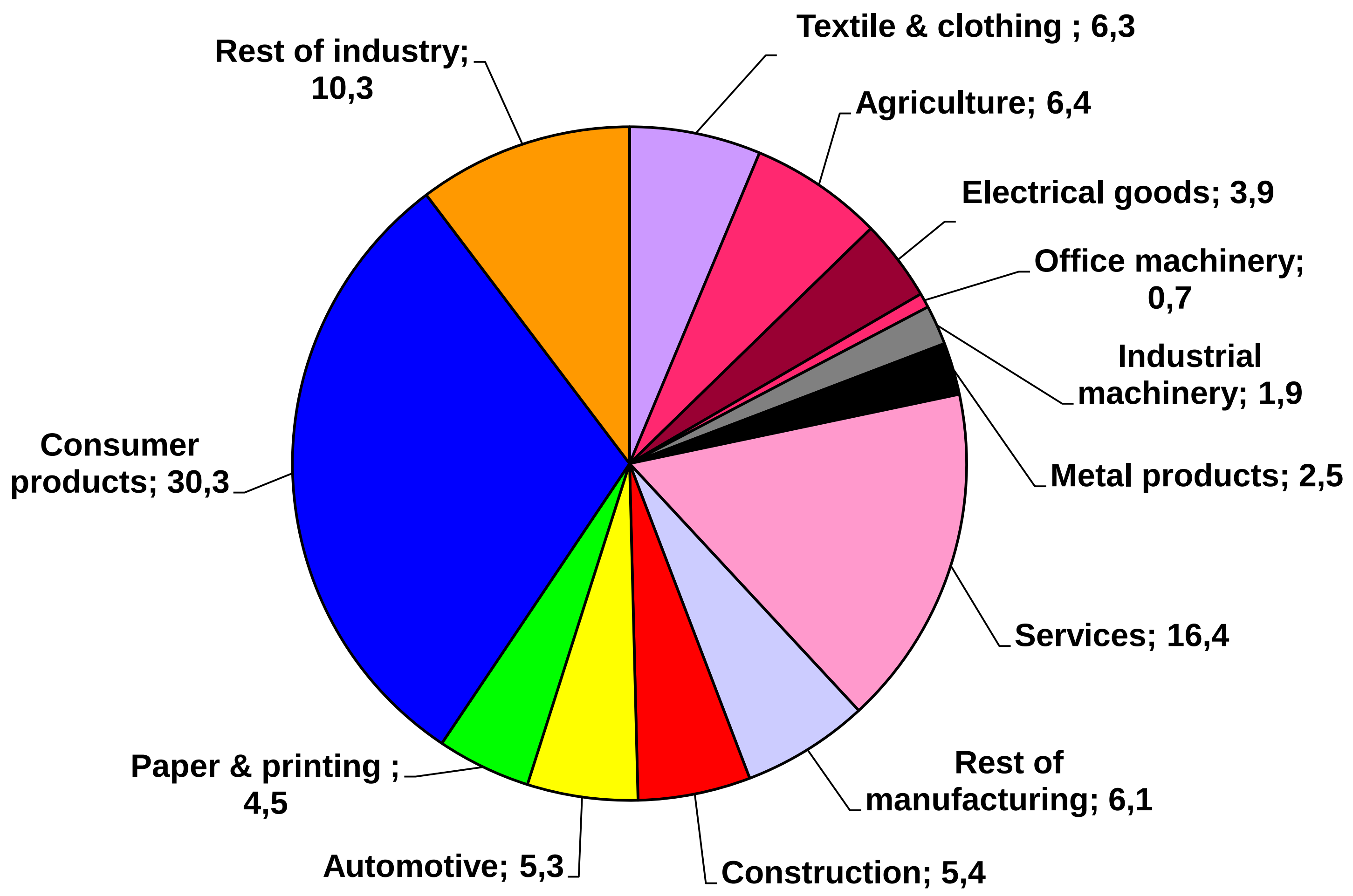
Prof. Attilio Citterio
Dipartimento CMIC "Giulio Natta"
https://iscamapweb.chem.polimi.it/citterio/education/course-topics/

Chemistry Permeates Other Sciences!



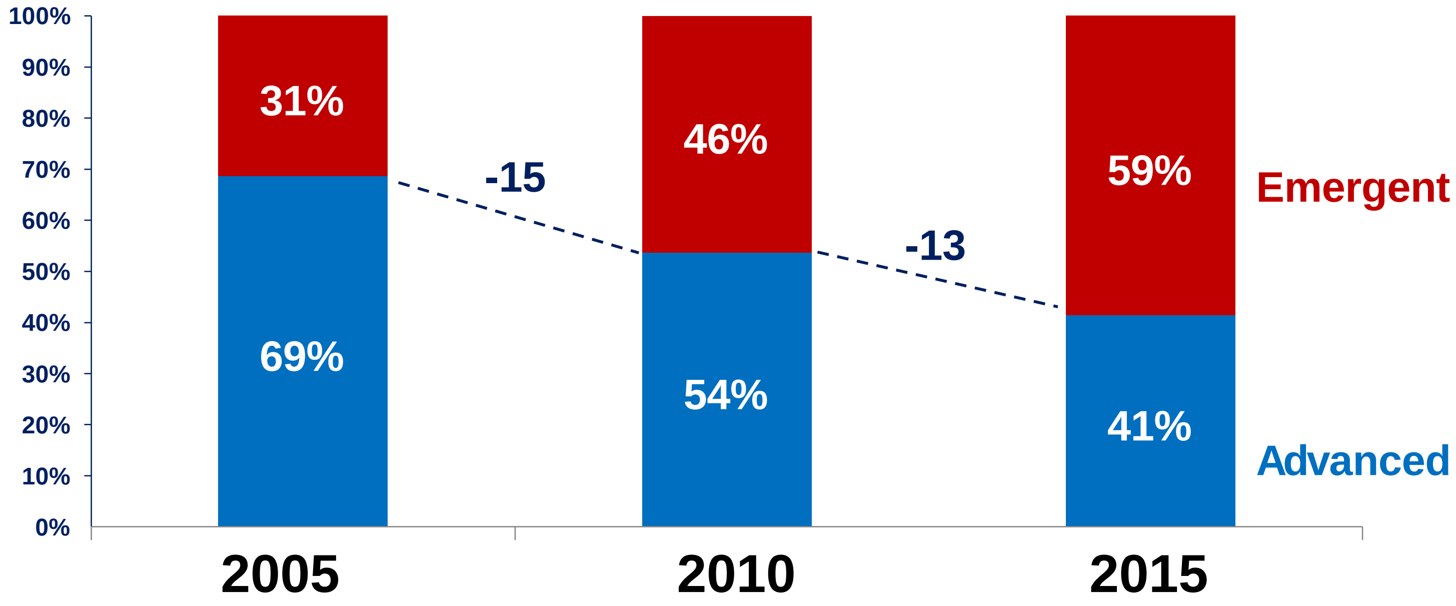
"embedded sustainability"

Chemistry is Everywhere!



http://www.chemistryandyou.org/

Developments in Quotas of World Chemical Production (% on production value).

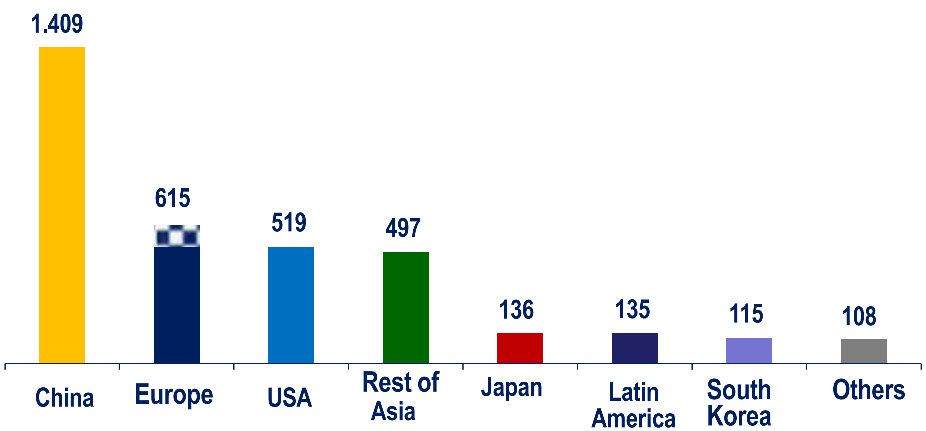


	2005	2010	2015
European Union	28%	21%	15%
USA	22%	16%	15%
China	12%	24%	40%
Others	38%	39%	31%

Chemical Industry:
World and European Scenery.

Geographic distribution of the world chemical production
(billion euro, 2015 year)

World = 3.534 billion euro

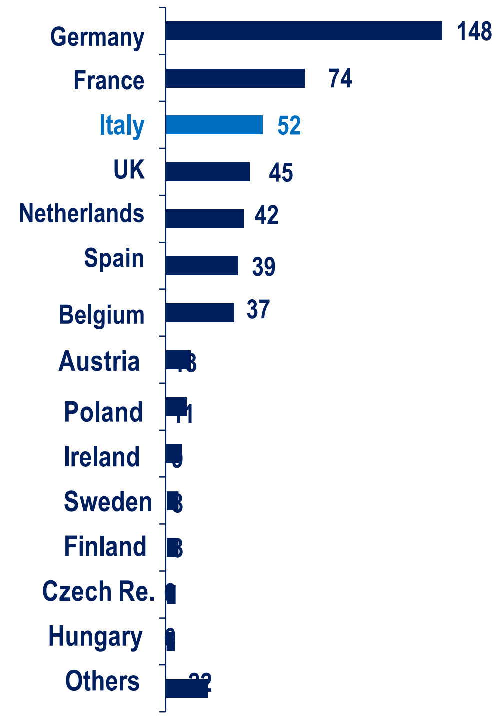


Note: Europe
= UE and not UE (Russia, Turkey, Switzerland, Norway, Ukraine)
Rest of Asia
= Asia excluded China, Japan and South Korea

Data for Netherlands include several purely commercial activities.

Geographic distribution of the EU chemical production
(billion euro, 2015 year)

UE = 520 billion euro



http://www.federchimica.it/docs/default-source/la-chimica-in-cifre/l'industria-chimica-in-cifre_giugno-2017.pdf

European Chemical Industry (2016).

Number of companies

28,221

Turnover

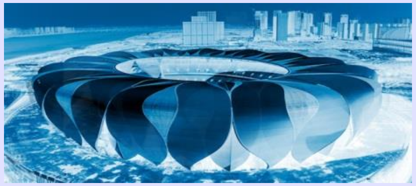
€ 520.2 billion

Direct employment

1,155,000

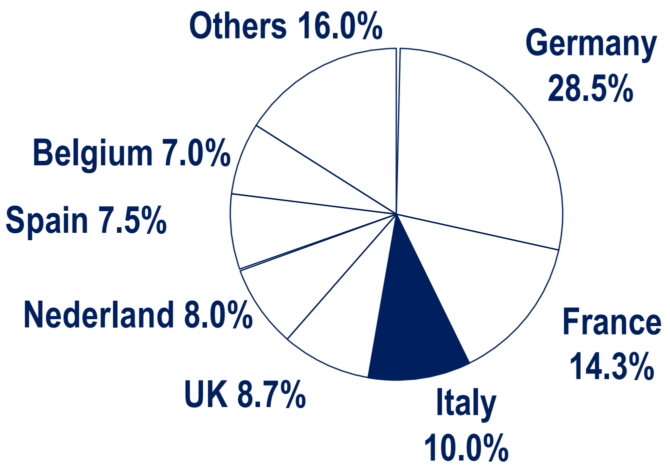
R & D costs

€ 9.14 billion



Dimension of Chemistry in the Italy, 2016 year.
(billion euro, unless otherwise indicated)

	Chemical Industry	Chemical and Pharmaceutical
Production	51.6	81.6
Exportation	27.5	48.8
Importation	34.6	57.4
Trade balance	-7.1	-8.6
Internal demand	58.6	90.2
companies (number)	2.810	3.256
Employed (thousands)	108.1	172.1
Investments	1.7	2.8
R&D expenses	0.5	1.2
Impact on manufacturing industry		
Revenue	6%	9%
Export	7%	12%

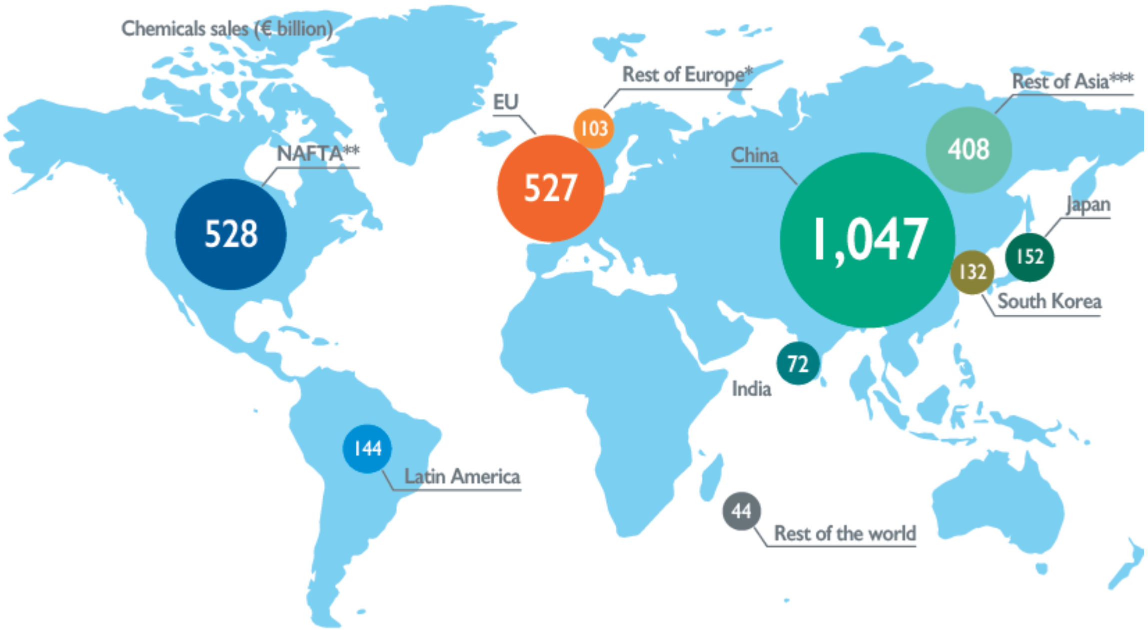


Note: R&D expenses and investments, last available year 2014
Source: Federchimica / elaboration and estimates on Istat bases

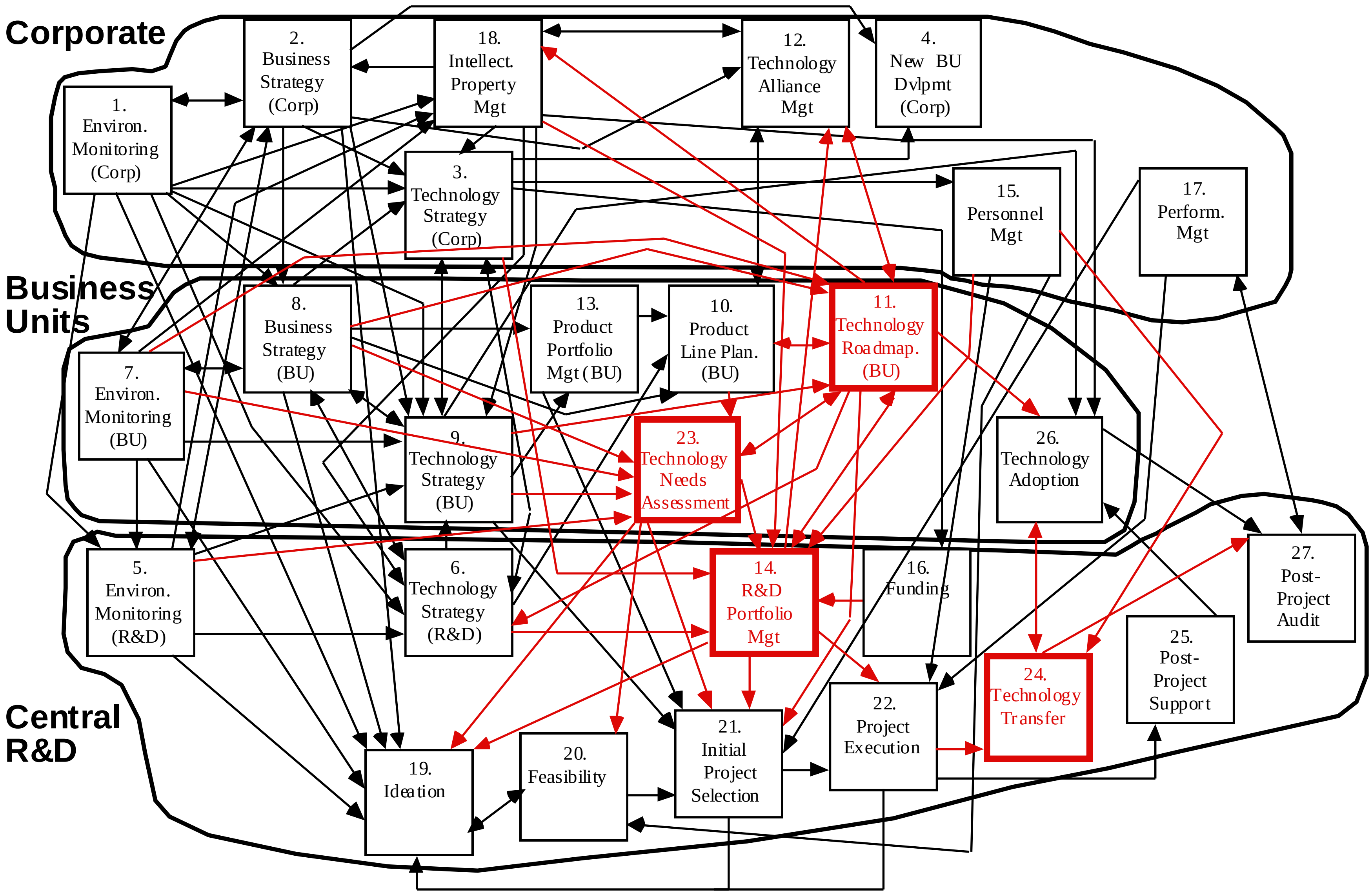
World Chemicals Market.

- World chemicals turnover was valued at € 3,156 billion in 2013 and grew 2.4%
- The sales growth rate was considerably lower compared to the 10 year trend, when average annual sales expanded by 10.3 per cent from 2003 to 2012
- The EU chemical industry ranks second, along with NAFTA in total sales, but has lower growth than Asia and NAFTA

World chemicals sales in 2013 are valued at €3,156 billion.
The European Union accounts for 16.7% of the total.



Technological Management Processes.



Chemistry Contributes on Three Levels to Sustainable Development.

Chemistry has to contribute on three levels to sustainable development:

1. Provision of chemical products that establish and ensure social and economic wealth.
2. Conservation of resources by developing:
    a. More effective chemical processes
    b. Renewable energy sources
    c. Chemical products that enhance significantly the effectiveness of production processes and products in other areas,
    d. Products that allow the consumer to use resources more effectively,
    e. A product design that fits into a recycling concept, and
    f. Products that are based on renewable resources.
3. Management of resources, substances and materials in a safe and in an environmentally benign manner.

M. S. Reisch, *Chem. Eng. News* 79(36), 17 (2001).

Estimated Numbers of Chemicals. (EPA and EU estimates, 2010)

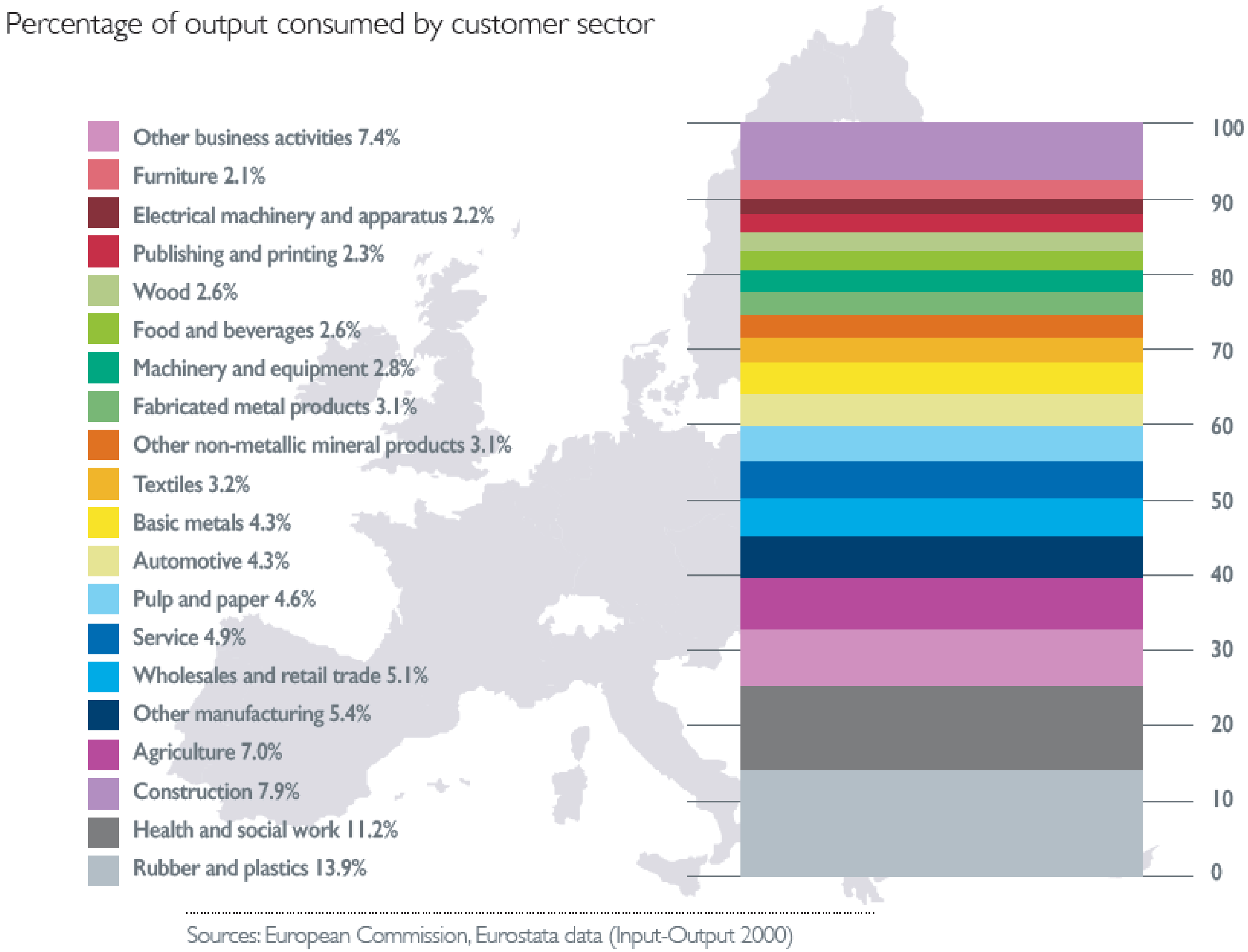
Number of Chemicals:	28,000,000	
Chemicals in Commerce:	10,000,000	
Industrial Chemicals:	240,000	(millions of products)
New Chemicals:	3-4,000	/year (1,000 in US)
Pesticides:	800	(21,000 products)
Food Additives:	9,500	
Cosmetic Ingredients:	8,500	(50,000 products)
Medicines to humans:	3,500	

- By limiting synthesis strictly to combinations of 30 atoms of just C, N, O, or S, **more than 10^{60} structures are possible !**
- Expanding the elements to other heteroatoms (e.g., P and halogens), the limits to the numbers of possible structures defies imagination. Also known as "chemical space"

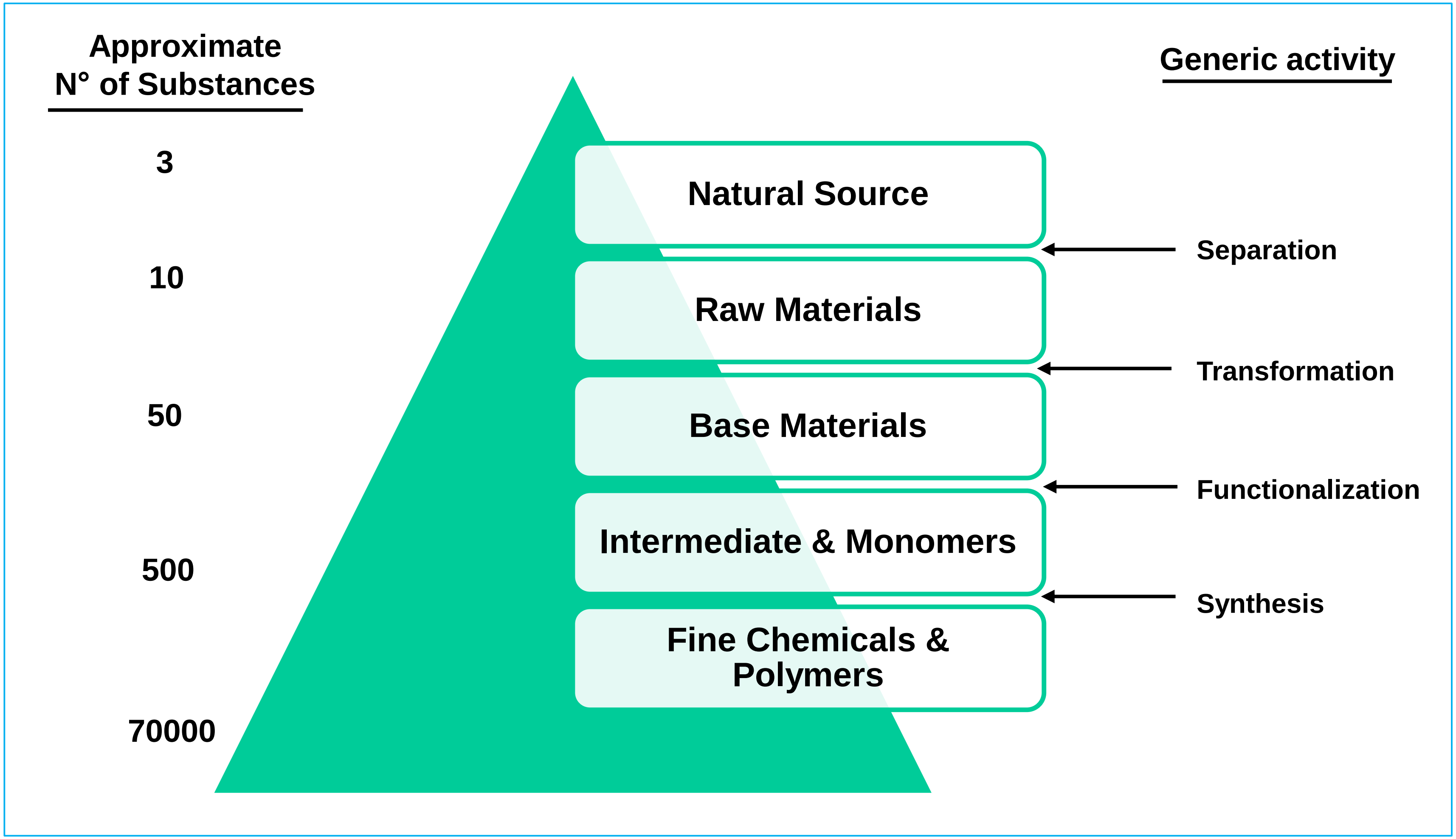
Chemical Market – Europe.

- Chemical industry underpins virtually all sectors of the economy and its strategies impact directly on downstream chemicals users.

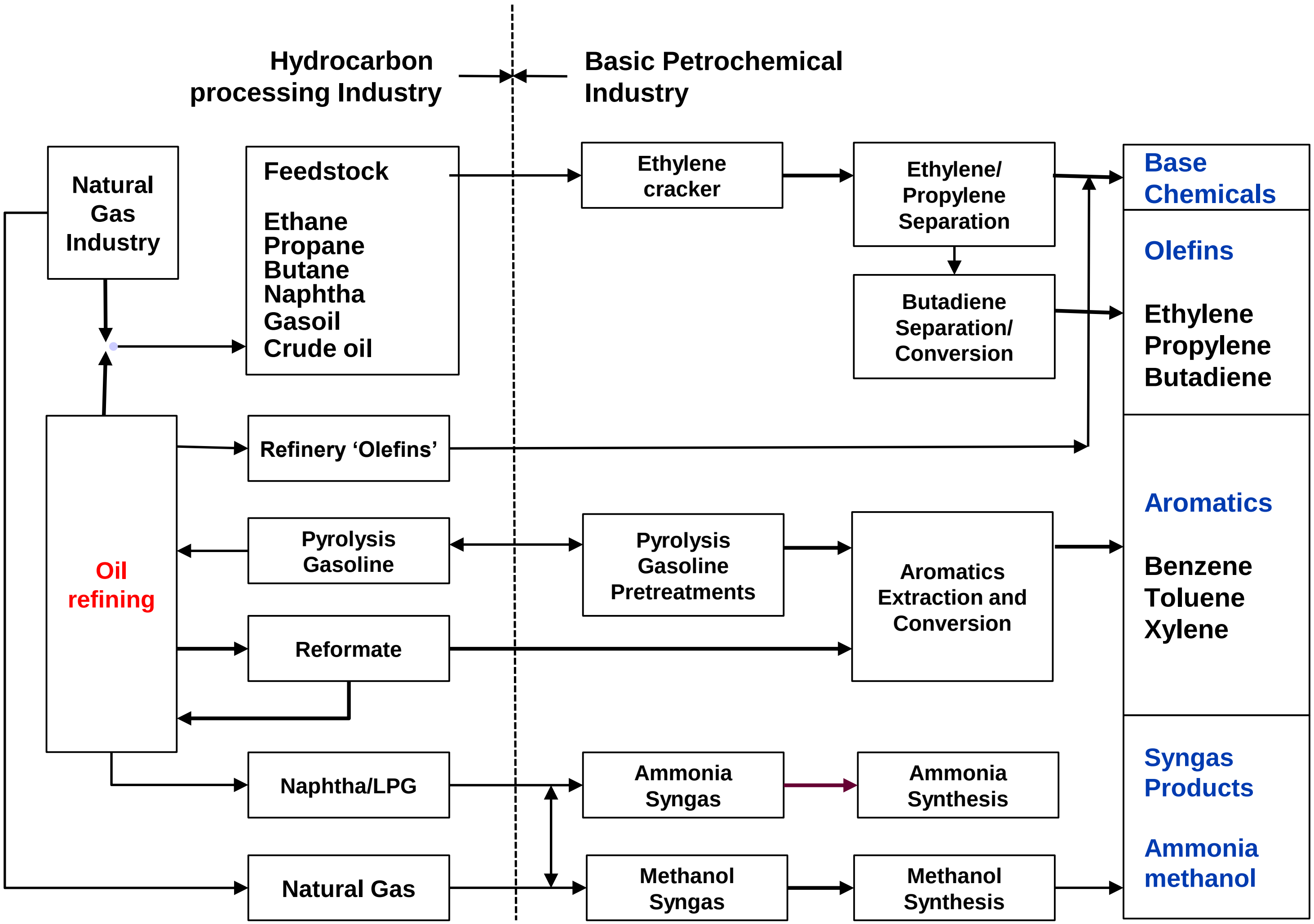
- The big industrial users of chemicals are rubber and plastics, construction, pulp and paper, and the automotive industry.



Structure of the Industrial Organic Chemistry.



Oil as Source of Base and Intermediate Organic Chemicals.



Source:[EC DGXI, 1993 #8]

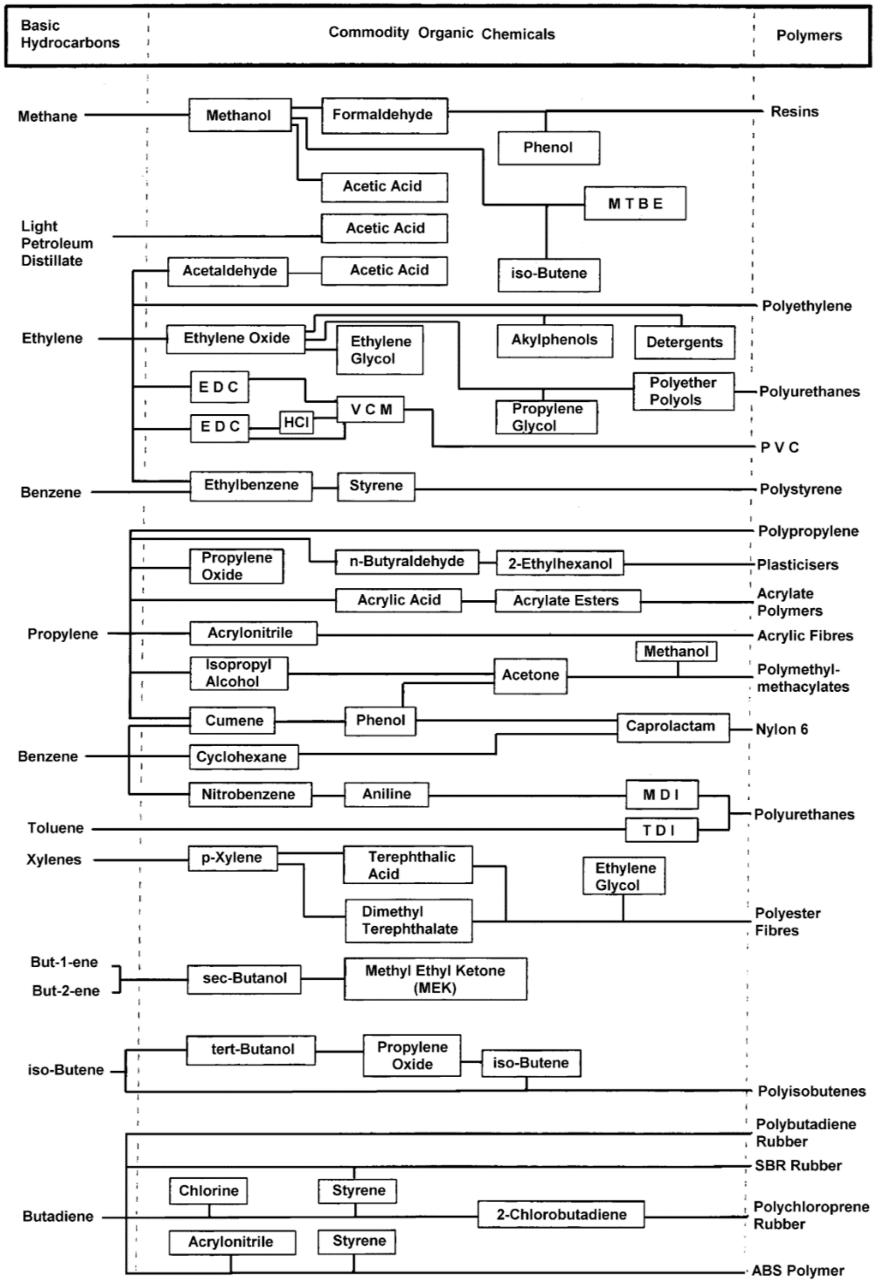
Pathways in the Organic Chemistry Industry.

Figure illustrates the complexity of the industry by showing the range of products that result from the basic hydrocarbon raw materials.

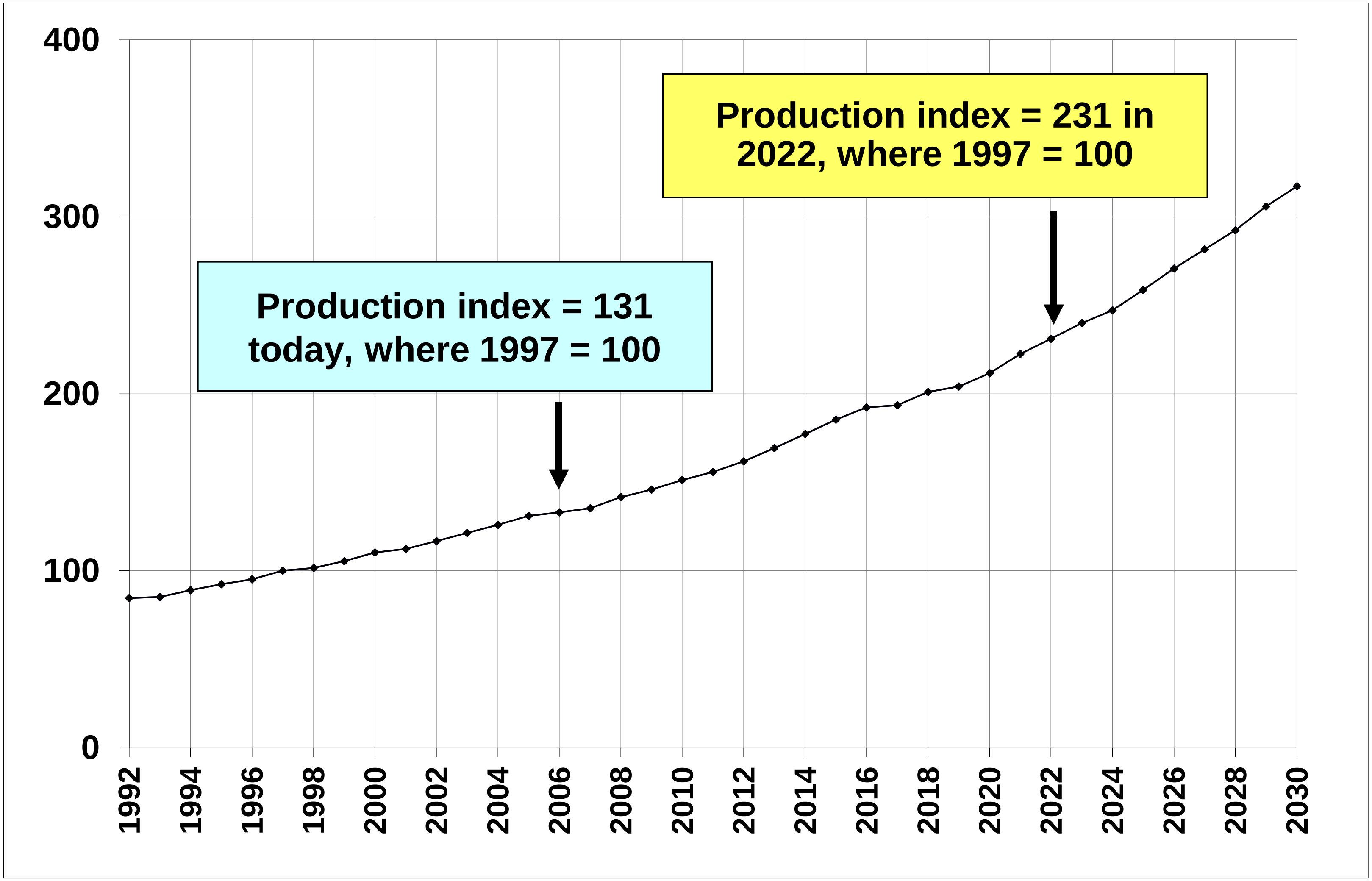
Many of the products are intermediates for the rest of the chemical industry and have limited use in their own right.

As a consequence of this complex step-by-step synthesis of products, there are rarely stand-alone manufacturing units producing just one product. Instead, chemical installations are usually large, highly integrated production units that combine many diverse plants.

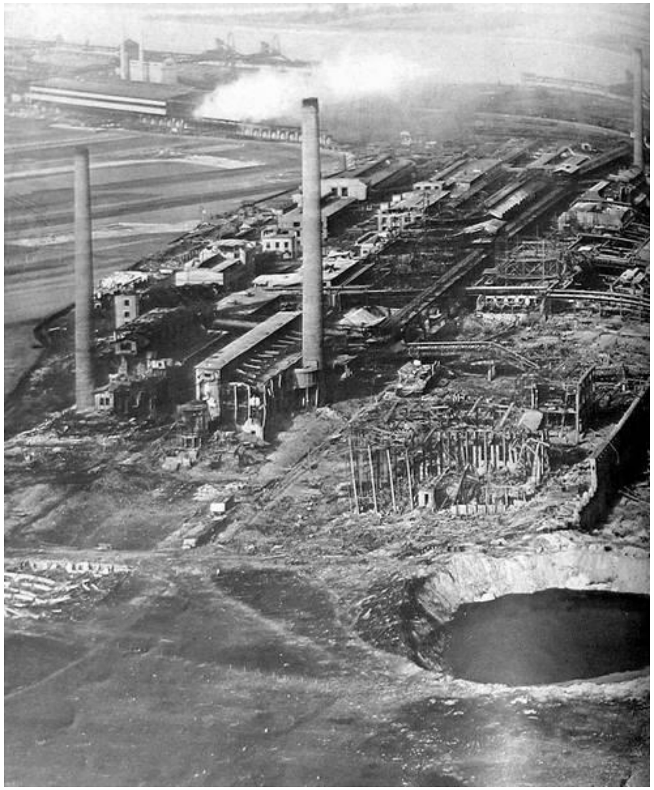
Products in these stages are called Commodity Organic Chemicals.



Global Chemical Production is Doubling Every 25-Years.



But …..
Relevant Accidents: Past and Recent !!



BASF,
Oppau/Ludwigshafen,
September 21, 1921

Crater: 80 m diameter,
16 m deep

450 dead

80 years after

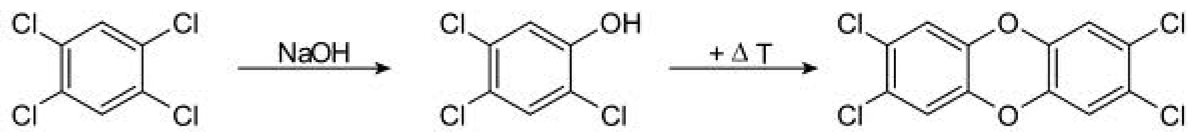
AZF, Toulouse,
September 21, 2001

Crater: 50 m diameter,
10 m deep
29 dead

Environmental Disasters.

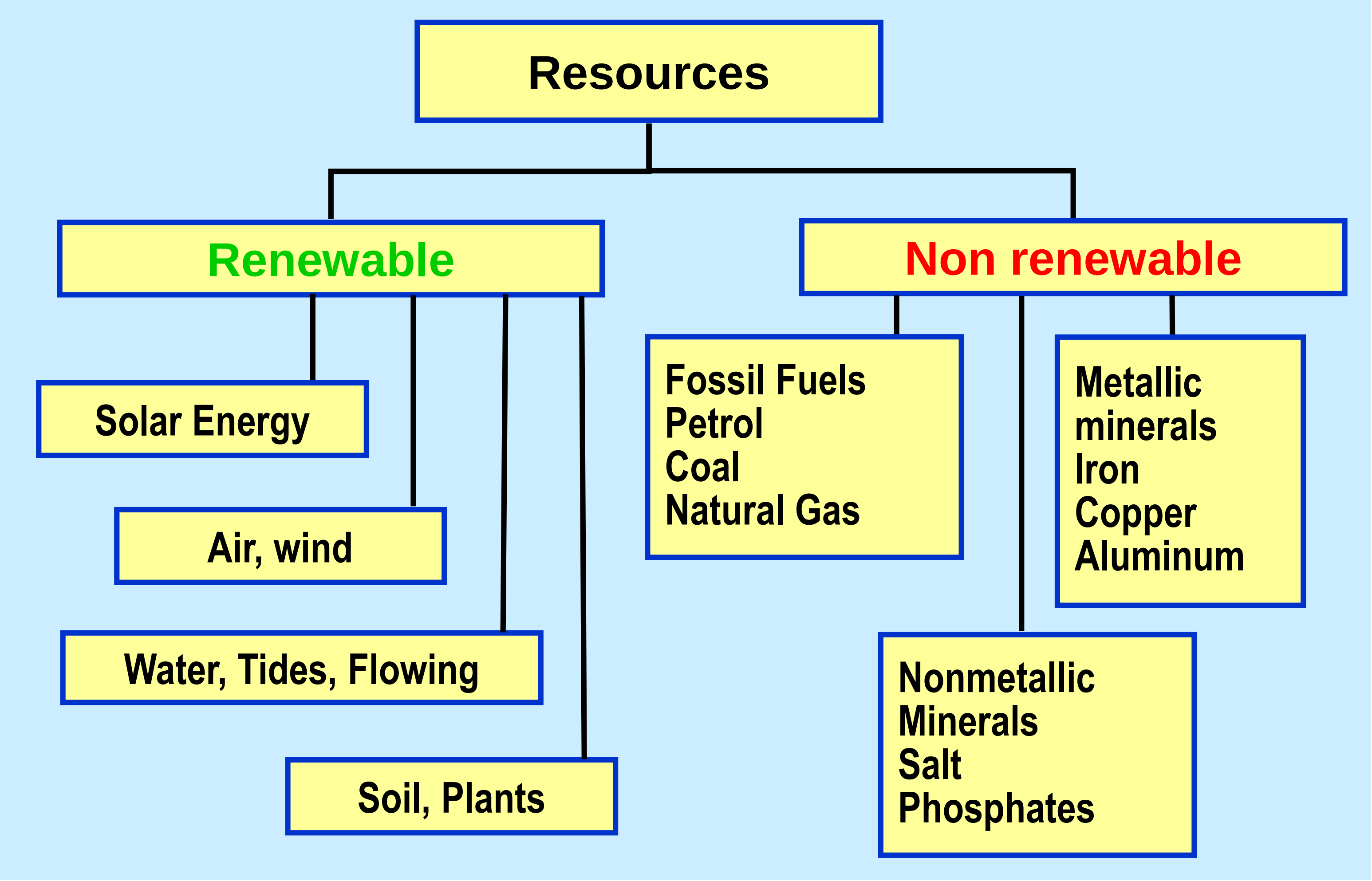
On Saturday 10th July 1976 a bursting disc on a chemical reactor ruptured at ICMESA. Maintenance staff heard a whistling sound and a cloud of vapors was seen to issue from a vent on the roof. A dense white cloud, of considerable altitude drifted offsite. The release lasted for 20 minutes. About an hour after the release the operators were able to admit cooling water to the reactor.

Among the substances of the white cloud released was a deposit of TCCD, a highly toxic material. The nearby town of Seveso, located 15 miles from Milan, had some 17,000 inhabitants. No human deaths were attributed to TCCD but many individuals fell ill. A number of pregnant women who had been exposed to the release had abortions. In the contaminated area many animals died.



TCCD = 2,3,7,8-tetraclorodibenzo-p-diossina

Resource = Matter Obtained from Environment (living or not) to Meet Human Needs.



Non Renewable and Renewable Material Resources.

<u>Non Renewable Resources</u> : Those extracted from the earth

Some energy is needed to:

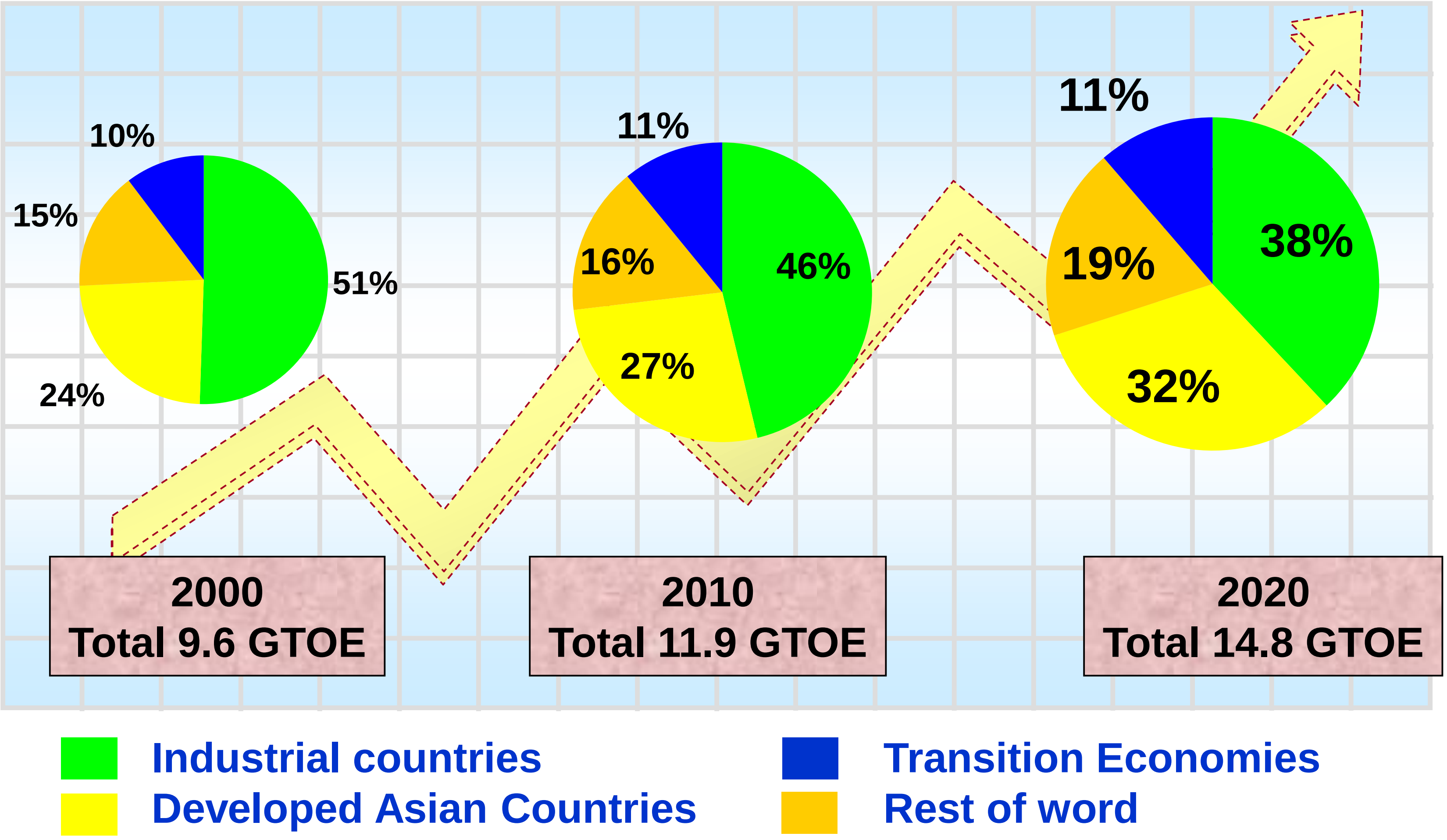
- Extract and process resources into usable forms
- Capture processed resources and convert them to an usable form

<u>Renewable Resources</u> : those which are regenerated in natural cycles

- Arising from living organisms (plants, animals)
- Arising from biogeochemical fast cycles (water, CO_2, soil)

Energy Word Use by Geographical Areas.

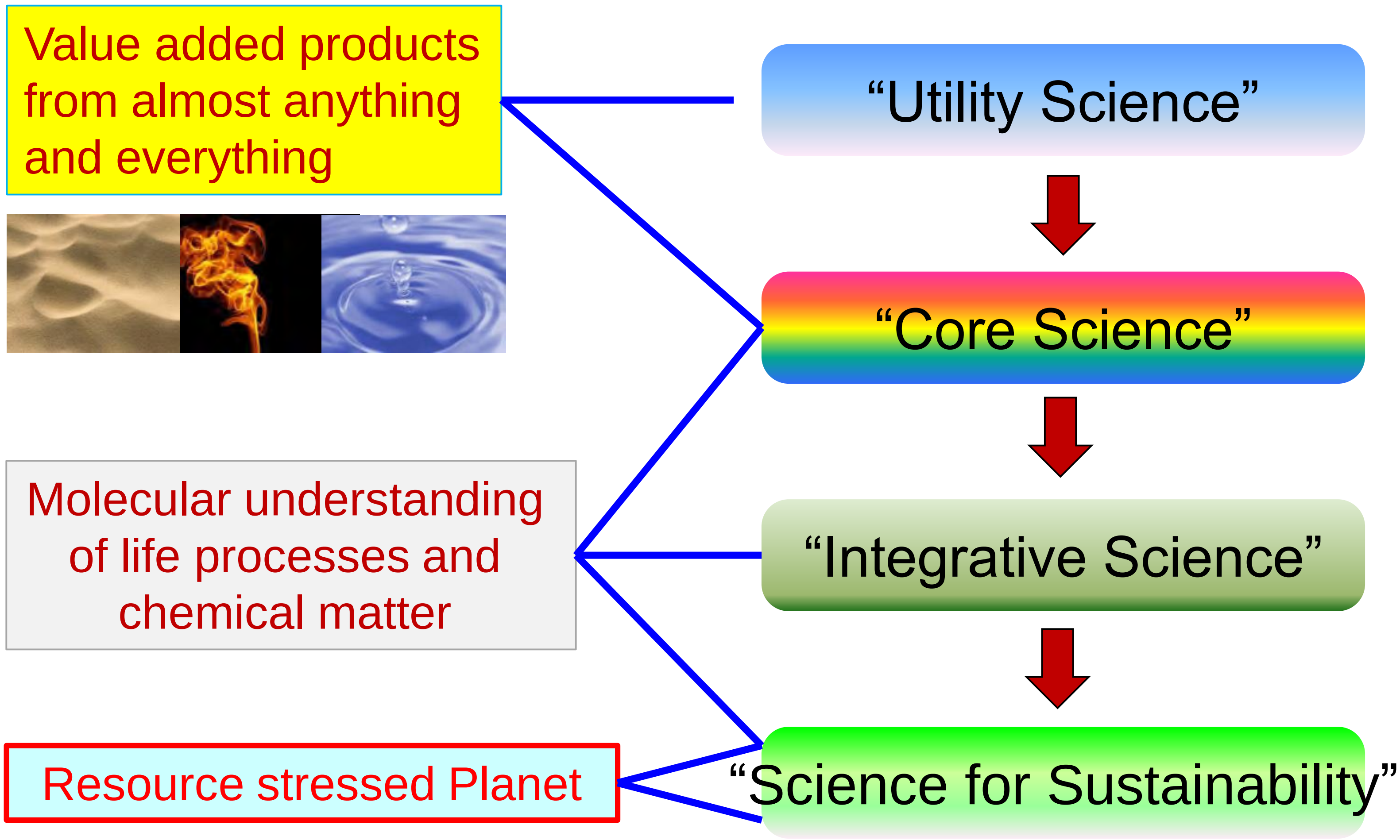
GTOE = Giga-ton of oil equivalent



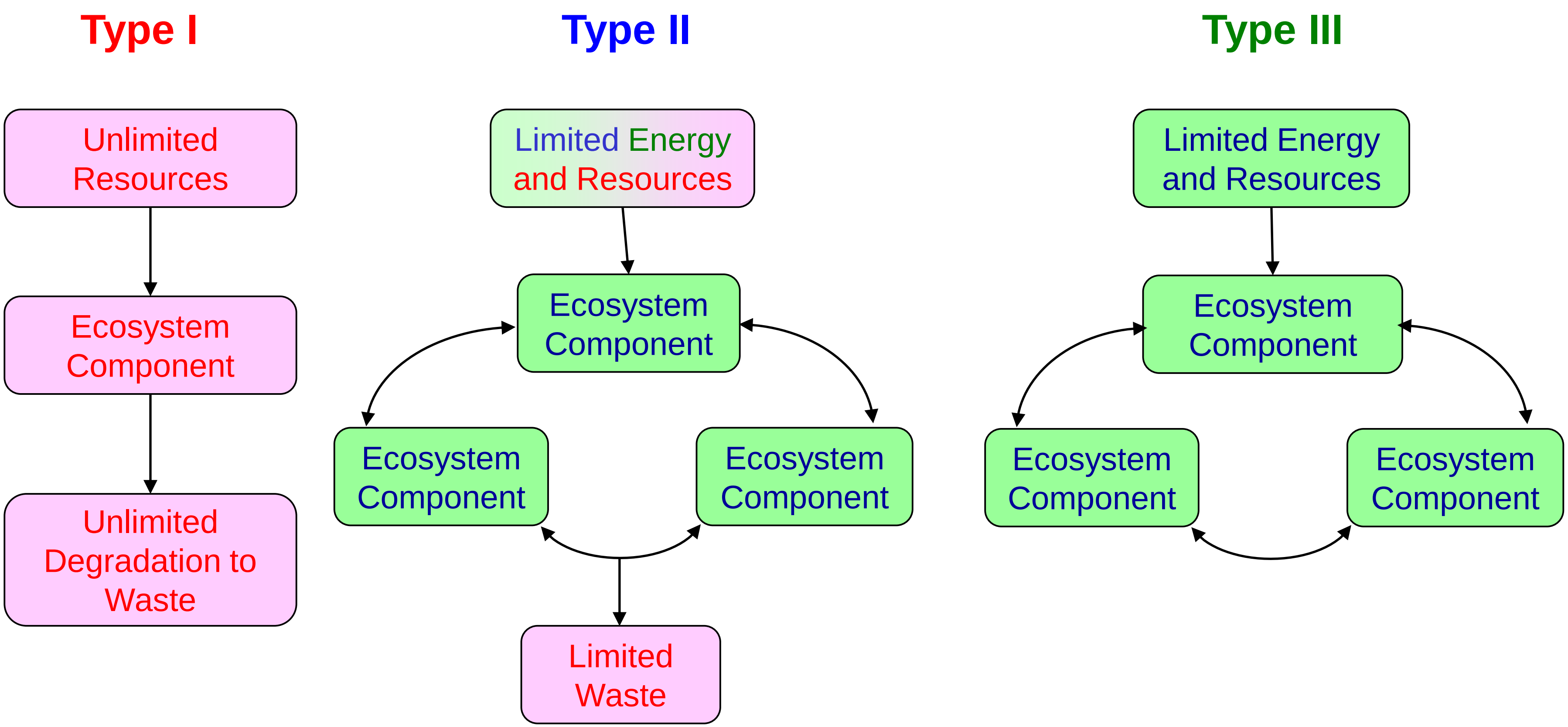
It is <u>Essential</u> that Chemists, Engineers and Public Managers Would Place a Major Focus on the Environmental Consequences of Chemical Products and the Processes by which these Products are Made.

We must consider our chemical ecological footprint.

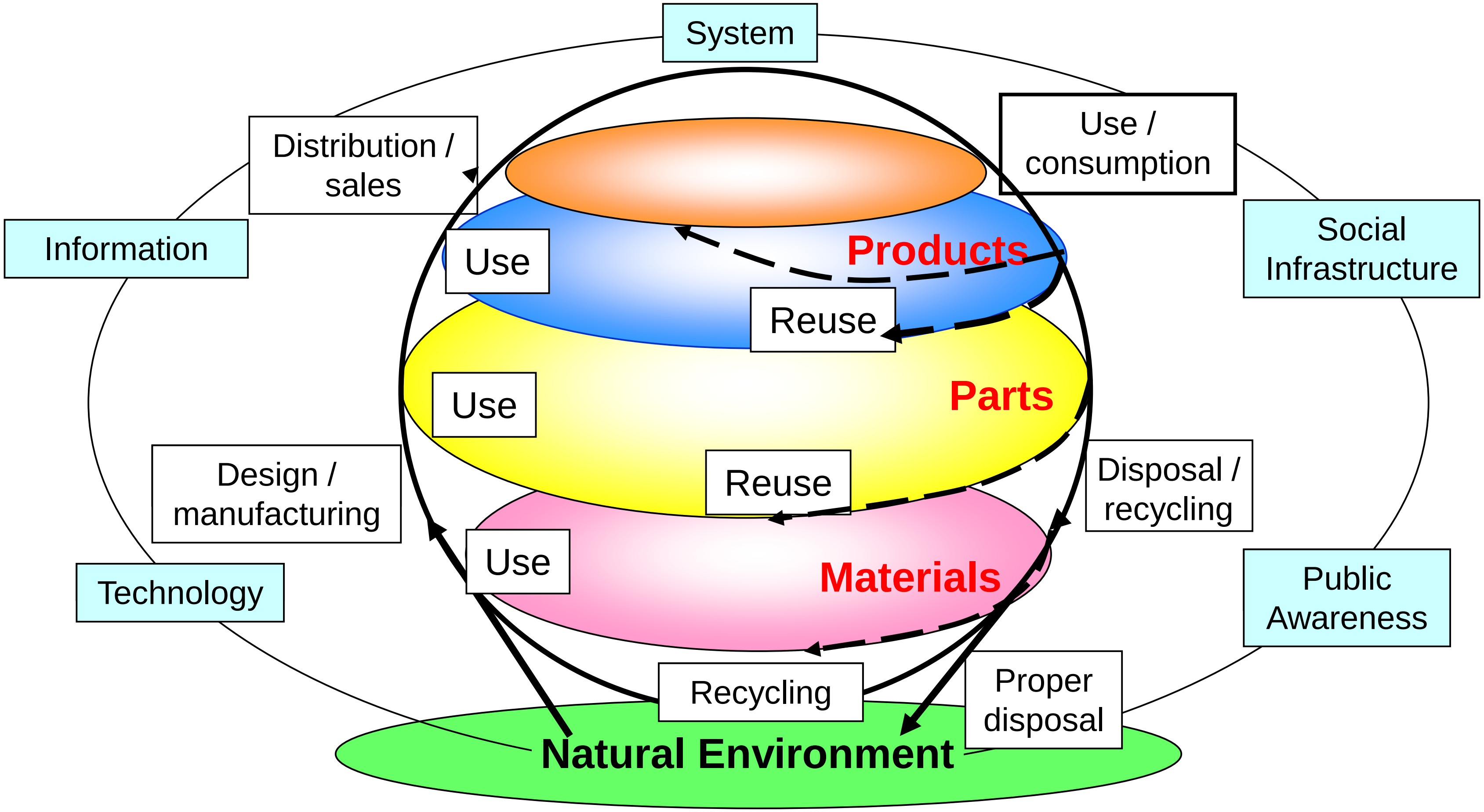
The Evolving Perception of Chemistry.



Industrial Ecology (Goal).



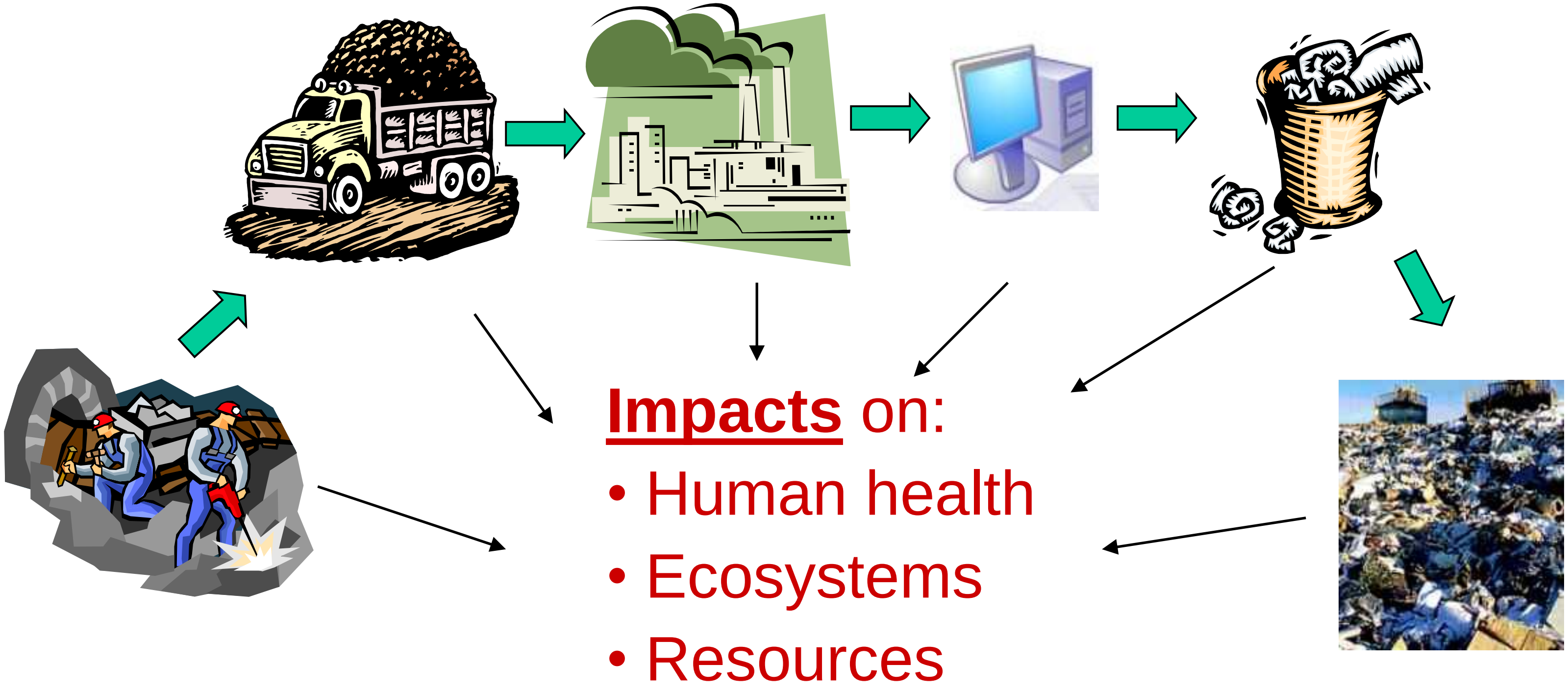
Sustainability Chain Valorization.



Source: Kitakyuchu Ecotown, 2001

Life Cycle Analysis.

”From cradle to grave”



Life Cycle Thinking.

Life Cycle Thinking → **Sustainability Decision Support**

The process of taking into account in decision making, as far as possible, all resources consumption, environmental, health, social, and economic implications that are associated with the life cycle of a product (good or service), considering i.e. the extraction of resources, production, use, transport, recycling, and waste disposal. This process helps to avoid the "shifting of burdens", i.e. of impacts or resource consumption, among life cycle stages, geographic areas, and environmental and human health problem fields such as Climate Change, Summer Smog, Acid Rain, etc.

Life Cycle Thinking and Pollution Prevention.

Life cycle thinking expands pollution prevention to include the complete product life cycle and sustainability. Source reduction in a product life cycle perspective is then equivalent to eco-design principles and what had been called the "**6 RE philosophy**":

- **Re-think** the product and its functions. The product may be used more efficiently, thereby reducing use of energy and other natural resources.
- **Re-duce** energy and material consumption throughout a product's life cycle.
- **Re-place** harmful substances with more environmentally friendly alternatives.
- **Re-cycle**. Select materials that can be recycled, and build the product such that it is disassembled easier for recycling.
- **Re-use**. Design the product so parts can be reused.
- **Re-pair**. Make the product easy to repair so that the product does not yet need to be replaced.

Environmentally preferable, well managed, sustainable

Recycled Content

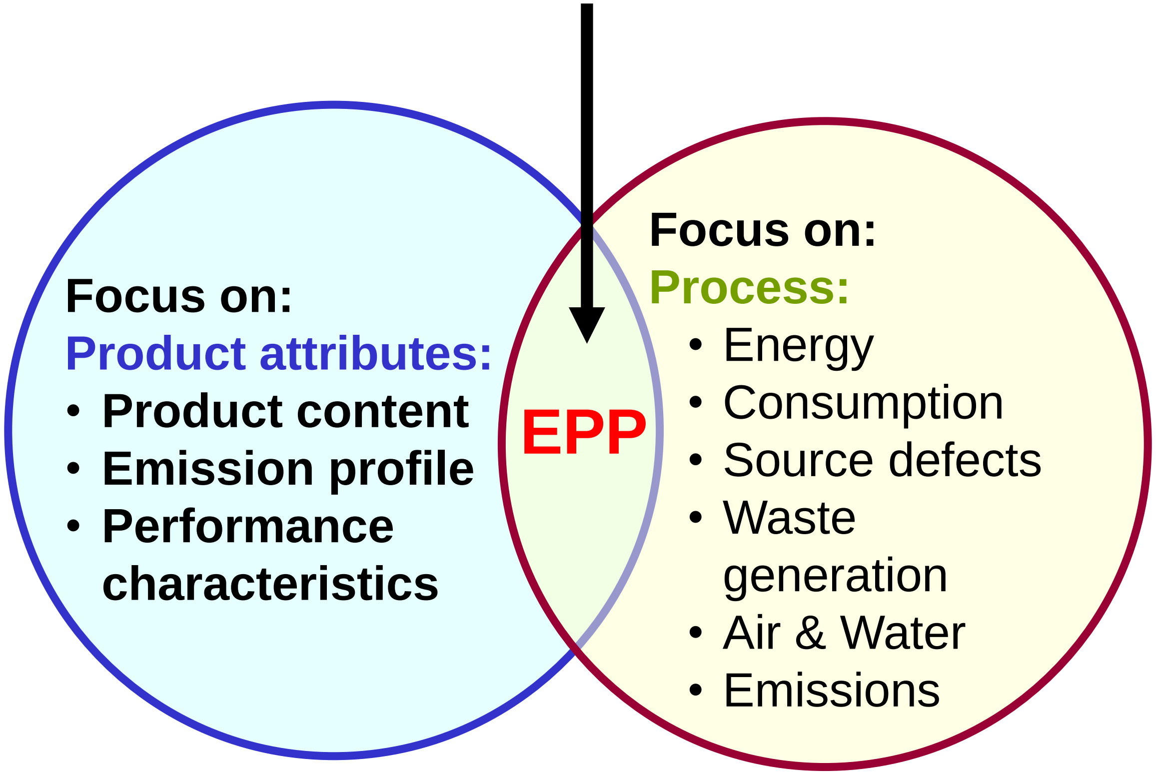
Organic

Low emitting

Energy efficient

Biodegradable

Low/0 toxicity



Renewable Energy

ISO 14000

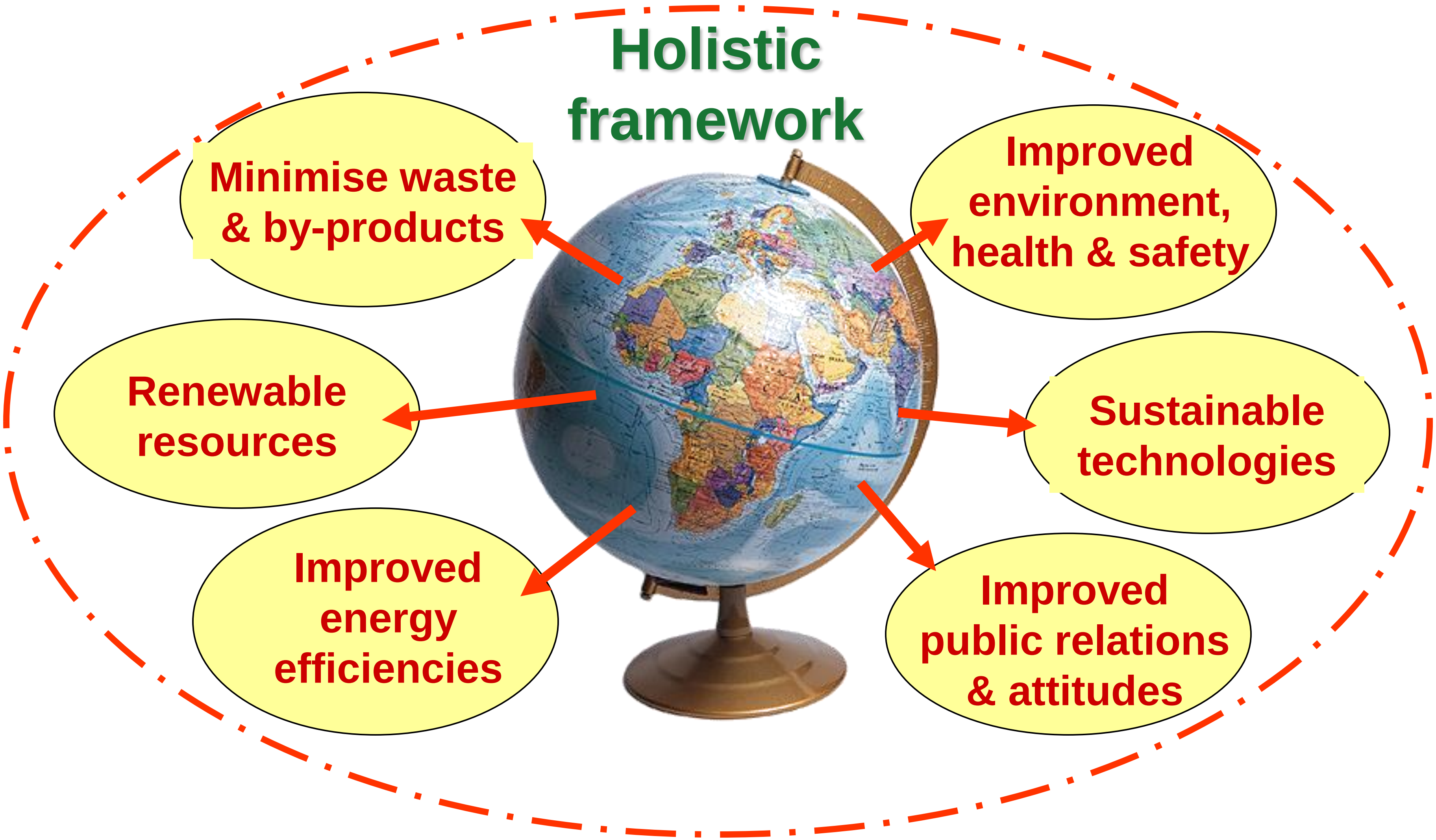
ISO 9000

LCI/LCA

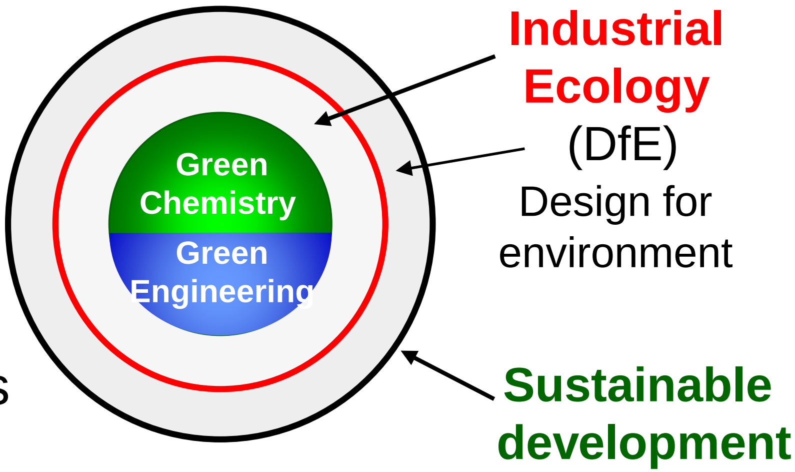
GHG registry

Green Chemistry: Socio-Economic Drivers.

Unacceptable environmental impact from inefficient process chemistry



Industrial Ecology = science of sustainability with emphasis on the careful use and reuse of resources

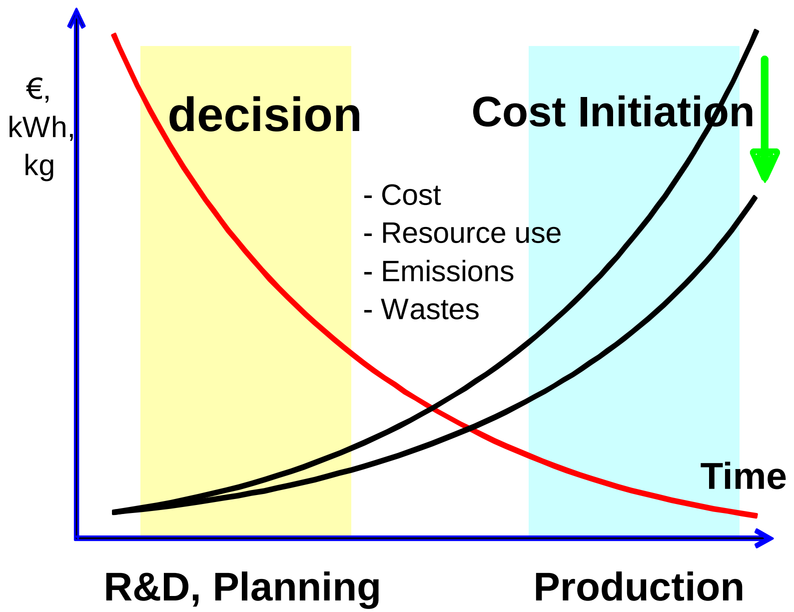


Green Chemistry for Sustainability = science of chemical transformation concerned with developing processes and products to reduce or eliminate hazardous substances and use efficiently resources and energy.

Intrinsic Safety and Green Engineering = Science and technology devoted to reduction / elimination of concerns associated to materials used and processing, with permanent and inseparable insertion into industrial processes.

Design for Environment (DfE): Where to use Environmental Information best?

Design is responsible for the technical, environmental, and economical performance of a system life cycle.
It is a basic principle that products and processes must be designed to have an eco-compatible function. The cost expenditure (70%) takes place in the production, but with only minor influence on the actual amount.
This makes the 'design for environment' a critical key factor of a product competitivity.



- Life Cycle related considerations therefore have to be included in the design process.
- If used properly, life cycle considerations save money and burdens.

GREEN CHEMISTRY (FOR SUSTAINABILITY).

DEFINITION ("U.S.")

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. Green chemistry is also known as sustainable chemistry.*

Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry

CHEMISTRY FOR SUSTAINABILITY DEALS WITH:

- Minimize Waste, Energy and Resource Use
- Recycle Products and Materials (Utilize Catalysts instead of Reagents)
- Applies innovative scientific solutions to real-world environmental problems (Prevents pollution at the molecular level)
- Reduces the negative impacts of chemical products and processes on human health and the environment
- Designs chemical products and processes to reduce the intrinsic hazards

** Green Chemistry Theory & Practice, P T Anastas & J C Warner, Oxford University Press 1998*

“European” Definition.

“The Green and Sustainable Chemistry aim to reach *significant improvements* in the eco-efficiency of chemical processes, products and services, so as to achieve a sustainable, cleaner and healthier environment and a *competitive advantage*”

“Design of products for sustainable applications, and their production by molecular transformations that are energy efficient, minimize or preferably eliminate the formation of waste and the use of toxic and/or hazardous solvents and reagents and utilize renewable raw materials where possible. It is therefore the discovery and application of new chemistry/technology leading to prevention / reduction of environmental, health and safety impacts **at source** at molecular level”

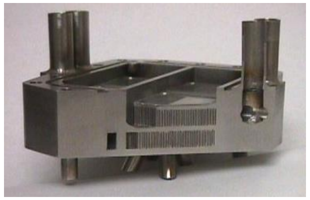
EU, COST Action D29 on Sustainable/Green Chemistry and Chemical Technology, 2003

Aspects of Sustainable Chemistry.

Minimise Risk and Accidents

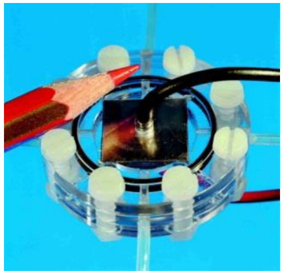
Energy Efficiency

Use of Alternative, Cleaner Solvents



Micro-reactors

Minimise Waste Production



Atom Efficiency

GREEN CHEMISTRY

Design to Degrade

Alternative energy sources

Minimise the Use of Toxic and Hazardous Chemicals

Use of Renewable Resources

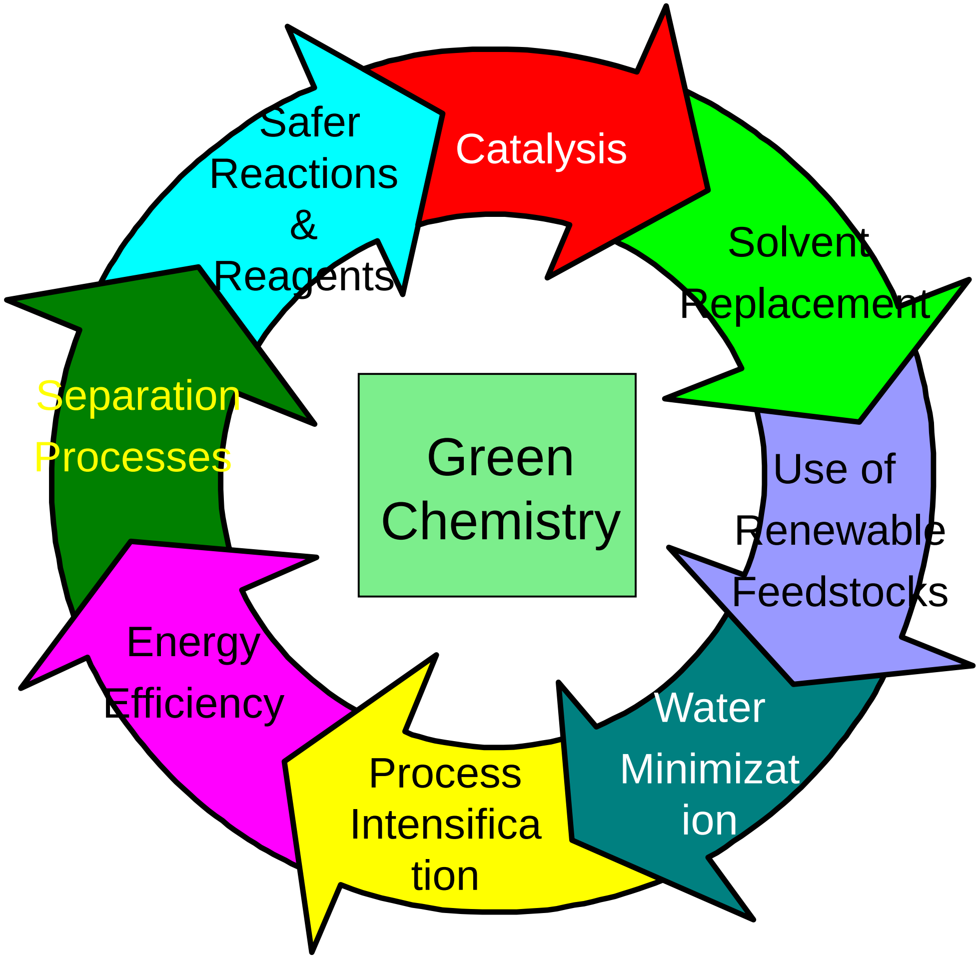
Biodegradable Plastics

Fuel cells

Recycle where possible

Some Aspects of Sustainable Chemistry.

- Design “Green” benign products for humans and environment;
- Renewable raw materials
- New reactions
- New catalysts
- Solvent substitution
- Process improvement
- Separation Technologies
- Enabling technologies, i.e. modelling, analysis,..
- Sustainable energy sources

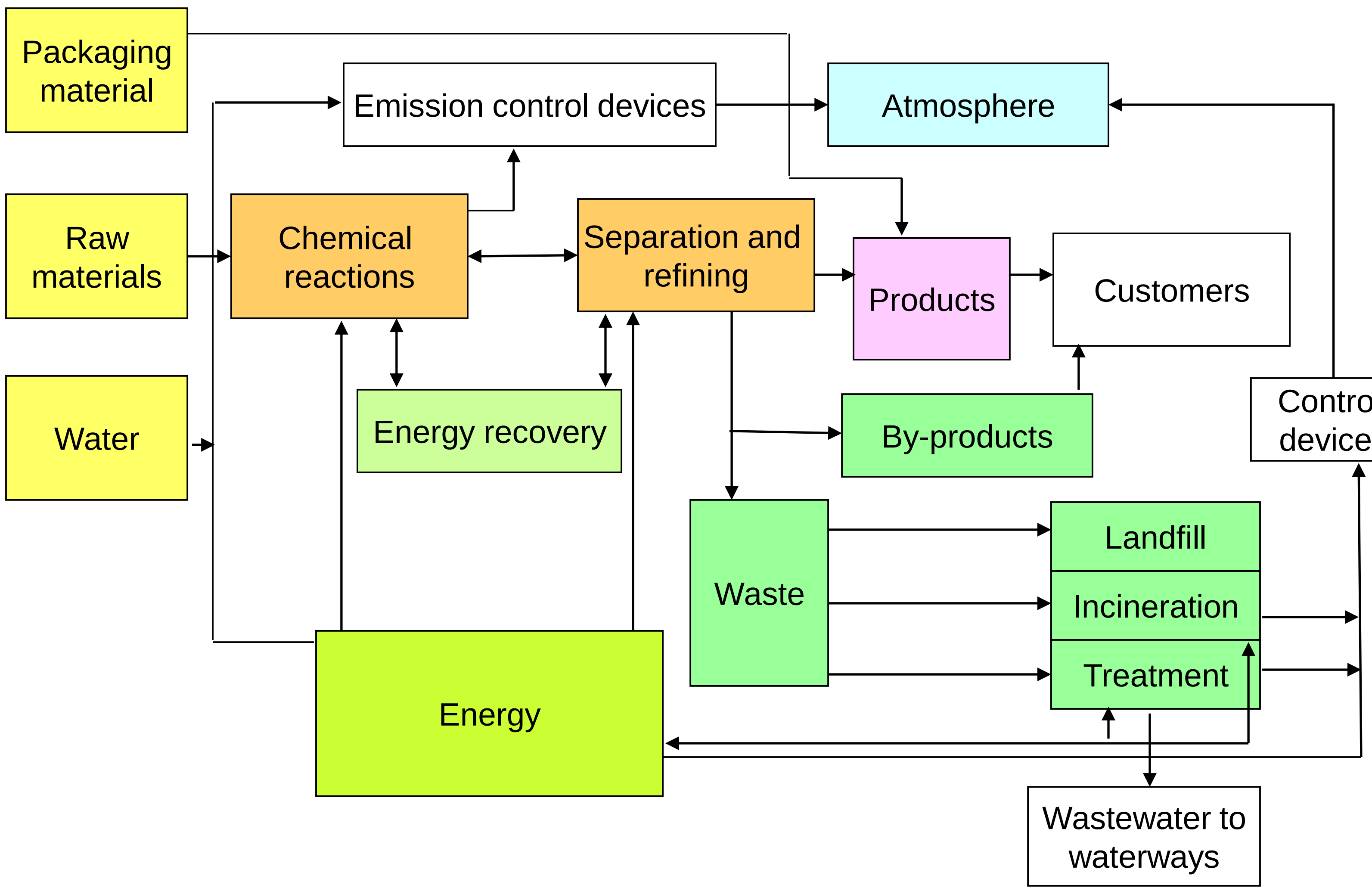


Key Technology Opportunities.

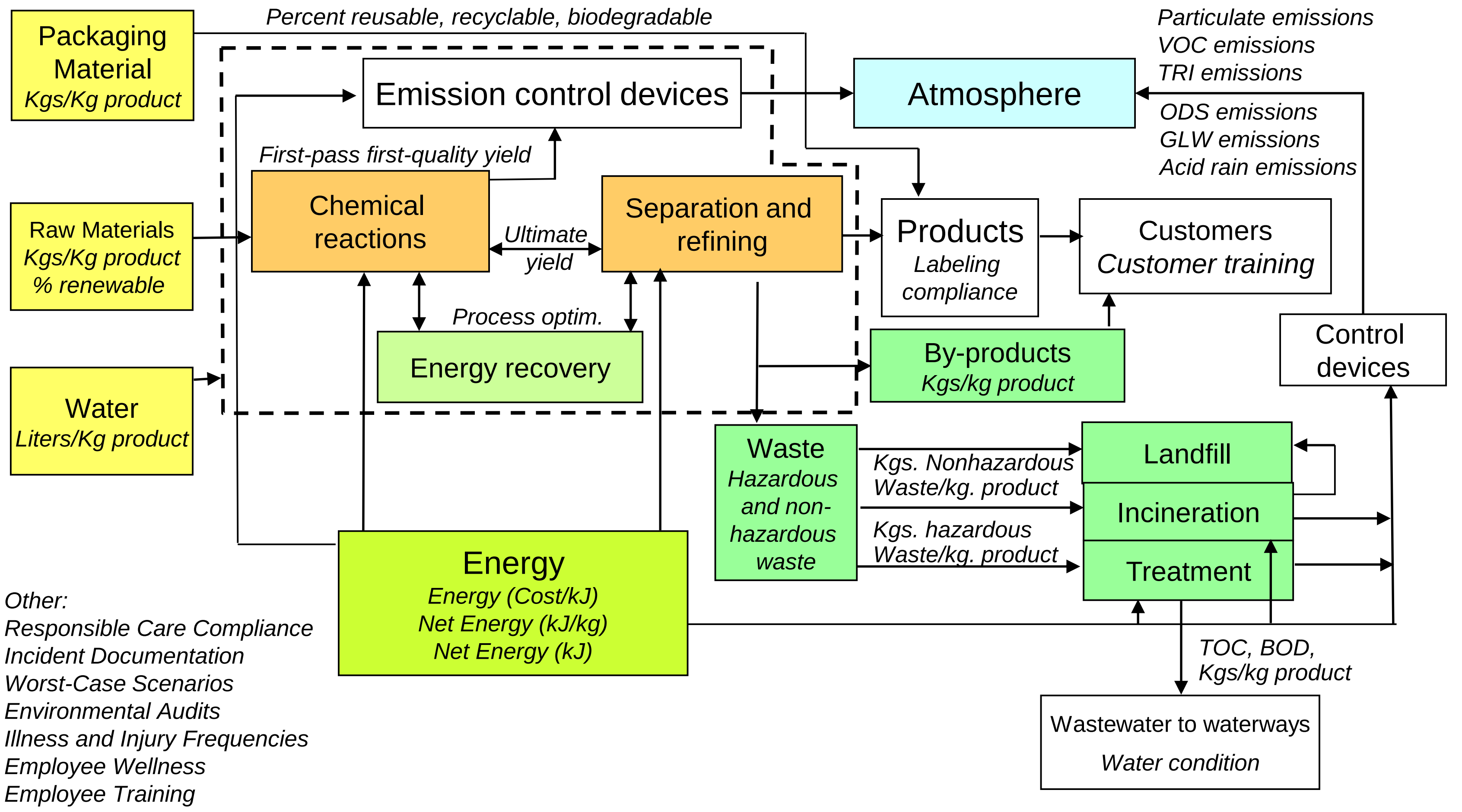
1. Green Product Design	2. Feedstocks	3. Novel Reactions	4. Novel Catalysts	5. Solvents	6. Process	7. Separations	8. Enabling
Life-cycle design	Olefins from alkanes	Combine bio- & chemical	Solid catalysts	**Closed-loop systems**	**Exploit process synthesis**	**Better data on membranes**	Integrated modelling
Extended recycling	Recycling plastics	Viable greener reagents	Practical enzyme reactions	**Supercritical fluids**	**Alternative energy sources**	Membranes for organic solvents	Fast, online analysis
Design for recycle & reuse	Waste to feedstock	Membrane driven reactions	Chiral synthesis	Practical ionic liquids	**Spinning disc reactors**	Lower cost affinity chromatog.	Easier life cycle analysis
Integrated product & process		Better routes to small & nanoparticles	Develop and scale-up	Solvent free reactions	**Real-time control**	Bioseps for fermentation	**Exploit existing HTE**
Understand downstream					New reactors e.g. microchannel		Improved High Throughput Experiments
Small & nano particles					**Exploit process modelling**		
					Easier, better models		

(Green/bold cells:) Existing technology in need of greater exploitation

Schematic Diagram of a Typical Manufacturing Chemical Process.

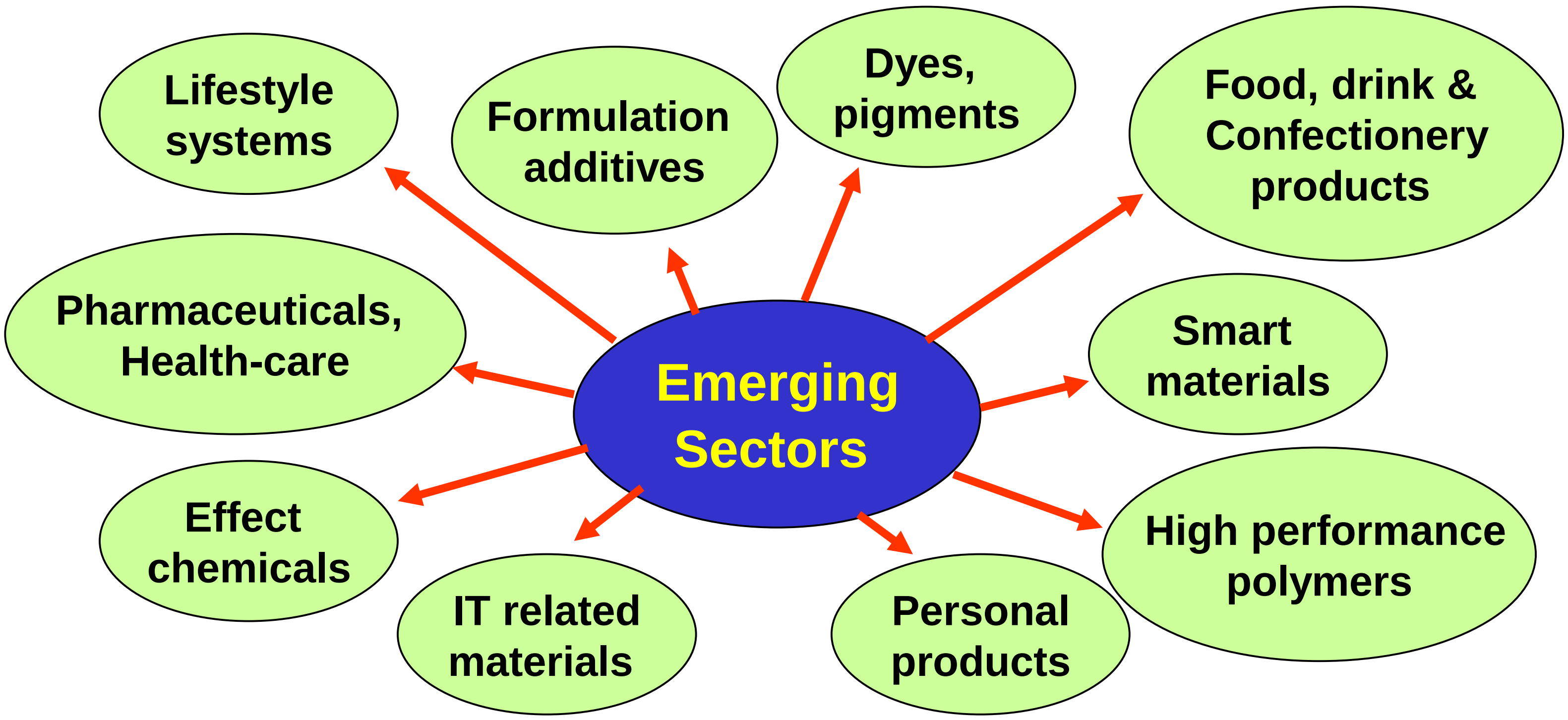


Measures Used in Chemical Production.



NOTE: VOC = volatile organic compound, TRI = toxic release inventory, ODS = ozone depleting substances, GLW = Great Lakes waste, TOC = total organic carbon, BOD = biological oxygen demand.

Relevant Product Areas in New Millennium.



… small fraction of these areas of product associated with sustainable & green process technology …

"The Principles of Sustainable Chemistry"
(example: ideal chemical synthesis).

Atom Efficient

Safe

Simple

THE IDEAL SYNTESIS OF A COMPOUND

One step

100% yield

No wasted reagents

Available materials

Environmentally acceptable

Clark, J.H. Green Chemistry, 1999

The 12 Principles of Sustainable Chemistry - (1-6).

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

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 methodologies 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 preserve efficacy of the 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,.

6. **Design for Energy Efficiency**
   Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be preferably conducted at ambient temperature and pressure.

Source: Green Chemistry Theory and Practice, Anastas & Warner, OUP, 1998.

The 12 Principles of Sustainable Chemistry - (7-12).

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 group, protection/de-protection, temporary modification of physical/chemical processes) should be minimized 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.

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 so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

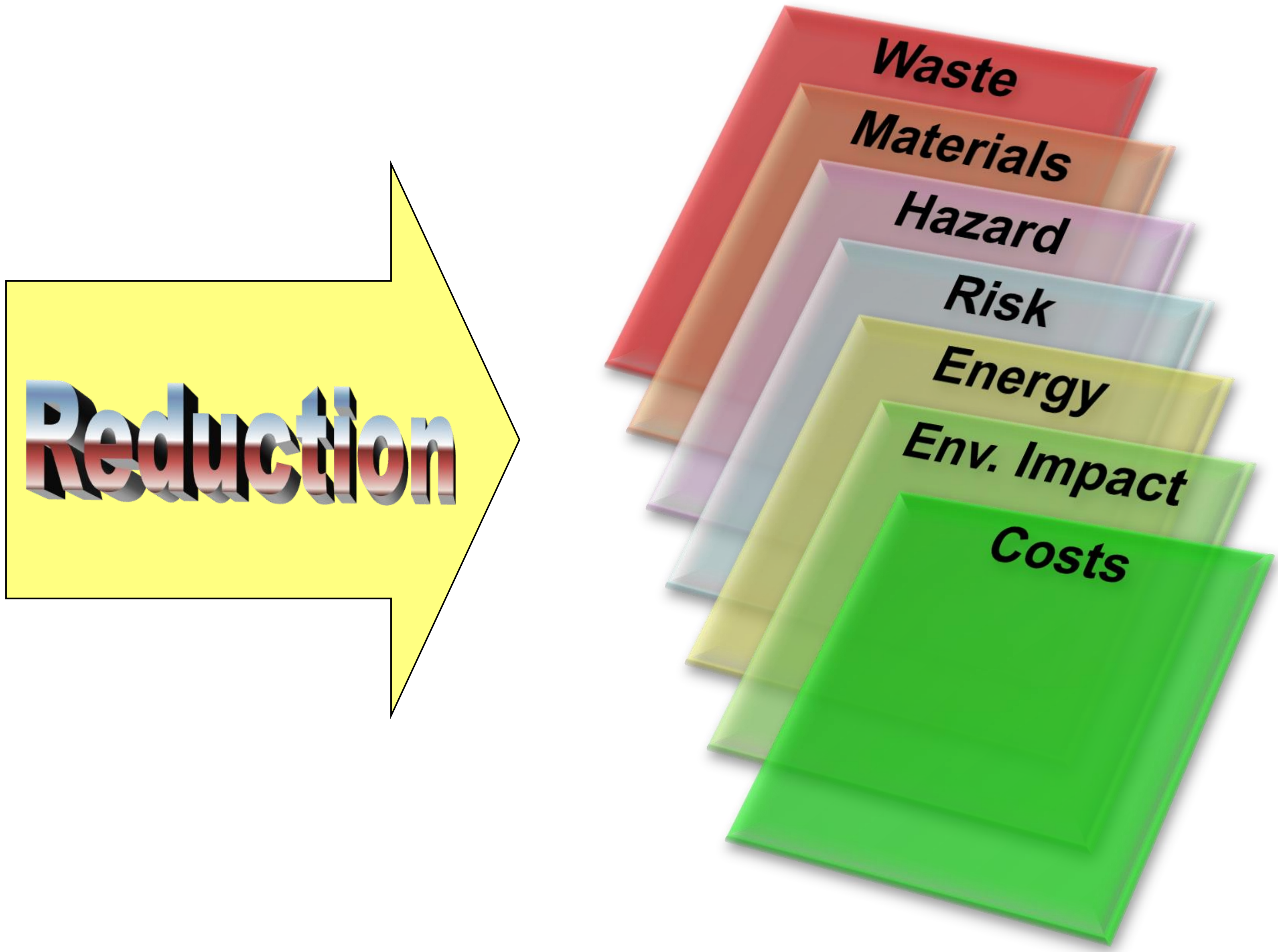
Further Needs for Greenness of Chemical Reactions.

When a more exhaustive determination of the greenness of a chemical reaction is required, many other factors than mass balances should be considered.

- **energy balances**, including the energy used to perform the reaction itself (J/kg of product) but also the energy used to extract or prepare and to recycle or destruct reagents, solvents, or auxiliaries.
- **prices**,
- **renewability**,
- **ease and safety of handling**,
- **recyclability,**
- **air, water and soil emissions**,
- **environmental risks.**

[Studies "from cradle to grave" i.e., "life cycle analyses" (LCA)]

Main Target of Green Chemistry:



Green and Sustainable Engineering.

Green Engineering is the development / commercialization of industrial processes that are economically feasible and reduce the risk to human health and the environment.

- Design, discovery, and implementation
- Molecules, products, processes, systems
- Maximize Inherency
- Maximize mass, energy, time, and space efficiency

A chemical manufacturing process is described as inherently safer if it reduces or eliminates hazards associated with materials used and operations, and this reduction or elimination is a permanent and inseparable part of the process technology.

(Kletz, 1991; Hendershot, 1997)

Aims of Green Engineering.

- Provide a framework
  - Applicable
  - Effective
  - Appropriate
- Apply across disciplines
  - Chemical, Civil, Environmental, Mechanical Systems…
- Apply across scales of design
  - Molecular architecture to construct chemical compounds
  - Product architecture to create a “product”, i.e. cell phone
  - Urban architecture to build a city

**Green Engineering, Anastas, P.T., ACS (2000) "Design Through the 12 Principles of Green Engineering", Anastas, Zimmerman, ES&T (2003)*

The 12 Principles of Green Engineering*.

1. **Inherent Rather than Circumstantial**
   Designers need to strive to ensure that all materials and energy inputs and outputs are as inherently nonhazardous as possible.
2. **Prevention Instead of Treatment**
   It is better to prevent waste than to treat or clean up waste after it is formed.
3. **Design for separation**
   Separation and purification operations should be designed to minimize energy consumption and materials.
4. **Maximize efficiency**
   Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.
5. **Output-Pulled versus Input-Pushed**
   Products, processes, and systems should be "output pulled" rather than "input pushed" in the use of energy/materials.
6. **Conserve Complexity**
   Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or disposition.

*Anastas, P.T.; Zimmerman, J.B. Design through the 12 principles of engineering. Environ. Sci. Technol. 2003, 37, 94A–101A.

The 12 Principles of Green Engineering – (7-12)

7. **Durability Rather than Immortality**
   Targeted durability, not immortality, should be a design goal.
8. **Meet Need, Minimize Excess**
   Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw.
9. **Minimize Material Diversity**
   Material diversity in multicomponent products should be minimized to promote disassembly and value retention.
10. **Integrate Material and Energy Flows**
    Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.
11. **Design for Commercial "Afterlife"**
    Products, processes, and systems should be designed for performance in a commercial "afterlife."
12. **Renewable rather than Depleting**
    Material and energy inputs should be renewable rather than depleting.

Alternative vision: The 9 Principles of Green Engineering in the Sandestin Declaration*.

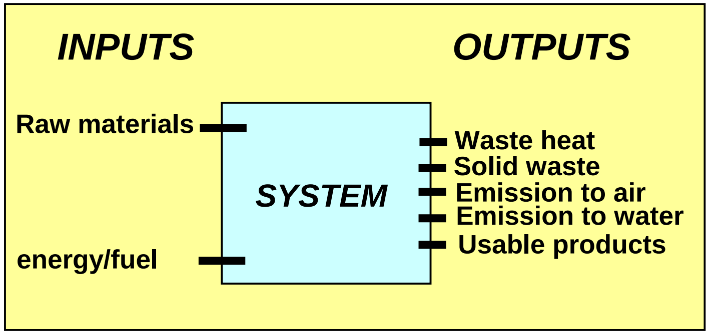
1. Engineer processes and products holistically, use systems analysis, and integrate environmental impact assessment tools.
2. Conserve and improve natural ecosystems while protecting human health and well-being.
3. Use life-cycle thinking in all engineering activities.
4. Ensure that all material and energy inputs and outputs are as inherently safe and benign as possible.
5. Minimize depletion of natural resources.
6. Strive to prevent waste.
7. Develop and apply engineering solutions, while being cognizant of local geography, aspirations, and cultures.
8. Create engineering solutions beyond current or dominant technologies, improve, innovate, and invent (technologies) to achieve sustainability.
9. Actively engage communities and stakeholders in development of engineering solutions.

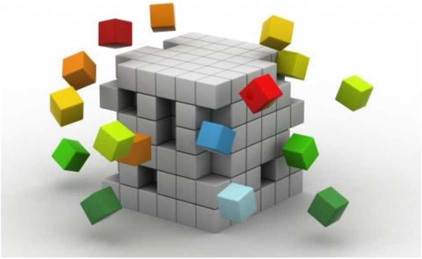
Fundamental Problems in the Application of Principles of Green Engineering.

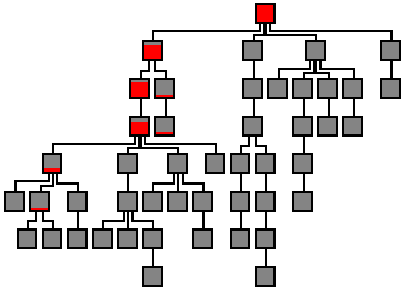
- Inherency

- *Life cycle foundation across all principles*.

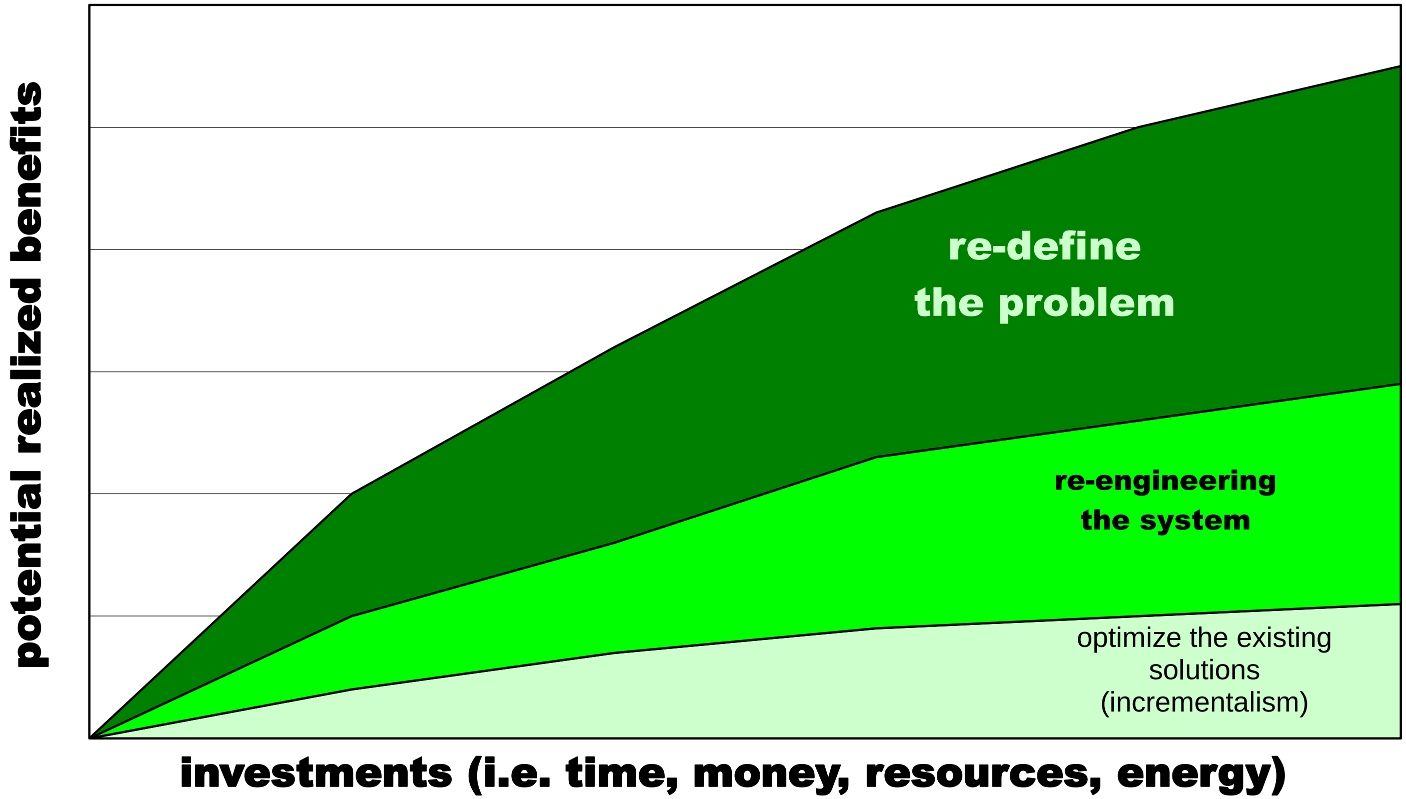
- Holistic or so-called "systems thinking" should be applied to avoid the unintended consequence of doing the wrong things, but doing them very well.







Applying the Principles of Green Engineering:
schematic of potential benefits vs. investments.



- Create engineering solutions beyond current or dominant technologies; improve, innovate and invent (technologies) to achieve sustainability

Principles 1, 2 and 3.

- Designers need to strive to ensure that all material and energy inputs and outputs are as **inherently non-hazardous and benign** as possible.
- It is better to prevent waste than to treat or clean up waste after it is formed.
- Separation and purification operations should be a component of the design framework.
- Engineer processes and products holistically, use **systems analysis**, and integrate environmental impact assessment tools
- Conserve and improve natural **ecosystems** while protecting **human health** and well-being.

Principles 4 e 5.

4. System components should be designed to maximize mass, energy and temporal efficiency.
   - Process intensification
   - Sophisticated actuator-control systems

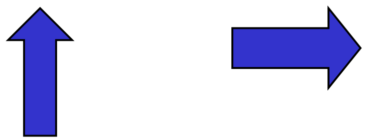
5. System components should be output pulled rather than input pushed through the use of energy and materials. *(approaching design through Le Chatelier's Principle)*

Le Chatelier's Principle
"If a system in equilibrium is subjected to a stress the equilibrium will shift in the direction which tends to relieve that stress."

Peculiarity of Principle 5.

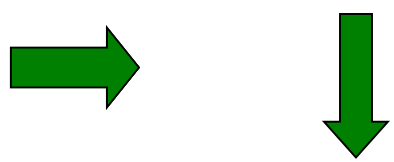
Often “drive” a reaction or transformation to completion by adding materials or energy.

$$A + B \rightleftarrows C + D$$



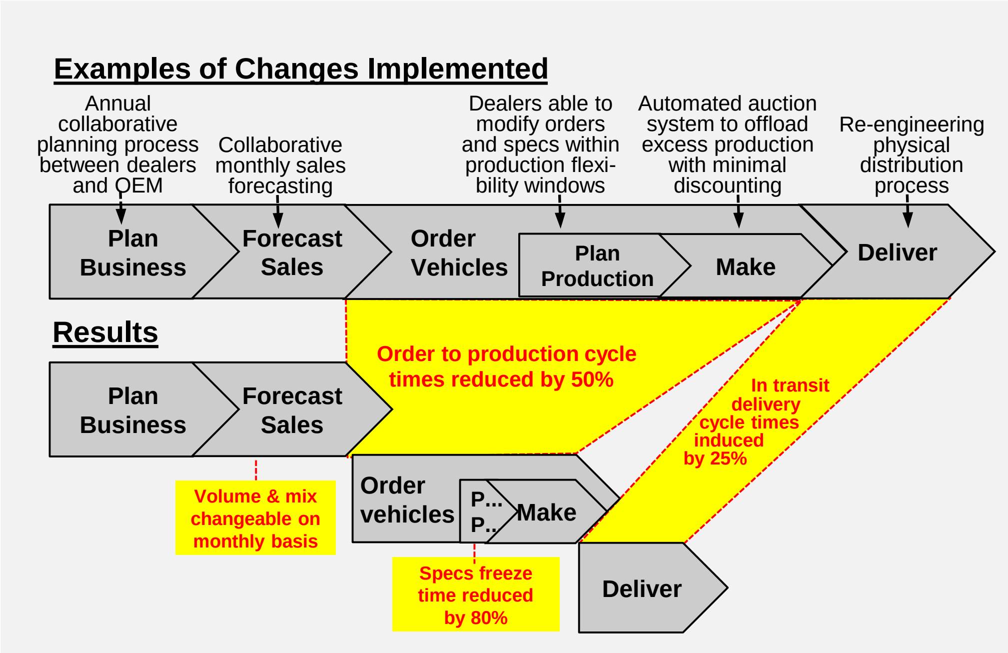
Similarly, a reaction can be “pulled” to completion by removing the product without adding materials or energy.

$$A + B \rightleftarrows C + D$$



Peculiarity of Principle 5 (cont.).

- "Just in time" manufacturing
  - Production is based on demand
  - eliminates waste overproduction and lowers warehousing costs
  - suppliers are closely monitored and quickly altered to meet changing demands
  - small and accurate resupply deliveries must be made just as they are needed



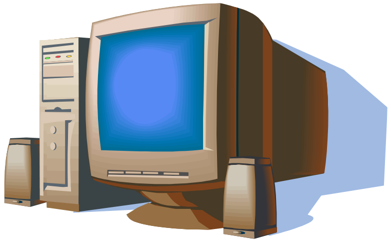
Grocery stores use RFID to track sales

Principle 6.

6. Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse or beneficial disposition.

- The amount of complexity built into a product whether at the macro, micro, or molecular scale is usually a function of resource expenditures.
  - High complexity, high entropy – reuse
  - Lower complexity – value-conserving recycling where possible or beneficial disposition
- Natural systems can also be recognized as having complexity

- **Why not reuse computers?**
  - **make modular**
  - **replace processors, memory…**
  - **economics...**



Principle 7.

7. Targeted durability, not immortality, should be a design goal.

- Products that last well beyond their useful commercial life often result in environmental problems ranging from solid waste to persistence and bioaccumulation.
- Repair and maintenance must also be considered
- Must balance targeted lifetime with durability and robustness in anticipated operating conditions.!
- Example

$C_xH_yF_zCl_q$
Non-flammable
Non-toxic
Inexpensive
Effective
Stable

Long-lived, migrate to upper atmosphere

UV-induced fragmentation in upper atmosphere leads to ozone depletion

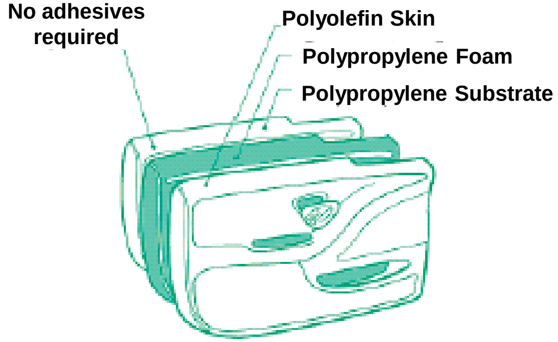
Principle 8.

8. Design for unnecessary capacity or capability should be considered a design flaw. This includes engineering "one size fits all" solutions.
   - While product agility and product flexibility can be desirable, the cost in terms of materials and energy for unusable capacity and capability can be high.
   - There is also a tendency to design for the worst case scenario such that the same product or process can be utilized regardless of spatial or temporal conditions.
   - A single laundry detergent formulation that is intended to work anywhere in the US and must be designed to work in the most extreme hard water conditions
     - Phosphates were added as builders to remove hardness of water
     - Phosphates, by their high nutrient value, can cause eutrophication in water bodies

Principio 9.

9. Multi-component products should strive for material unification to promote disassembly and value retention. *(minimize material diversity)*

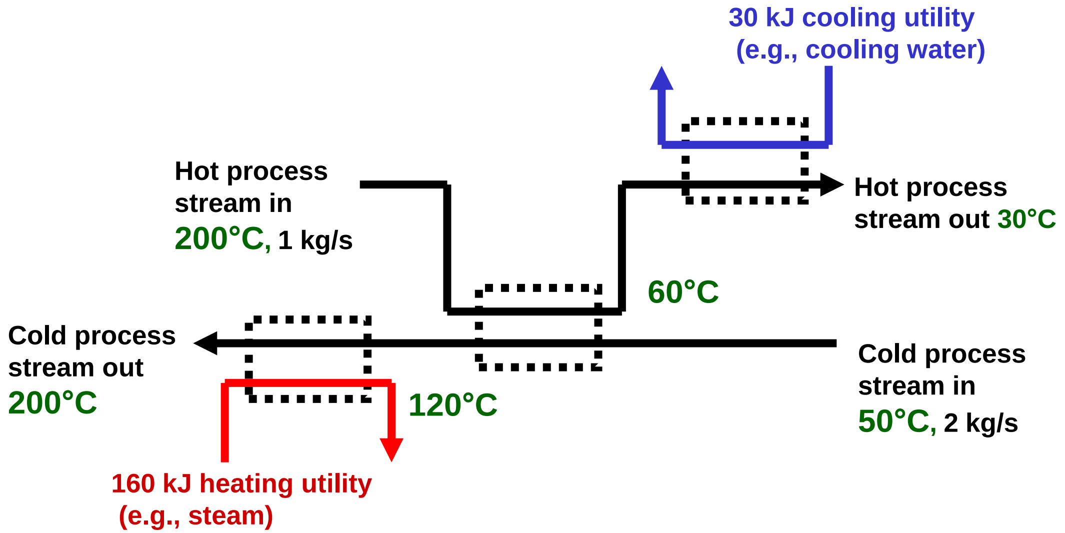
- Selected automobile designers are reducing the number of plastics by developing different forms of polymers to have new material characteristics that improve ease of disassembly and recyclability.
- This technology is currently applied to the design of multilayer components, such as door and instrument panels.
- Through the use of this monomaterial design strategy, it is no longer necessary to disassemble the door or instrument panel for recovery and recycling



Principles 10, 11, and 12.

- Design of processes and systems must include integration and interconnectivity with available energy and materials flows.
- Performance metrics include designing for performance in commercial "after-life".
- Design should be based on renewable and readily available inputs.

Example:
heat integration



Example of Principle 12.

With cooperative development from Mitsui Chemicals Inc. and Cargill-Dow, LLC, SANYO achieved the world's first bio-plastic (polylactic acid) optical disc in 9/2003.

Use corn as feedstock to derive polylactic acid with its optical property and exact structure.

Roughly 85 corn kernels is needed to make one disc and one ear of corn to make 10 discs. The world corn production is about 600 million tons, less than 0.1% is needed to make 10 billion discs (current annual worldwide demand).

LCA of Chemical Reactions: an highly simplified but indicative approach (EcoScale)*.

The analysis id simplified via six parameters characterizing a reaction:

1) yield,
2) prices of the components,
3) safety,
4) technical set-up,
5) temperature and time,
6) work-up and purification.

Within each of these parameters, individual penalty points are associated to particular situations. The ideal score is attributed to an ideal reaction in which a compound A (substrate) undergoes a reaction with (or in the presence of) inexpensive compounds B to give the desired product C in 100% yield at room temperature with a minimal risk for the operator and a minimal impact for the environment. The actual EcoScale score is then calculated by lowering the ideal score of 100 by those penalty. (> 75 good, 50 -75 medium, < 50 non acceptable)

*Van Aken, K.; Strekowski, L.; Patiny, L. *EcoScale, a semi-quantitative tool to select an organic preparation based on economical and ecological parameters*. Beilstein J. Org. Chem. 2006, 2.
Dash, R.; Song, J.J.; Roschangar, F.; Samstag, W.; Senanayake, C.H. The eight criteria defining a good manufacturing process. Org. Process Res. Dev. 2012, 16, 1697–1706.

Penalty Points Used in the EcoScale.

Parameters	Penalty Points
Yield	**(100 - Effective Yield)/2**
Price of reaction components (to obtain 10 mmol)	
Inexpensive (< 10 US$)	**0**
Expensive (between 10 and 50 US$)	**3**
Very expensive (> 50 US$)	**5**
Safety (adapted for Globally Harmonized System of Classification and Labeling of Chemicals)	
GHS09 (dangerous for the environment)	**5**
GHS06 (toxic)	**5**
GHS02 (flammable)	**5**
GHS01 (explosive)	**10**
GHS07, GHS08 (extremely toxic)	**10**

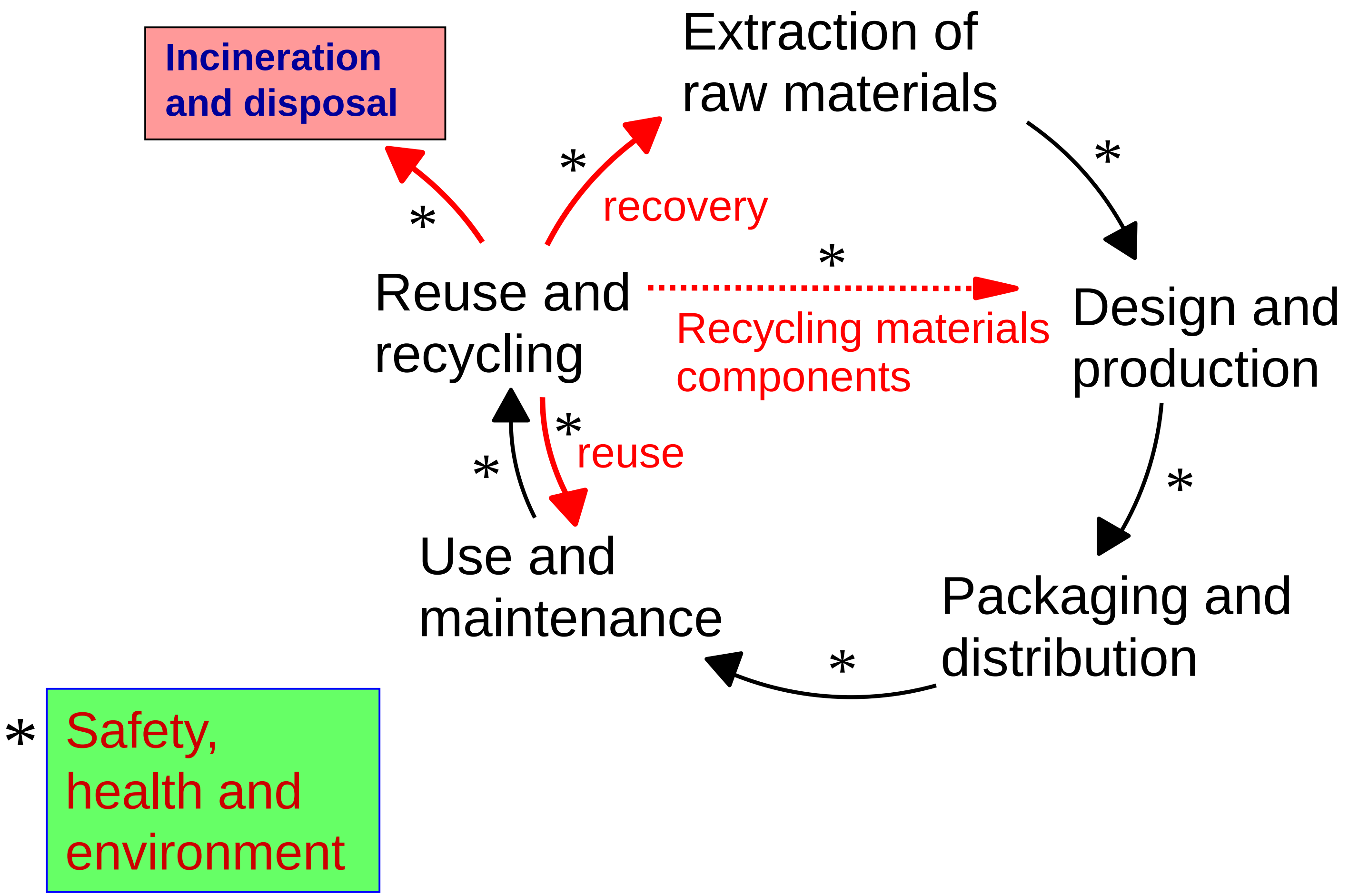
Penalty Points Used in the EcoScale (cont.).

Parameters	Penalty Points
Technical setup	
Common setup	0
Instruments for controlled addition (funnel, etc.)	1
Unconventional activation technique (microwave, etc.)	2
Pressure equipment > 1 atm	3
Any additional special glassware	1
(Inert) gas atmosphere	1
Glove box	3
Temperature/Time	
Room temperature, < 1 h	0
Room temperature, < 24 h	1
Heating < 1 h	2
Heating > 1 h	3
Cooling to 0°C	4
Cooling < 0°C	5

Penalty Points Used in the EcoScale (cont.)

Parameters	Penalty Points
Workup/Purification	
None	**0**
Cooling to room temperature	**0**
Adding solvent	**0**
Simple filtration	**0**
Removal of solvent with bp < 150 °C	**0**
Crystallization and filtration	**1**
Removal of solvent with bp > 150 C	**2**
Solid phase extraction	**2**
Distillation	**3**
Sublimation	**3**
Liquid-liquid extraction	**3**
Classical chromatography	**10**

Product Life Cycle Thinking
Safety/health/environment.

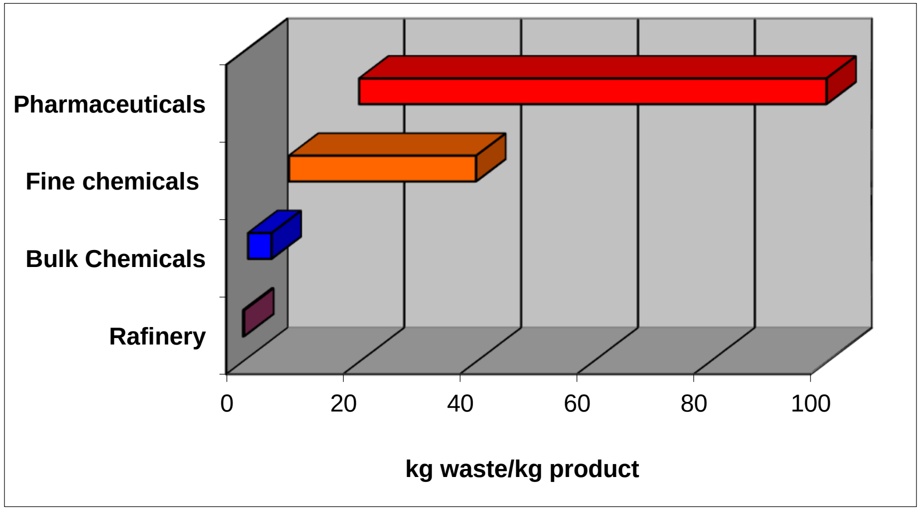


Wastes and Chemical Industry.

Can be quantified according to industry:

Industry Segment	Ton/year	Ratio Kg Byproducts/Kg Product
Oil refining	10^6 - 10^8	<0.1
Bulk chemicals	10^4 - 10^6	1 – 5
Fine Chemical	10^2 - 10^4	5 – 50
Pharmaceuticals	10 - 10^3	25 - 100+

- Areas traditionally thought of as being dirty (oil refining & bulk chemical production) are relatively clean - they need to be so because margins per Kg are low.
- Newer industries with higher profit margins and employing more complex chemistry produce relatively much more waste.

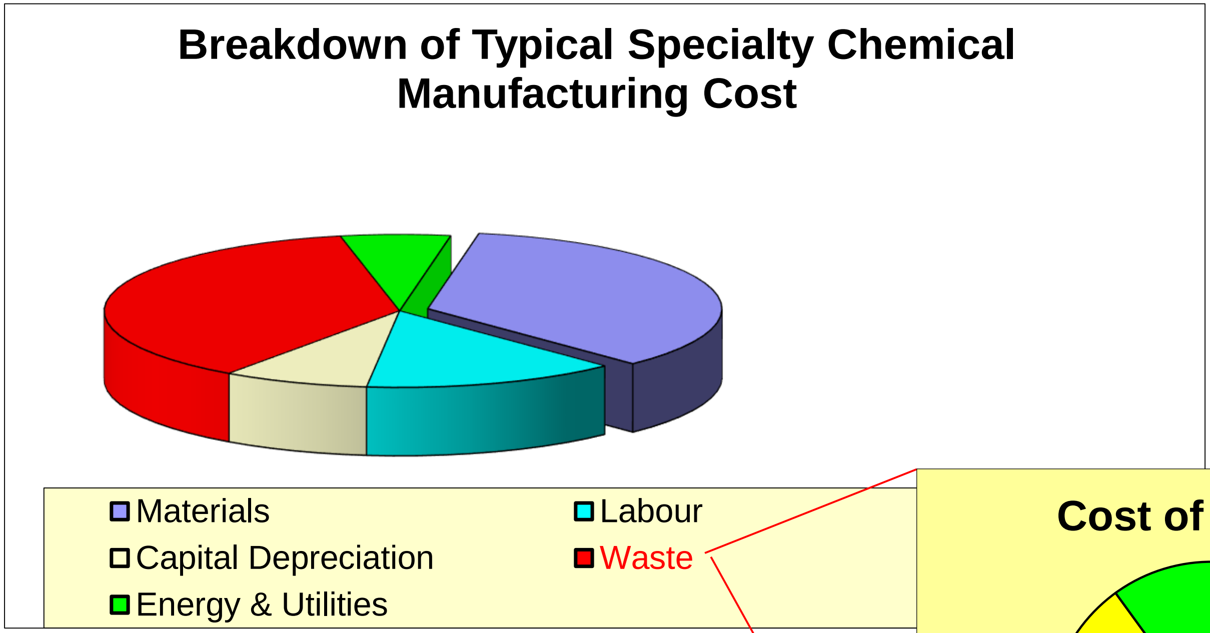


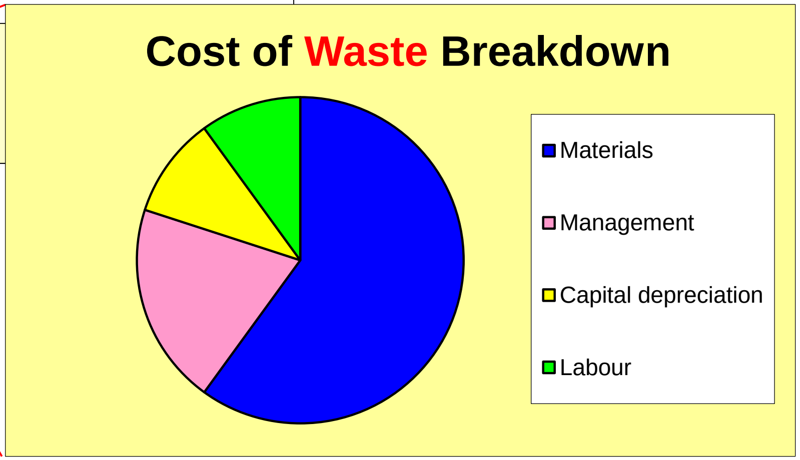
R A Sheldon *J. Chem. Tech. Biotech*. 1997, 68, 381

Wastes in the Past.

- **1,000 millions kg of hazardous chemicals released into air, water and land according to US Environmental Protection Agency (EPA) toxic release inventory.**
- **69% air; 13% land; 3% surface water; 15% underground**
- **2,000 millions kg transferred offsite for recycling, remediation (including energy recovery), treatment and disposal (often incineration)**
- **5 out of the top 10 chemicals released or disposed of were solvents or volatile organic compounds (VOCs), including MeOH, toluene, xylene, methylethylketone, and dichloromethane.**
- **As a result, an increasing proliferation of environmental regulations appeared to combat such releases.**

Waste in the Specialty Chemicals Industry.



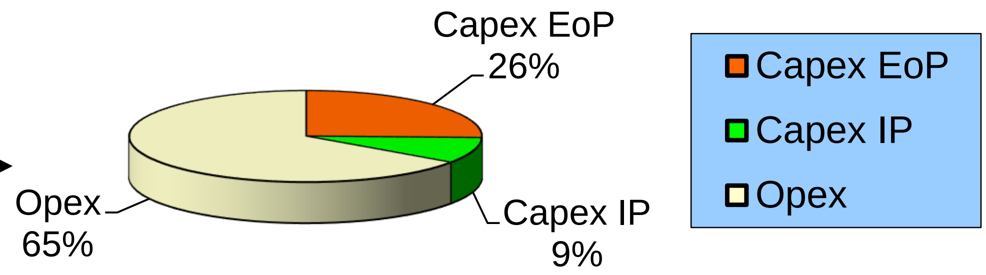


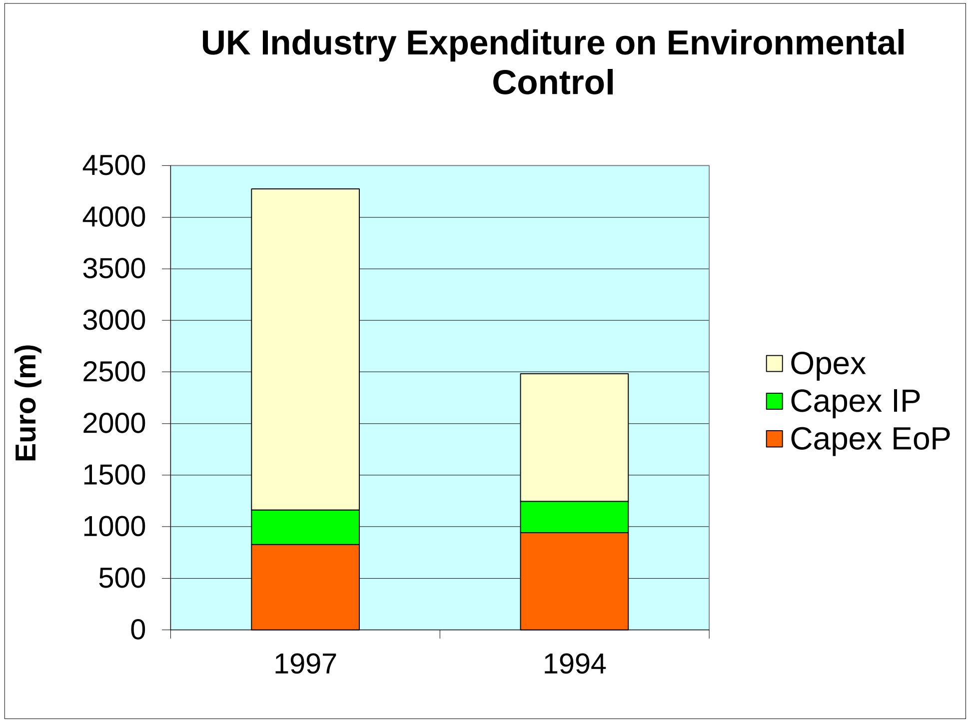
Expenditure on Environmental Control.

2007 Total Euro 2300 m

1997 Total Euro 1250 m →

1994 Total Euro 747 m





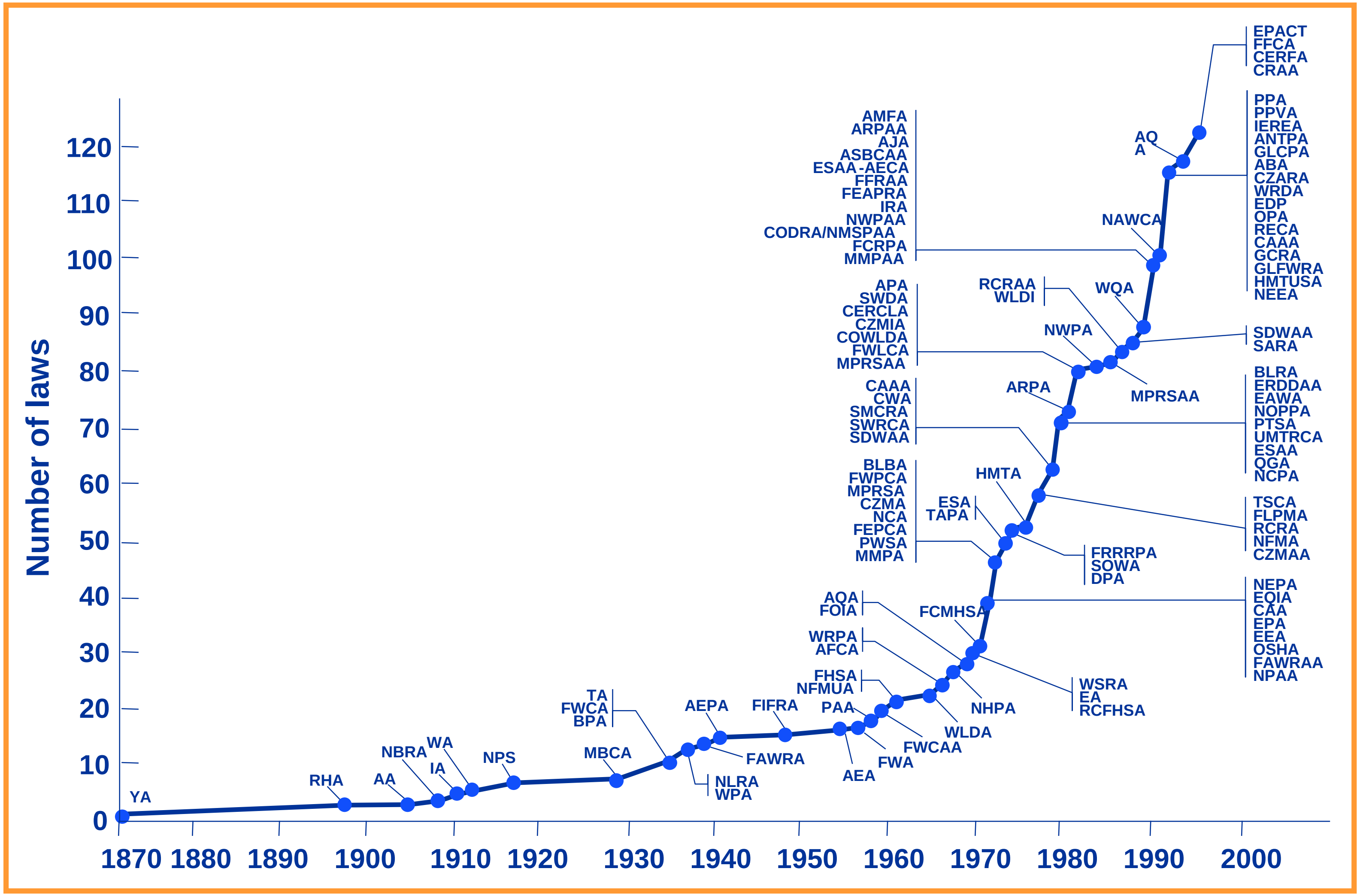
Capex EoP: expenditure for end of pipe technology

Capex IP: Expenditure for integrated process technology

Opex: Expenditure for operating expenditure

M Lancaster
Green Chemistry, 2000, 2, G65

Cumulative Growth in Environmental Regulation (US).



Chemical Risk and Law.

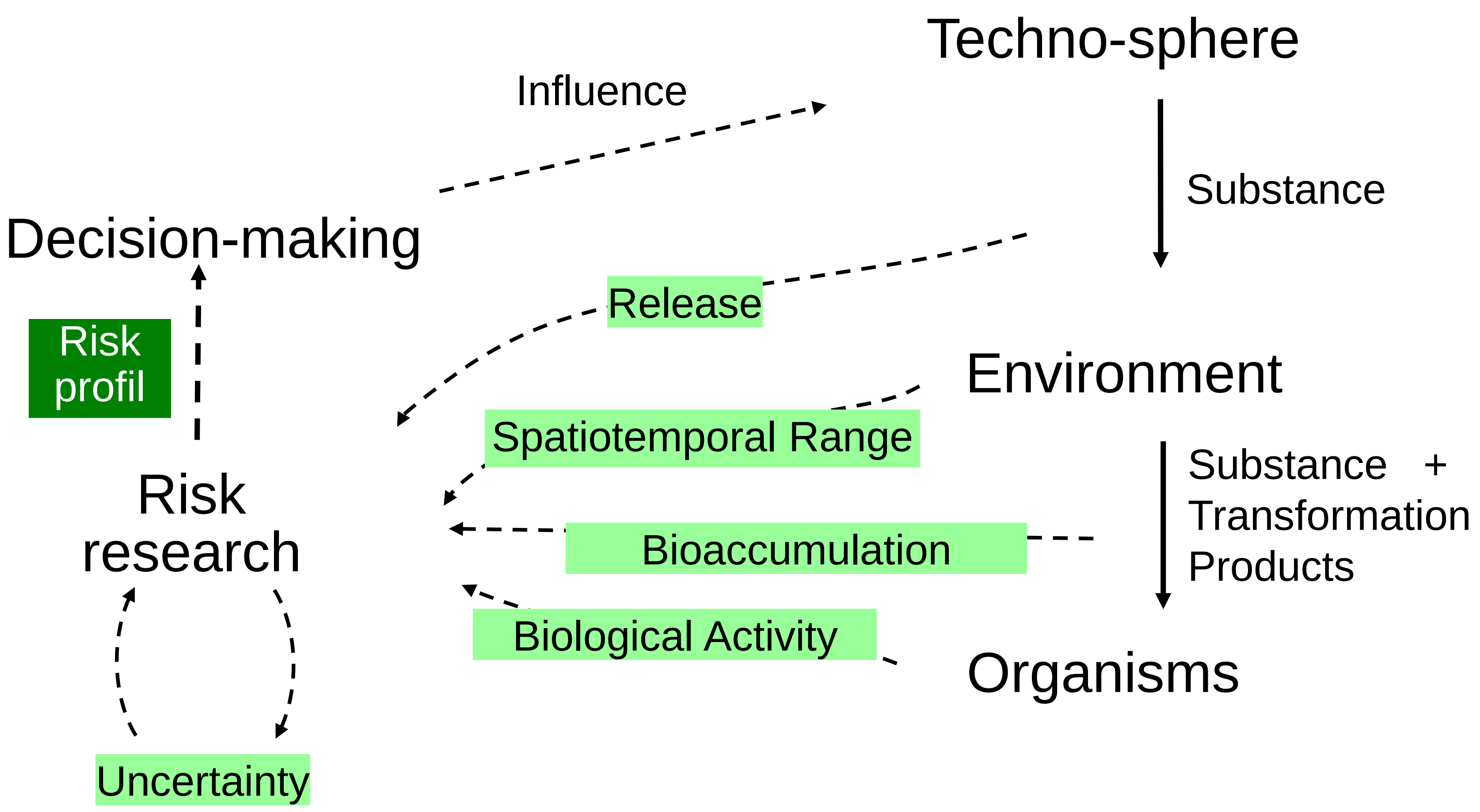
All of these acts, with few exceptions, deal with pollution after it is formed. These laws are in general focused on the treatment or abatement of pollution and are become know as “command and control” laws. In many instances these laws place limits on pollution and timetables for compliance, with little regard to whether the science/technology could attain these goals and with little regard to the economic costs of these laws.

Risk associated with a toxic chemical is a function of Hazard and Exposure.

The “end of the pipe” laws attempt to control Risk by dealing with the prevention of the Exposure to toxic hazardous chemicals. Of course all to often prevention of Exposure has failed.

Risk = f(Hazard, ~~Exposure~~)

Risk Management Cycle and Eco-toxicological Information on Chemical Products.



Focus on Hazard Elimination!

- Green Chemistry, instead of limiting Risk by controlling our Exposure to hazardous chemicals, attempts to reduce and preferentially eliminate the Hazard, thus negating the necessity to control Exposure. The bottom line is, if we don't use or produce hazardous substances then the Risk is zero, and we don't have to worry about the treatment of hazardous substances or limiting our exposure to them.
- Green chemistry has gained a strong foothold in the areas of research and development in both industry and academia. Several conferences and meetings are held each year with green chemistry and technology as their focus.

Risk = f(~~Hazard~~, Exposure)

Control the hazard, no need to worry about the exposure!

Precautionary Principle.

Where, following an assessment of available scientific information, there are reasonable grounds for concern for the possibility of adverse effects but scientific uncertainty persists, provisional risk management measures based on a broad cost/benefit analysis whereby priority will be given to human health and the environment, necessary to ensure the chosen high level of protection in the Community and proportionate to this level of protection, may be adopted, pending further scientific information for a more comprehensive risk assessment, without having to wait until the reality and seriousness of those adverse effects become fully apparent.

Fisher, E., J. Jones, R. von Schomberg (Eds). Implementing the Precautionary Principle: Perspectives and Prospects, Cheltenham, UK : Edward Elgar (2006)

AEA – Agenzia europea dell'ambiente (2001), Late Lessons From Early Warnings: The Precautionary Principle 1896-2000, Environmental issue report No 22.

Ref: http://habitat.igc.org/agenda21/rio-dec.html

EU Chemicals Legislation.

Publication proposal REACH regulation

REACH in force

Dangerous Substances Directive 1999/45/EEC

White Paper

Notification new substances
92/32/EEC – 7e Amendment

Year

65. . . .70. . . .75. . . .80. . . .85. . . .90. . . .95. . . .00. . . . 05 . .

EINECS list

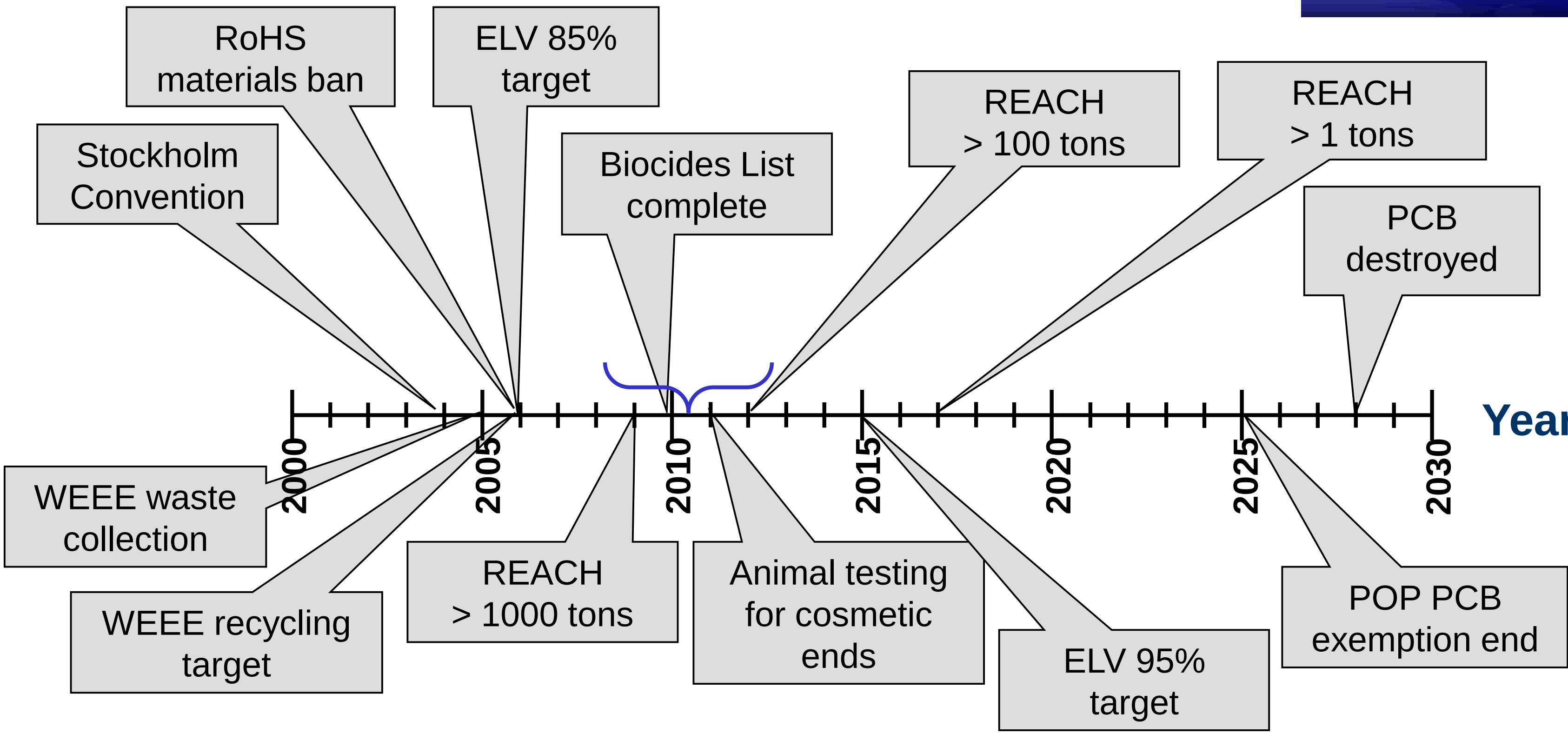
Risk assessment:
93/67/EEC (new substances)
Reg. 793/93 (existing subst.)

Hazard assessment:
67/548/EEC
Classification,
Packaging & Labelling
dangerous substances

Restrictions of marketing and use of certain chemicals / preparations: 76/769/EEC

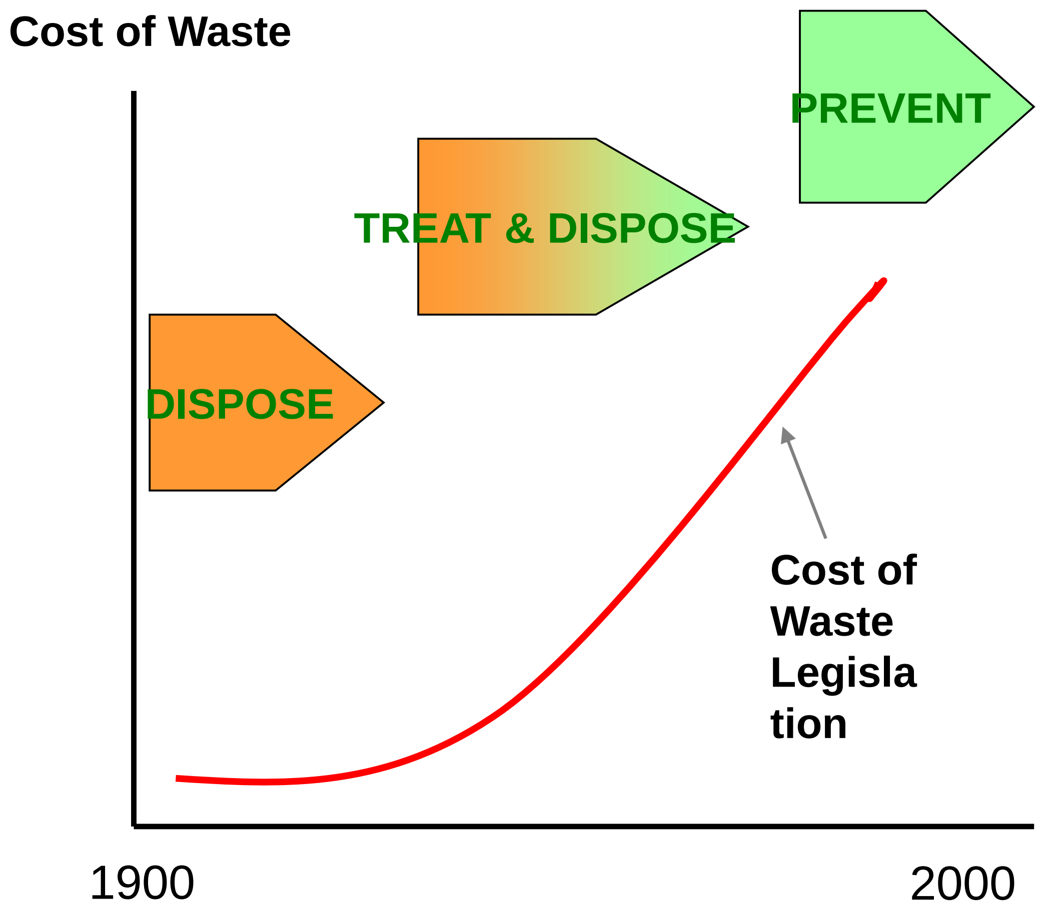
EU-REACH Legislation Timeline.

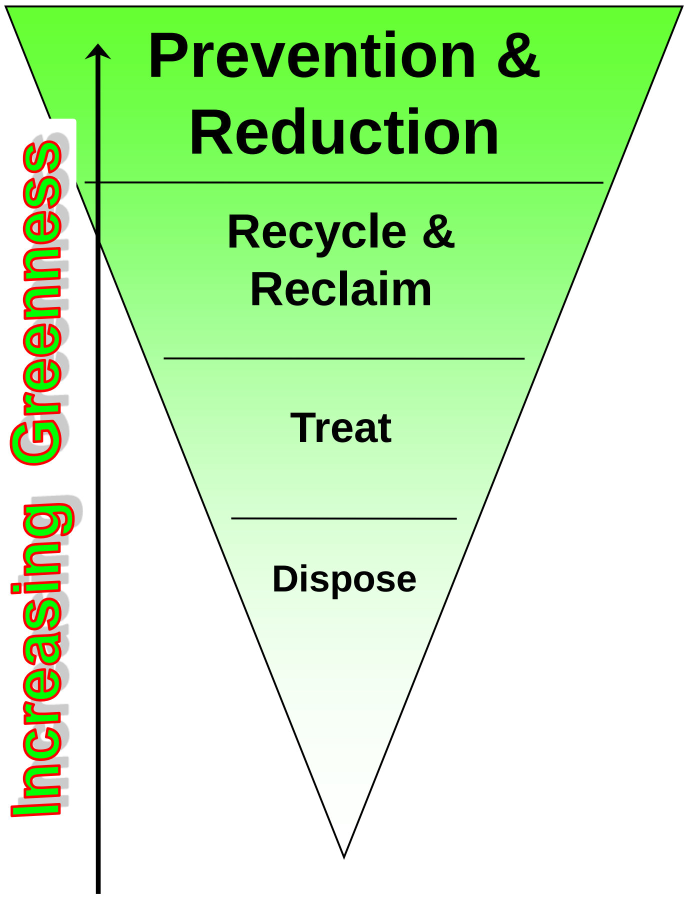
Chemical Products: Registration
Evaluation
Authorization



http://www.ec.europa.eu/environment/chemicals/reach/reach_intro.htm; EC 1907/2006

Waste Treatment and Pollution Prevention Hierarchy





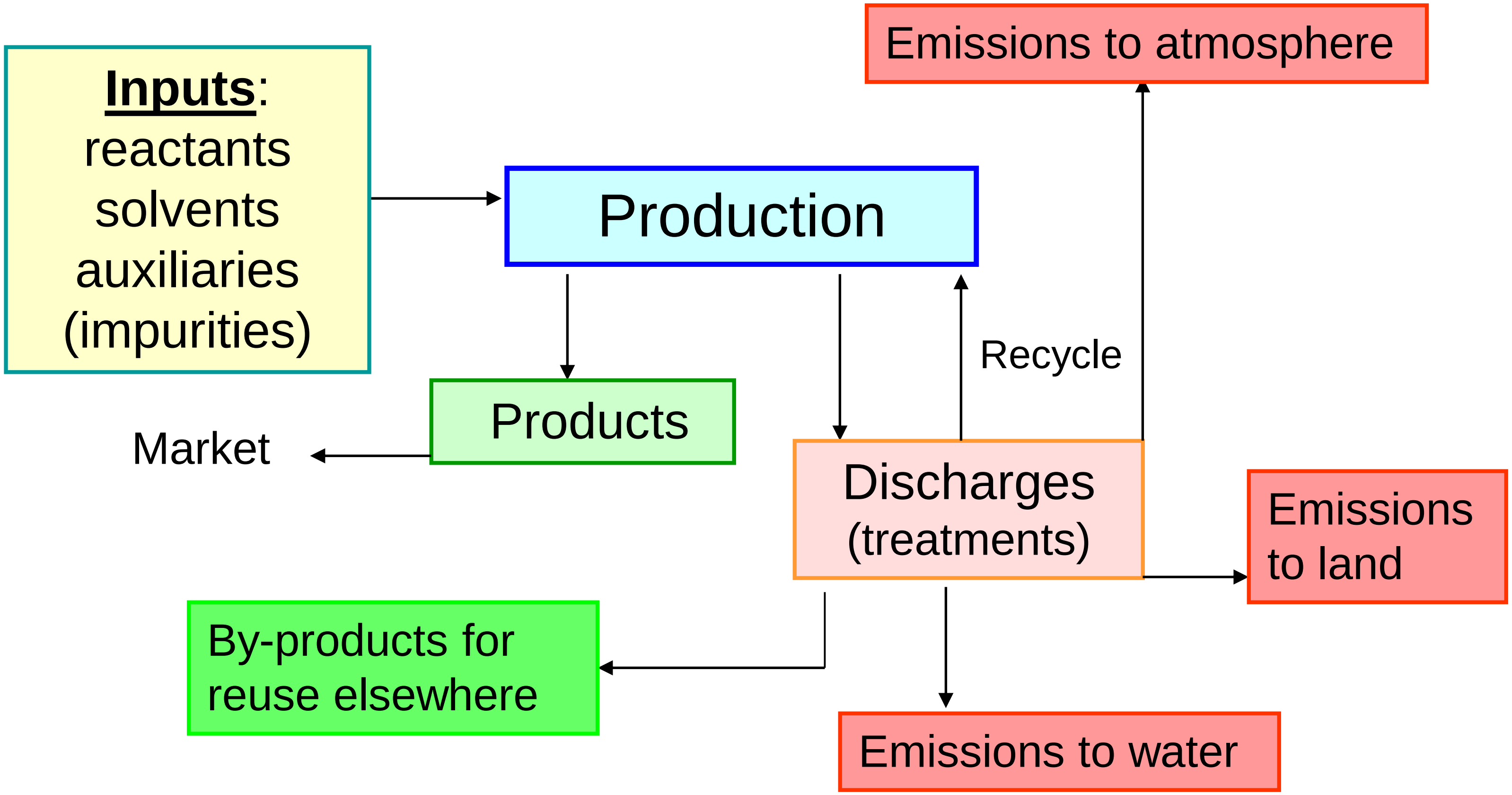
Waste Minimization Techniques.

- Prevention is better than cure
- Get it right at the R&D stage
- Chemists do not have all the answers!
- The answer lies within a multi-disciplinary team:
  - ✓ chemists
  - ✓ chemical engineers
  - ✓ production
  - ✓ business
  - ✓ health, safety, environment specialists
  - ✓ control engineers, environmental scientists, consultants/ etc.

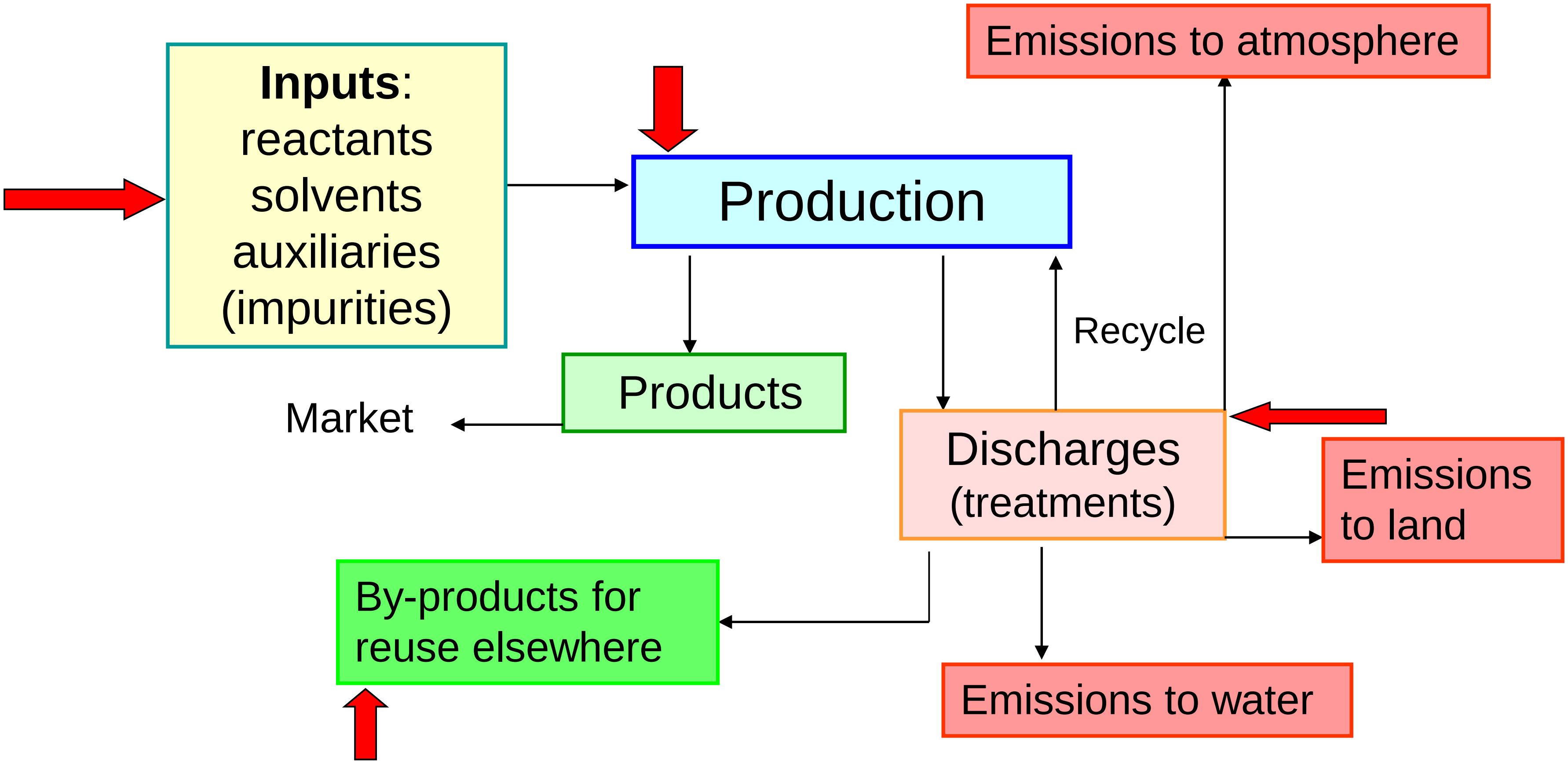
Role of Teams in Developing a New Process Selection.

Chemistry	**Production**	**SHE**	**Business**	**Chem.Eng.**
Yield	Operability	Emissions	Production cost	Flow sheet
Purity	Convenience for shifts	Waste treatment	Waste disposal cost	Heat & mass transfer
Selectivity	Operator safety	Regulatory compliance	Product packaging	Process costs
Identification by-products	Materials handling	Operator safety	Product liability	Equipment choice
Mechanism			Product quality	Product isolation

Waste & Production.



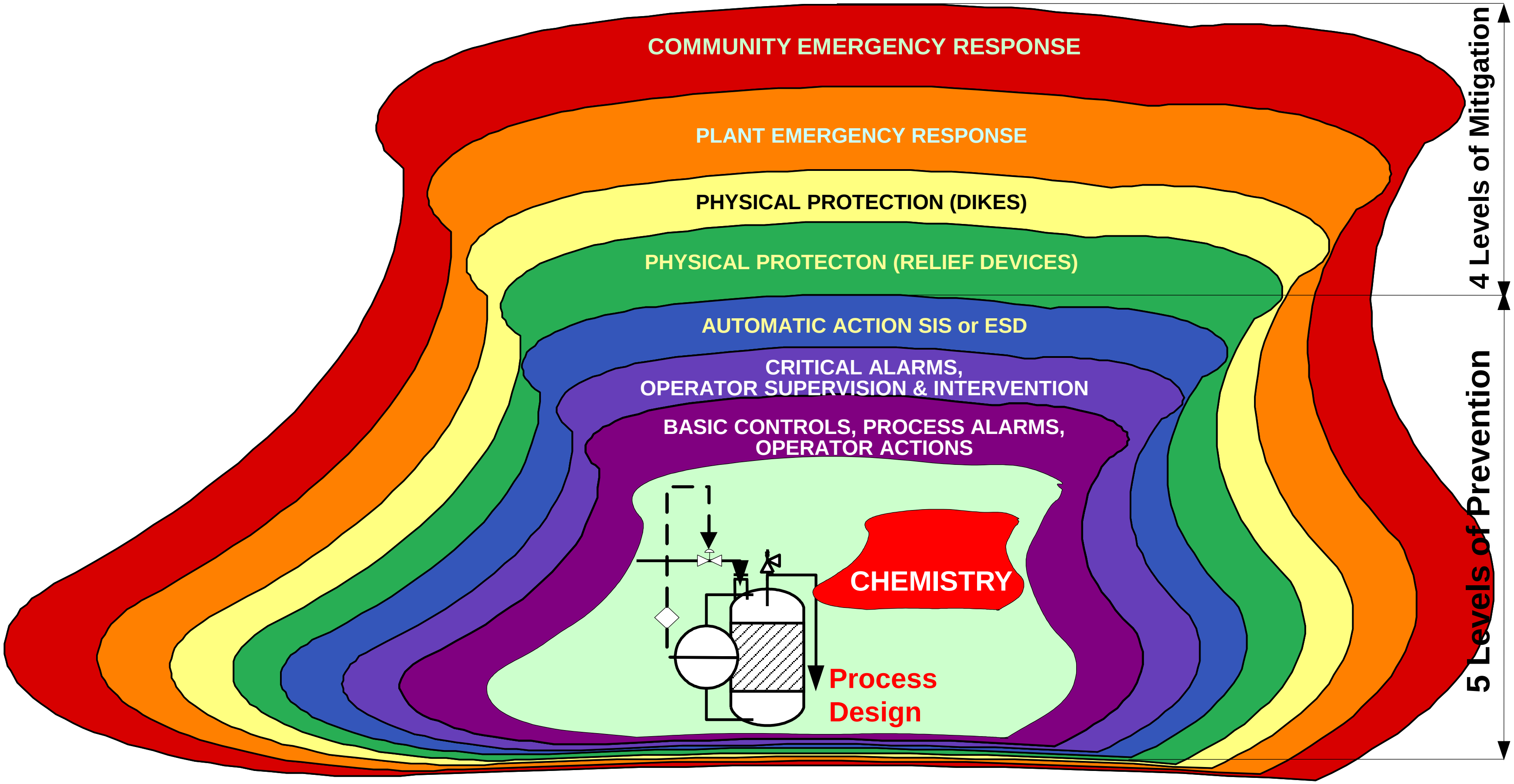
Waste Reduction Possibilities



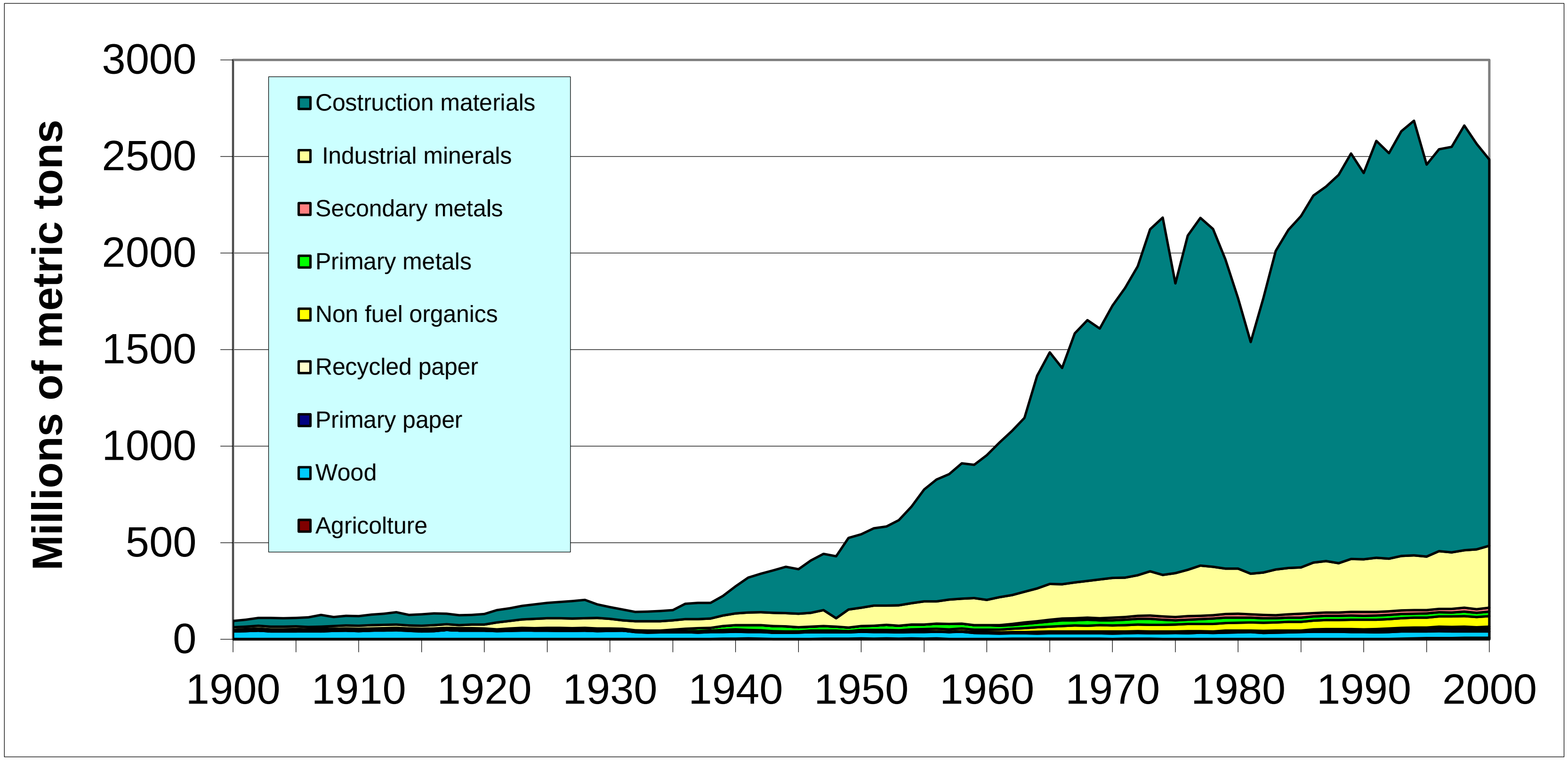
Waste Reduction Possibilities.

- Inputs
  - ✓ eco friendly solvents, high purity reagents, recyclable auxiliaries, lass hazardous materials
- Production
  - ✓ change time, T&P, reactor types, mixing, heat transfer
  - ✓ new route, appropriate cleaning
- Discharges
  - ✓ reduce water volume, improved scrubbers, waste water clean up, mineralization of organics
- By-products
  - ✓ Maximize use, R&D, marketing, site integration

Prevention/Mitigation: Layers of Protection for a Chemical Plant.

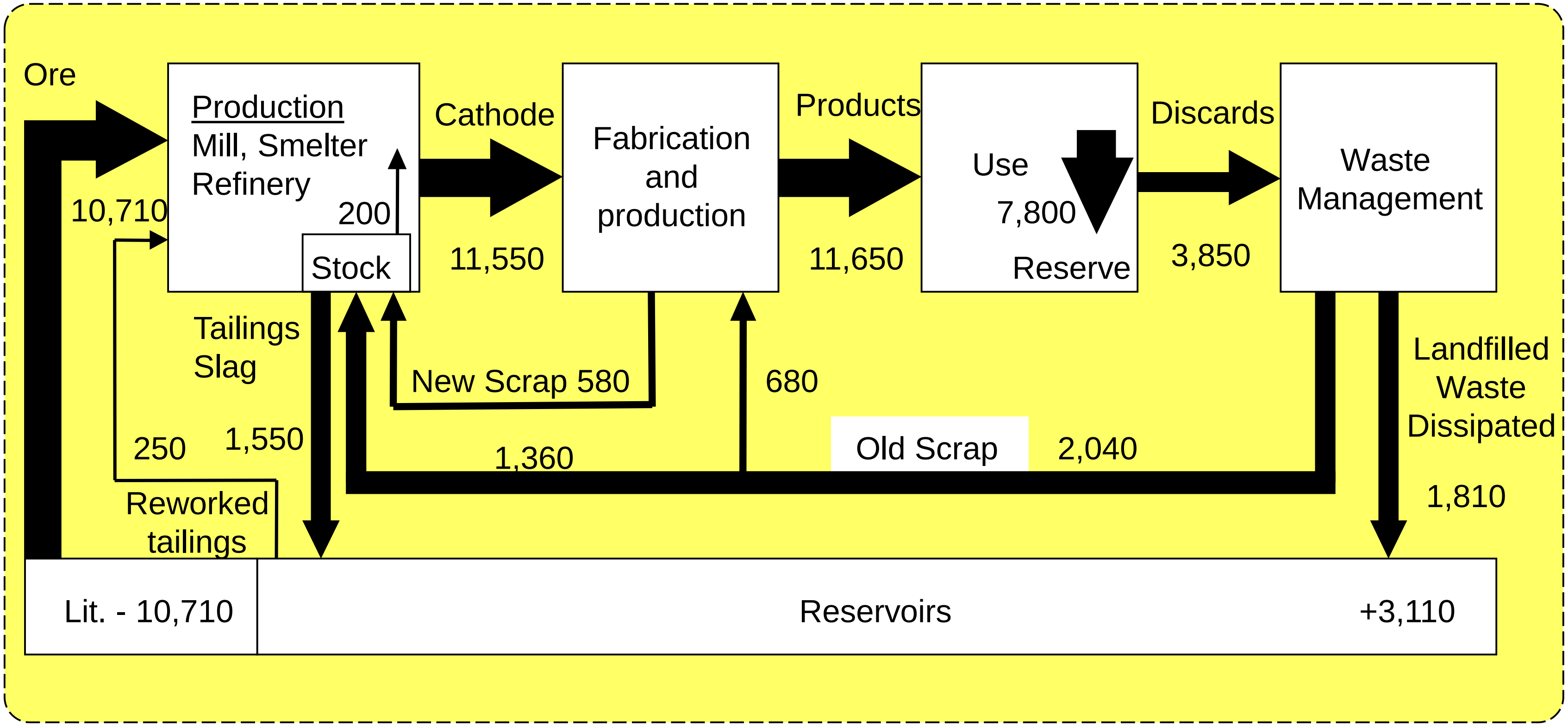


Trend in Use of Raw Materials (1900-2000).



Source: US Geological Survey

Substance or Material Flow Analysis: The Global Copper Cycle, 1990-2000.

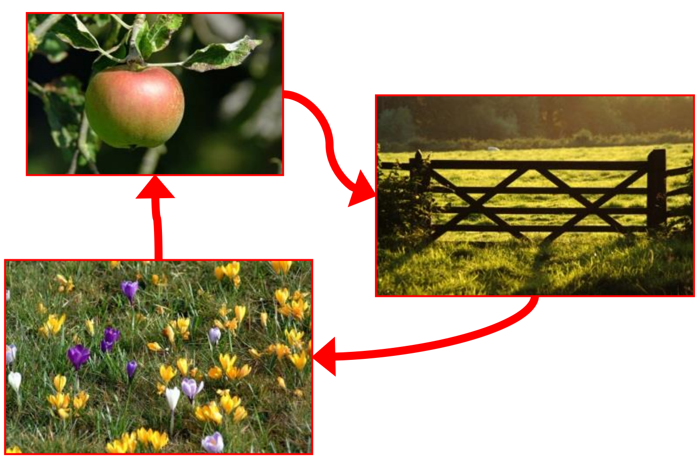


System Boundary (Closed System): "STAF World"

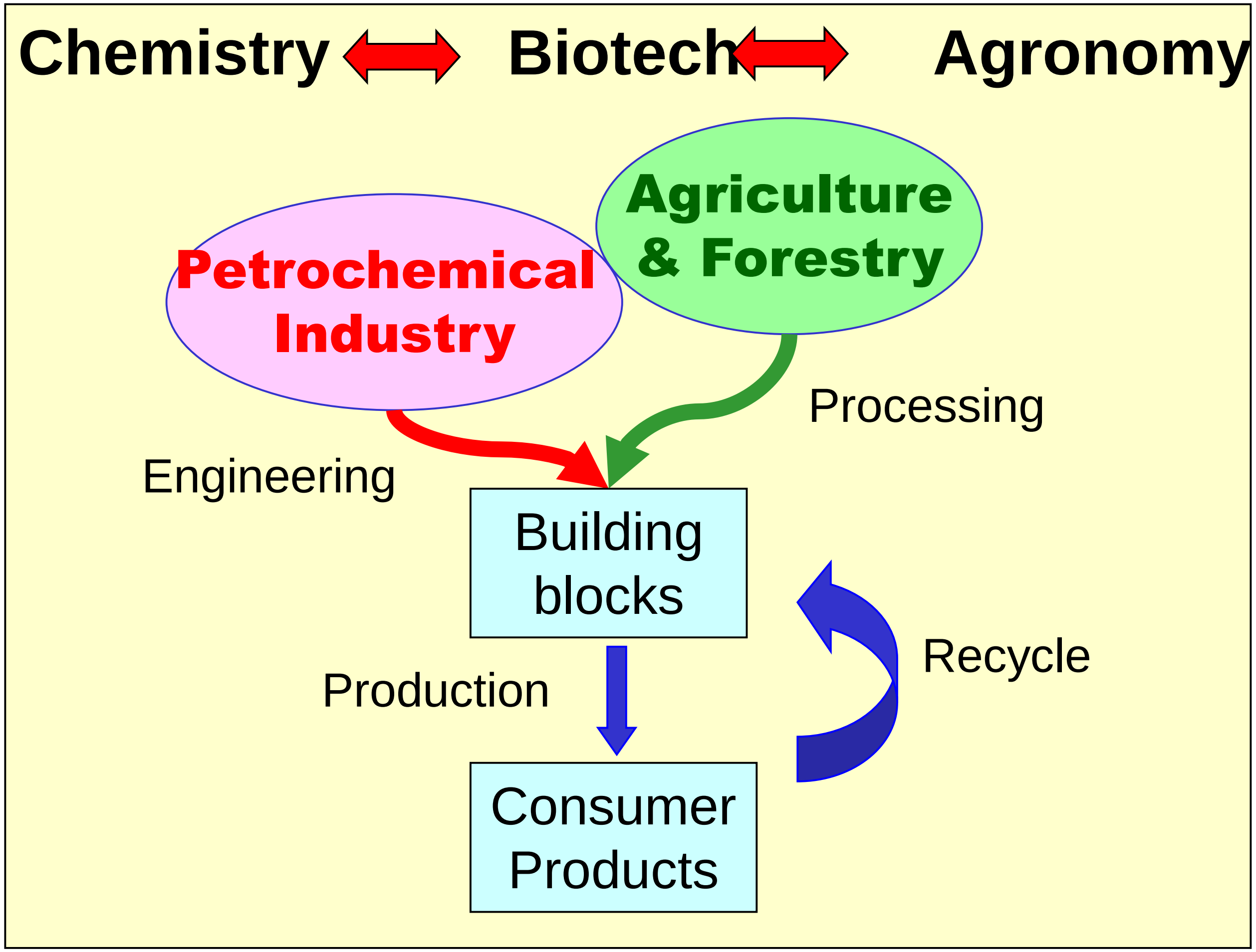
Natural and Industrial Ecosystems: Industrial Metabolism.

The analogy of industrial systems to natural systems:

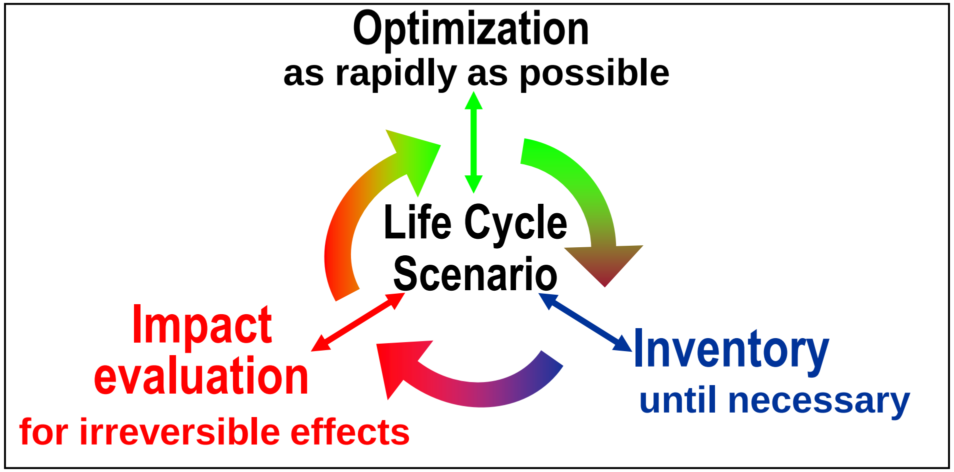
- Both have cycles of energy and nutrients/materials.
- Strategies of nature to meet sustainability:
  - recycling/decomposing
  - renewing
  - conservation and population control
  - toxins stay in place
  - multiple function of the organism

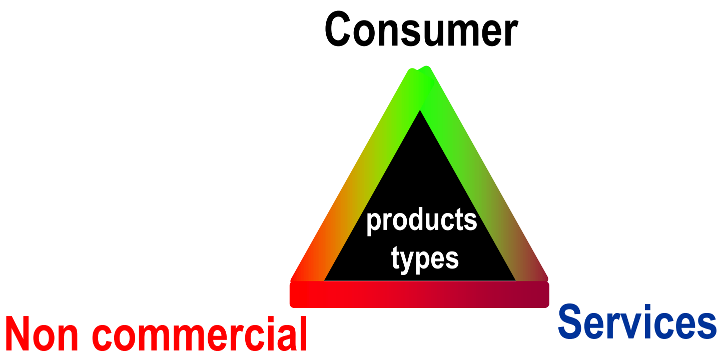


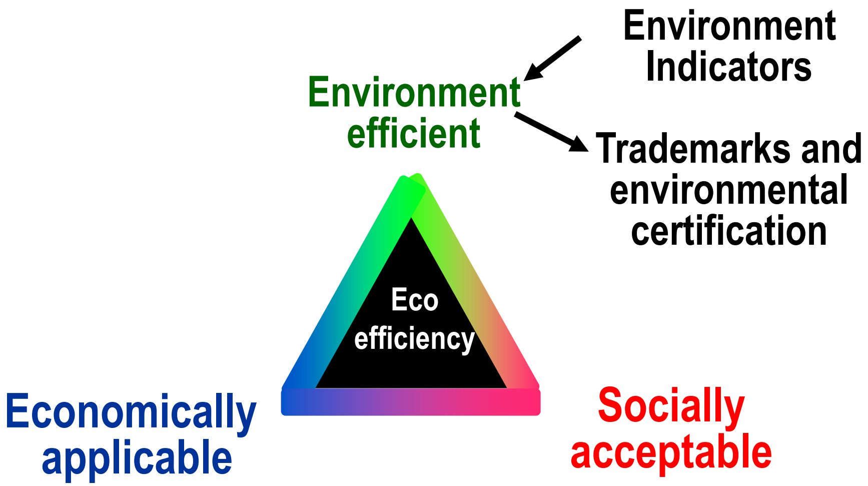
Renewable Sources of Chemicals.



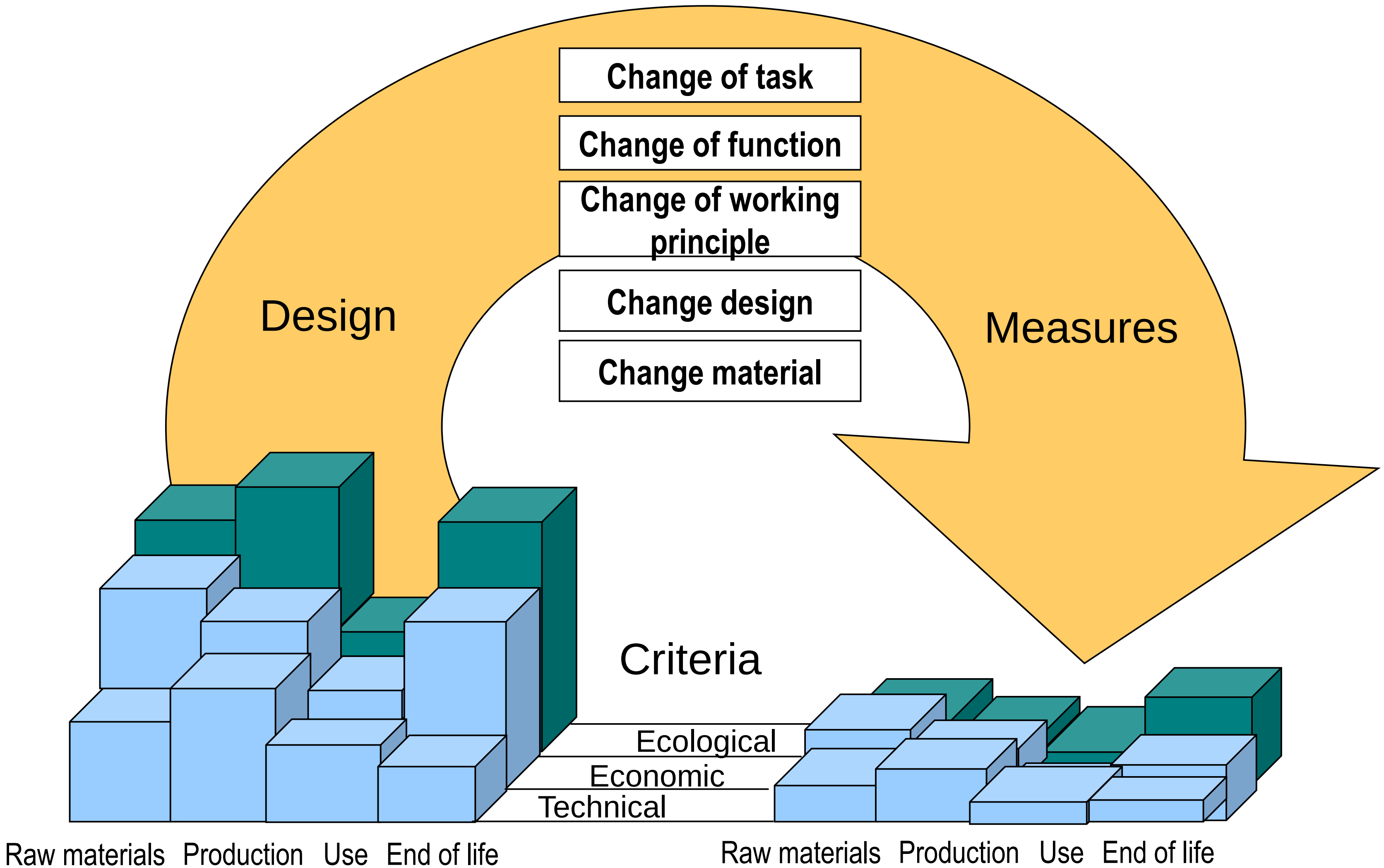
Cleaner Production: Products - Eco-efficiency – Life Cycle.







Design for Environment (DfE): Integrated Product Development.

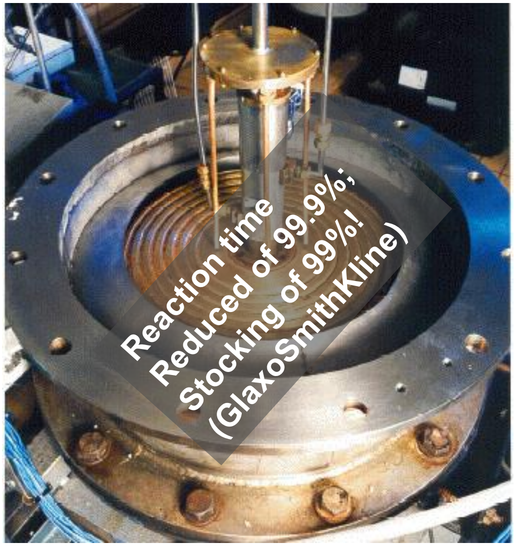


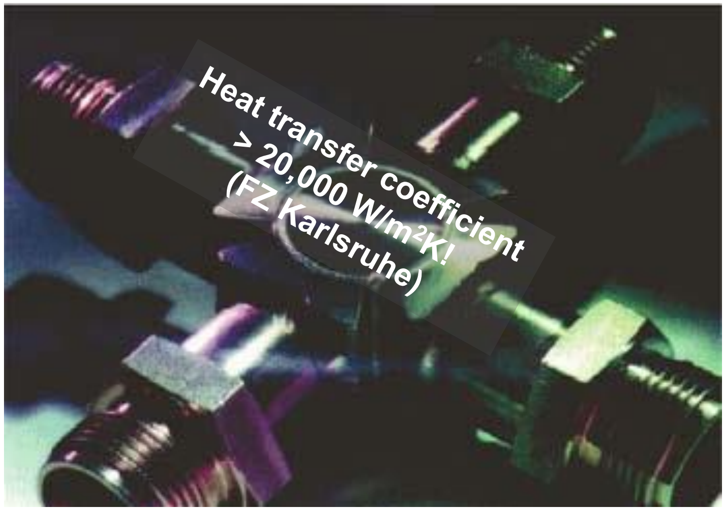
Chemical Industry Aims on Sustainability.

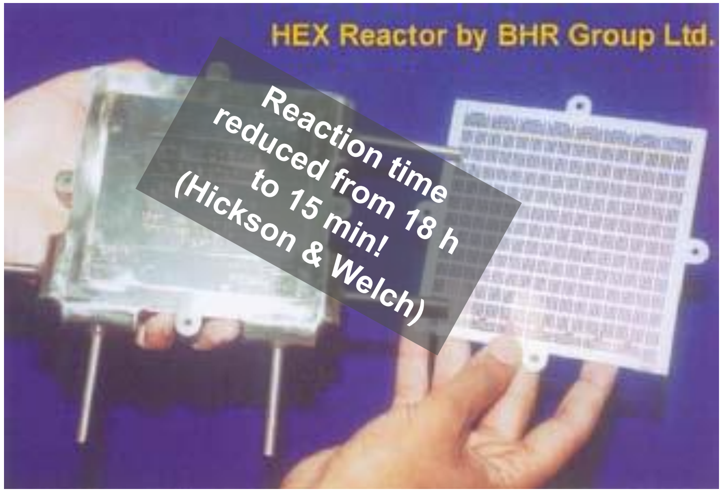
Where we are...

...and where we want to be

Some Examples of Intensified Equipment.



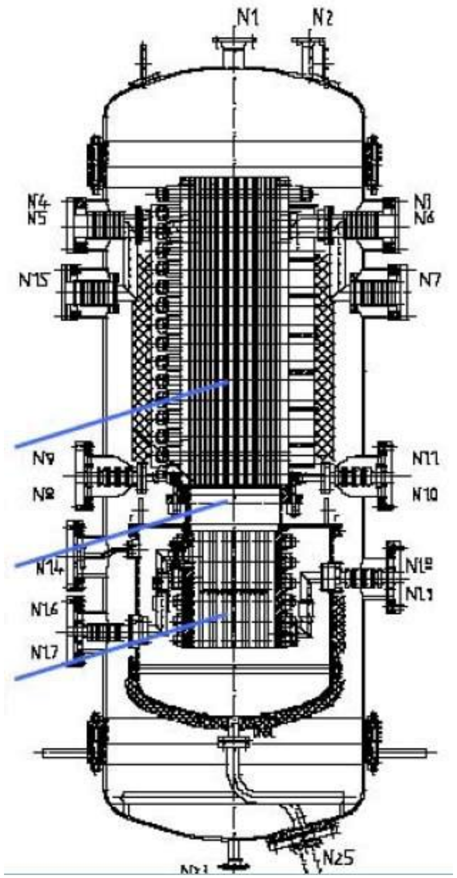




Process Improvement vs. Innovation.

	Aim	Focus	Interdisciplinarity
Process optimization	Performance improvement of existing concepts	Model, num. method Kinetics/Therm.	**Weak**
Process Systems Engineering	Multi-scale integration of existing/new concepts	Model, software	**Modest**
Process intensification	Development of new concepts of process, steps & equipment	Experiment, phenomenon, interphase PAT, QdB	**Strong** Chemistry/Catalysis, applied physics materials science, electronics

Micro-structured Epoxidation Reactor.

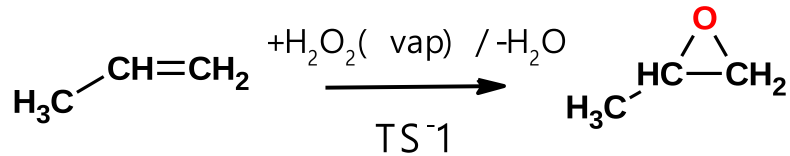


Reaction (micro-structured)

Mixing (micro-structured)

H_2O_2 evaporation (micro-structured)

Model Synthesis:



> 95%

Features:

- Modular (unit operations, capacity)
- Multi-purpose (catalyst and reaction)
- Reaction under pressure
- Reactions in the explosive regime

http://www.thyssenkrupp-industrial-solutions.com/fileadmin/documents/brochures/uhde_brochures_pdf_en_10000032.pdf

Circular Economy: Circularity Strategies within the Production Chain, in Order of Priority.

Circular economy

Increasing circularity

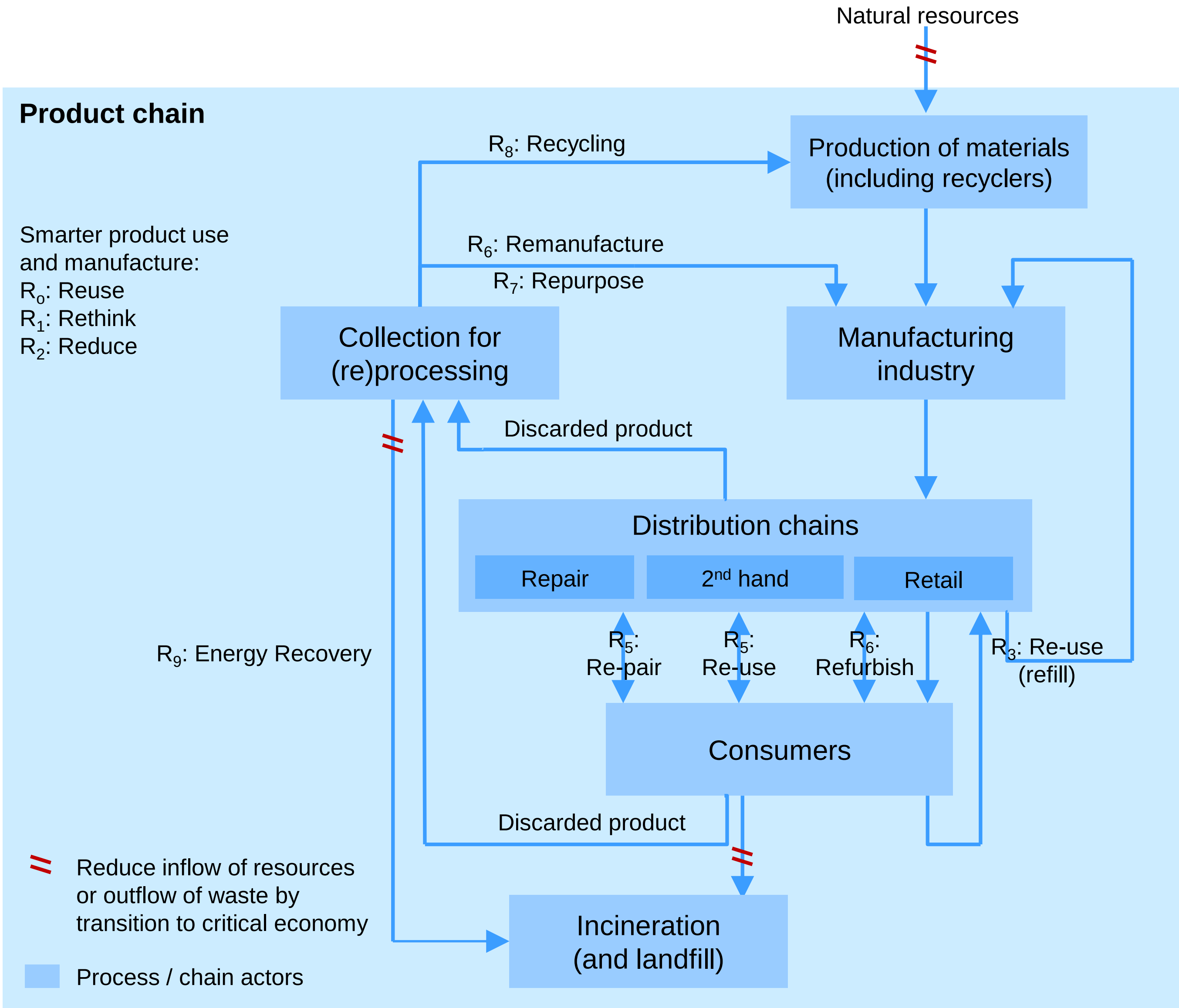
Rule of thumb: higher level of circularity = fewer natural resources and less environmental pressure

Linear economy

Strategies			
Smarter product use and manufacture	R_0	Refuse	Make product redundant by abandoning its function or by offering the same function with a radically different product
	R_1	Re-think	Make product use more intensive (e.g. through sharing products or by putting multi-functional products on market)
	R_2	Reduce	Increase efficiency in product manufacture or use by consuming fewer natural resources and materials
Extend lifespan of product and its parts	R_3	Re-use	Re-use by another consumer of discarded product which is still in good condition and fulfils its original function
	R_4	Repair	Repair and maintenance of defective product so it can be used with its original function
	R_5	Refurbish	Restore an old product and bring it up to date
	R_6	Remanu-facture	Use parts of discarded product in a new product with the same function
	R_7	Repurpose	Use discarded product or its parts in a new product with a different function
Useful application of materials	R_8	Recycle	Process materials to obtain the same (high grade) or lower (low grade) quality
	R_9	Recover	Incineration of materials with energy recovery

Source: RLI 2015; edited by PBL

Circularity Strategies and the Role of Actors within the Production Chain.



Source: PBL

Three Types of Innovation in Product Chains.

CE transitions may need innovation and socio-institutional change. Innovation can take place in technology, product design or revenue models. Socio-institutional change involves reviewing written/unwritten rules, customs or beliefs.

1. CE transitions in which the emergence of specific, radically new technology is central and shapes the transition. This means radical innovation in core technology, i.e. the specific technology central for a product. To give the new technology a place in society, socio-institutional change is needed.
2. CE transitions in which socio-institutional change is central and where technological innovation plays a secondary role (incremental innovation in core technology). A good, perhaps somewhat extreme example is that of packaging-free shops.
3. CE transitions in which socio-institutional change is central, but are facilitated by enabling technology. An example is the transition to what has become known as the sharing economy. This transition from owning a product to purchasing its services primarily involves socio-institutional change, but this is not possible without information technology to link service providers and users.

Diagnostic Questions to Measure the Progress of the Process and Effects of a CE Transition.

	Diagnostic questions
Means	**Mobilisation of means** - Are all relevant product chain partners actively involved in realising CE solutions? - Is there sufficient funding for realising CE solutions? - Are there specific physical means limiting the realisation of CE solutions?
	Knowledge development - Does the available knowledge suffice to develop CE solutions (with regard to technology, patents, consumer and chain actor behaviour)?
Activities	**Knowledge exchange** - Is the level of knowledge exchange on CE solutions high enough in the product chain?
	Experimenting by entrepreneurs - Are entrepreneurs experimenting sufficiently with CE solutions and revenue models? - Is upscaling of CE solutions already taking place?
	Giving direction to search (vision, expectations of governments and core-actors, regulation) - Is there a clear vision among product chain partners of the pursued circularity strategy? - Do product chain partners broadly share this circularity strategy? - Does this circularity strategy structure the activities of the product chain partners?
	Opening markets - Are product chain partners active in creating consumer awareness of CE solutions? - Are companies investing sufficiently? - Does the government have supplementary policies, and do they help in opening markets?

Diagnostic Questions to Measure the Progress of the Process and Effects of a CE Transition.

	Diagnostic questions
Achievements	**CE design** - What is the present lifespan of a product and has it increased from its original lifespan? - Have products become easier to disassemble? - Does the design foresee the use of recycled materials? - Are the components designed for high-grade recycling (no increase envir. pressure)?
	Production - Is the overall (primary and secondary) consumption of materials by companies decreasing? - Do companies use fewer substances which are hazardous to human health and ecosystems? - Is production moving towards lower levels of waste generation? - Are companies moving to CE revenue models with reuse of products and components, or models based on providing a service rather than offering a product?
	Consumption - Is the consumption of CE products increasing (compared to conventional products)? - Do CE products have a longer lifespan or are they used more intensively? - Is reuse of products leading to less waste?
	Waste - Is the volume of landfill decreasing in favor of incineration? - To what extent is high grade-recycling applied? - To what degree is recycling effective with regard to costs and environment?

Diagnostic Questions to Measure the Progress of the Process and Effects of a CE Transition.

	Diagnostic questions
Effects	**Circularity (resource efficiency)** - Is primary material consumption decreasing (in kg per functional product unit)? - Is primary material consumption decreasing for the whole sector (in kg)? - Is energy consumption in MJ_{pr} for recycling lower than cumulative energy consumption in MJ_{pr} ?
	Environment For all product groups (over the whole life cycle of a product): - Is cumulative energy consumption in MJ_{pr} decreasing per functional product unit? - Is cumulative energy consumption in MJ_{pr} decreasing for the whole sector? Environmental pressure caused by specific product groups (over the whole life cycle of a product): - Is cumulative environmental pressure decreasing per functional product unit? - Is cumulative environmental pressure decreasing for the whole sector?
	Economy - Is the added value of products and product services increasing? - Are employment levels in the product chain increasing?

Sources: EEA (2016) http://www.eea.europa.eu/data-andmaps/indicators#c5=&c0=10&b_start=0 **;**
Hekkert M, de Boer S and Eveleens C. (2011). Analysis of innovation system for policy analysists. A manual (in Dutch). Utrecht University, Utrecht.(2011)**;**
Huijbregts et al. Is Cumulative Fossil Energy Demand a Useful Indicator for the Environmental Performance of Products? Environmental Science & Technology, 40(3), 641-648(2006)

What is “Green”?

- ✓Sustainable
- ✓ More benign and compliant with people and planet