La chimica sostenibile: passato, presente, futuro

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Le origini del concetto di sviluppo sostenibile risalgono al 1987 con il *Rapporto Brundtland* “Our common Future”:

“sustainable is the development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”

*ovvero*

lo *Sviluppo sostenibile* è uno sviluppo che soddisfa i bisogni del presente senza compromettere la possibilità delle generazioni future di soddisfare i propri bisogni
Le 3 componenti del concetto 2/2

1) Le necessità della società (obiettivo sociale)
2) La gestione efficiente delle risorse poco disponibili (obiettivo economico)
3) La necessità di ridurre il carico sull’ecosistema per mantenere la base naturale della vita (obiettivo ambientale)
La Chimica è la Scienza che permette uno Sviluppo Sostenibile

- To make sustainable the *growing human impact* on the ecosystem it is necessary to **accelerate** the processes of *transformation of matter* to close the cycles

- chemistry → **catalysis**
- But in an *holistic* multidisciplinary integration of competences
  - **catalysis is a multidisciplinary science at the interface of many areas**
• Extremely fast growing of new economies with huge market potential
  ▪ altering the actual production model & depleting availability of natural resources / raw materials

• Globalization of environmental problems, from water to greenhouse gases
  ▪ necessary to avoid further delays in introducing new technologies to decrease the impact of industrial production on future society

• Climate changes & environmental problems
  ▪ decrease the local availability of critical resources for societal life → water availability
• Preserve the quality of life & environment → a key element for societal decisions
  ▪ requires changing to a new model of delocalized production and energy
• Securing and safeguarding raw materials, food, energy and resources
  ▪ crucial factors for decision strategies
• Progressive climate changes and poverty
  ▪ increase immigration problems

Riconsiderare la Chimica per permettere una transizione veloce a una Società Sostenibile
Chimica e Società

• Progressively reduction of the environmental impact of chemical production (mainly to comply with societal pressure & regulations)

BUT

• SLOW introduction of new processes and technologies
• FAST progressive decrease of production and market (Europe → Middle and Far East)

Necessità di riprogettare i processi chimici
F³ Factory

European Fed. of Chemical Industries


Novel Synthetic Pathways
Specialized Hardware
Production Facilities
Computer Models
Supply Chain Design

Renewable Resources

highly eco-efficient, scalable and adaptive process that have smaller physical and ecological footprints

modular design
closer introduction

f3 Factory
flexible • fast • future
Future Manufacturing - The $F^3$ Factory Task

- Taylor-made and local manufacturing
  - Differentiated or new products
  - Local markets and alternate feedstock

- Forward-integrated Manufacturing
  - New business models
  - New supply chain concepts

- Efficient and flexible Manufacturing
  - Sustainable, ecological
  - Globally competitive

$F^3$ Factory enhances competitiveness of the industries
Concepts of sustainable chemistry

- **Down-sizing and integrate** (chemical) production (minimize transport and storage, avoid large plants and concentration)

- **Smart use of resources, materials and energy** (reduce mater. & energy intensity of goods & services, increase durability)

- **Maximize recycle and minimize utilities**

- **Integrate processes** (multi-step reactions - catalysis, reaction & separation)
Nuovi approcci per un’energia sostenibile e la riduzione di gas ad effetto serra
Essential technology challenges of the society today and in the future

- Environment/Climate:
  - Efficient use of resources
  - CO₂-Prevention

- Energy:
  - Conversion
  - Storage
  - Efficient use

- Mobility

- Nutrition

- Health
Which scenario for renewable energy?

- **Short-term**: mainly energy saving and efficiency, and an increased use of biomass.
- **Medium term**: an increasing use of solar energy, that will become predominant for a longer-term energy scenario.
Short-medium term energy scenario

- energy saving and efficiency
- Increased use of biomass and unconventional fossil fuels
  - At the same time, there is the need to minimize the impact on the environment of the use/production of the actual or less conventional fossil fuels.

- Main drivers for catalysis research are from one side the possible options for transport fuels from less-conventional resources, such as coal, tar sands, and strained natural gas reserves, and on the other hand, the use of biomass resources, particularly waste biomass.

- This opens new creative options for novel catalytic processes which reflect in new possibilities also for chemical field
Biofuel Production Alternatives

Gasification to “syngas” (CO + H₂)

Pyrolysis, fast or slow

Dissolution

Liquid phase processing

Fischer-Tropsch methanol

Jets Fuel

Diesel

Gasoline

Ethanol

Butanol

Jet Fuel

Ethanol

Biodiesel

Paternal, 2010

Forest waste

Corn stover

Switch grass

Sugar/Starch

Corn grain

Sugarcane

Lipids

Alga

Soy beans

Sugarcane

Saccharification

Fermentation

Sugar

Lignin → Heat/Power

Hydrotreating

Transesterification

Regalbuto, 2010
Factors determining the strategic choices for future biomass scenarios

• The push to biofuels derives from a mix of factors (different from country to country), but in Europe CO₂ reduction is a key factor
  
  ▪ the target are liquid fuels which can well integrate into the existing energy infrastructure to store & transport energy
    • HC have a higher energy density than oxygenated
    • chemicals from biomass are an added-value bonus (not driving factor)
    • diesel components are better than gasoline; constrains in type products
    • integration between fossil fuels and biofuels

◆ C-efficiency of the biofuel production is a key element
  • avoid as much as possible loss of C (CO₂ fermentation or some chemical transformations)

◆ It is a short-medium scenario, highly depending on the investments costs and biomass transport costs
Possible feedstocks for biorefineries

**Oilseed crops**: rapeseed, sunflower, soy, palm, jatropha

**Sugar crops**: sugar beet, sugar cane, sweet sorghum

**Starch based crops**: maize and other cereals, cassava (for tropical climates)
Lignocellulose as raw material
200 billion tons produced annually

Because of the resistant structure of cellulose and natural composite structures of lignocellulosics, efficient pretreatment technologies are needed prior to the enzymatic hydrolysis.

**Agricultural residues**
- Cellulose 38%
- Hemicellulose 32%
- Lignin 17%
- Other 13%

**Wood residues**
- Lignin 22%
- Hemicellulose 23%
- Cellulose 60%
- Extractives 5%

**Sorted municipal solid waste**
- Cellulose 45%
- Ash 15%
- Lignin 10%
- Hemicellulose 9%
- Other carbohydrates 9%
- Protein 3%
- Other 9%

**Herbaceous energy crops**
- Cellulose 45%
- Hemicellulose 30%
- Lignin 15%
- Other 10%

Cellulosic biomass must first be ‘pre-treated’ to make the sugars available to chemical or biological hydrolysis.
Longer term perspective

Necessary that the energy for the reaction of CO₂ conversion is supplied from renewable energy, particularly solar energy.

Why solar energy

• Actual average global energy consumption ~ 16 TW (~ 25 TW by year 2050).

• Sunlight striking the Earth’s atmos. is $1.75 \times 10^5$ TW. If the irradiance on only 1% of the Earth’s surface could be converted into electric energy with 10% efficiency, → 105 TW.

• Estimated amount of energy extractable by wind is about 2-4 TW, by tides about 2-3 TW, by biomass 5-7 TW and by geothermal energy 3-6 TW.

• The use of solar irradiation to increase the use of renewable energy is a not-questionable necessity.
Storage: the critical energy gap

C-based energy vectors

H₂ liq.
H₂ gas
H₂ storage mater.
H₂ compr. (700 bar)
gasoline
LPG
NG
DMF
methanol
ethanol
Li-batteries
advanced Li-batteries
The energy density (per unit volume) of gasoline or other liquid fuels is by far larger than that possible for H\(_2\) and for electrical energy, even considering future possible developments in storage materials.

- **Storage and transport of energy are the critical factors**

- Realistic energy scenarios should consider, besides sustainability, the continuity in *usage of existing technologies* (and infrastructure) wherever possible.

- **Need to convert CO\(_2\) back to fuels using solar energy**
C-based solar fuels as energy vector

New routes to C-based solar fuels
Renewable H₂ from solar energy

- single step direct water photoelectrolysis
  - target to increase the cost-effectiveness of the process with respect to the two step process (PV followed by water electrolysis; actual reference in term of efficiency)

- photoreforming of waste streams deriving from agro-food or agro-energy production
  - many diluted waste streams containing ethanol and other organics, which are too diluted to be used as feed to make H₂ by catalytic routes or methane by anaerobic digestion, or to be used as feed in new generation fuel cells
Towards "artificial trees"

The device is suited to convert conc. CO₂ stream deriving either from CO₂ sequestration or from fluxes produced by thermal treatment of CO₂ solid adsorbents.

It is possible to develop artificial trees to capture CO₂ from air (using regenerable adsorbents) and convert back to fuels.
Lab-scale PEC device

Assembly of photoanode with the Nafion membrane

PEC cell

Filter

Solar simulator

Assembly of photoanode with the Nafion membrane

Proton Membrane

Photoanode

Electrocatalyst

Light

H₂O

O₂

H₂

2H⁺

CO₂

CO₂ reduction to fuels

or

CH₃CH(OH)CH₃

H₂ production

CO₂

2H⁺

H₂
Pd-CNF (sol immob.): TEM

Pd nano-particle
Catalisi ambientale e processi chimici sostenibili
Scientific interest then progressively moved from the cleanup approach to the other subjects.

- New catalytic processes for a sustainable production
- Catalytic approaches to clean energy and reduction of greenhouse gases

New problems and questions have recently renewed research activity also in the area of catalytic cleanup technologies

Negli ultimi anni c’è stato un radicale cambiamento nelle problematiche riguardanti la catalisi ambientale
Environmental catalysis

- **Sustainable processes & products**
  - Better use of resources
  - Catalytic upgrading of natural resources
  - Use of renewable energy
  - Eco-efficient catalytic processes
  - Gas & liquid emission cleanup
  - Conv. or reuse of waste
  - Reduction of the env. impact of non-chem. processes

- **Quality of life & Environment**
  - Increase efficiency in energy and resources use
  - Reduced impact of transport
  - Indoor & outdoor air purification
  - Soil & water remediation
  - Smart materials
  - Reduction of greenhouse gases

- **Reduction of greenhouse gases**
- **Indoor & outdoor air purification**
- **Soil & water remediation**
- **Smart materials**
- **Reduction of greenhouse gases**
Towards a new vision for industrial chemical production

• **Sustainability should become the driver for innovation and competitiveness**, making possible to maintain the vital role of chemistry for society.

• **Microreactor** technology and **catalysis** are two of the crucial pillars to foster this vision, and accelerate the introduction of new sustainable chemical processes.
  
  ▪ High cost of investment for new processes in a situation of instability of the market → new approach requiring lower development costs and investment, which can catalyze the introduction to the marked of safer and more sustainable technologies
Chemical industry and environment

- Chemical industry has made a considerable effort in recent decades to reduce the impact on the environment, and consumption of raw materials, including energy,
  - but mainly to comply with regulations.
- The fast evolving world scenario for energy and chemistry, however, has accentuated the need to put innovation at the core of the industrial competitiveness instead of the financial aspects.
  - However, it is necessary to rethink the development model of the chemical industry, by introducing new flexible and modular approaches.
Green Chemistry

- Safer Reactions & Reagents
- Catalysis
- Solvent Replacement
- Use of Renewable Feedstocks
- Waste Minimisation
- Process Intensification
- Energy Efficiency
- Separation Processes
### 12 Principles of green chemistry

<table>
<thead>
<tr>
<th>Principles on Green Chemistry</th>
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</thead>
<tbody>
<tr>
<td>Waste prevention is better than treatment or clean-up</td>
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<tr>
<td>Chemical synthesis should maximize the incorporation of all starting materials</td>
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<tr>
<td>Chemical synthesis ideally should use and generate non-hazardous substances</td>
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<tr>
<td>Chemical products should be designed to be nontoxic</td>
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<tr>
<td>Catalysts are superior to reagents</td>
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<tr>
<td>The use of auxiliaries should be minimized</td>
</tr>
<tr>
<td>Energy demands in chemical syntheses should be minimized</td>
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<tr>
<td>Raw materials increasingly should be renewable</td>
</tr>
<tr>
<td>Derivations should be minimized</td>
</tr>
<tr>
<td>Chemical products should break down into innocuous products</td>
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<tr>
<td>Chemical processes require better control</td>
</tr>
<tr>
<td>Substances should have minimum potential for accidents</td>
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</tbody>
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“It is better to prevent waste than to treat or clean up waste after it is formed”

Chemical Process → No waste
“Energy requirements should be recognised for their environmental impacts and should be minimised. Synthetic methods should be conducted at ambient pressure and temperature.”

Heat, Cooling, Stirring, Distillation, Compression, Pumping, Separation

Energy requirement (electricity)

Global warming

Burn fossil fuel

CO₂ to atmosphere
“A raw material of feedstock should be renewable rather than depleting wherever technically and economically practical”

Feedstock

Non-renewable
e.g. Fossil fuel based

Renewable e.g.
Plant based
# How Efficient is Chemical Manufacturing?

## E-factors

<table>
<thead>
<tr>
<th>Industry</th>
<th>Product tonnage</th>
<th>Kg by-products / Kg product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil refining</td>
<td>$10^6 - 10^8$</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Bulk Chemicals</td>
<td>$10^4 - 10^6$</td>
<td>1 - 5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>$10^2 - 10^4$</td>
<td>5 - 50+</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>$10 - 10^3$</td>
<td>25 - 100+</td>
</tr>
</tbody>
</table>
Tools and technologies for a Sustainable Process Development

Clean Technology Pool

- Catalysis
- Process Intensification
- Product Design and Life Cycle Assessment
- Alternative Solvents
- Solventless Reactions
- Innovative Engineering
- Renewable Feedstocks
**Traditional route:** Alkaline hydrolysis of allyl chloride, which generates the product and hydrochloric acid as a by-product

\[
\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{CH}_2=\text{CHCH}_2\text{OH} + \text{HCl}
\]

**Greener route,** to avoid chlorine: Two-step using propylene \((\text{CH}_2=\text{CHCH}_3)\), acetic acid \((\text{CH}_3\text{COOH})\) and oxygen \((\text{O}_2)\)

\[
\text{CH}_2=\text{CHCH}_3 + \text{CH}_3\text{COOH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_2=\text{CHCH}_2\text{OCOCH}_3 + \text{H}_2\text{O}
\]

\[
\text{CH}_2=\text{CHCH}_2\text{OCOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_2=\text{CHCH}_2\text{OH} + \text{CH}_3\text{COOH}
\]

**Added benefit:** The acetic acid produced in the 2\textsuperscript{nd} reaction can be recovered and used again for the 1\textsuperscript{st} reaction, leaving no unwanted by-product.

**Example 1**

*Production of allyl alcohol \((\text{CH}_2=\text{CHCH}_2\text{OH})\)*
**Traditional route:** Start with phosgene (COCl₂), which is extremely toxic, and end with methyl chloride (CH₂Cl), which is harmful, as a by-product.

\[ \text{COCl}_2 + \text{Biphenol A} + \text{NaOH} \rightarrow \text{Polycarbonate} + \text{H}_2\text{O} + \text{CH}_2\text{Cl} \]

**Greener route,** to avoid phosgene:

Biphenol A + Diphenylcarbonate → Polycarbonate

(This process was developed by Ashai Chemicals Co. in Japan.)

Example 2

**Production of polycarbonate (polymer)**
Alternative feedstocks (renewable)

- Renewable resource (corn)
- Microbial production of PDO from glucose from cornstarch
- Balance of carbon, redox, and energy with respect to microbial growth & product formation
- Aerobic fermentation using 40% less energy than chemical route to PDO

Commercializing 2006
The Question of Solvents

- Toxicity / atmospheric emissions of volatile solvent (e.g. chlorinated hydrocarbons)
- Toxicity / ground water contamination by non-volatile, polar solvents
- Solvents contribute ca.85% of non-aqueous mass in processes in the pharma industry.
- Current recovery efficiencies typically 50-80%.
Solvent Replacement

**Benzene**

- Excellent solvent but it is a Genotoxic human carcinogen
- Limit in drinking water of 5ppb (US EPA)
- In 1990 Perrier water found to have 12-20ppb (cigarette smoke has 2000 times more benzene than this) - 160 million bottles withdrawn
- EU limit in petrol 5% before 2000, now <1%
Solvent Replacement

**Halogenated Solvents**

**Dichloromethane CH₂Cl₂:**
- a suspected human carcinogen
- widely used in synthesis and extractions
- extraction of caffeine from coffee (<10ppm residue)

**Perchloroethylene CCl₂CCl₂:**
- a suspected human carcinogen
- main use in dry cleaning (85% of all solvents)
- also found in printing inks, typewriter correction fluid and shoe polish
Strategies to reduce waste solvent production in chemical processes

• Solvent-free synthesis
• Use of water as a solvent
• Use of supercritical fluids as solvents
• Use of ionic liquids as solvents
• Fluorous biphasic catalysis
Water as a reaction medium

- Economically & Environmentally attractive
  - Inexpensive and abundantly available
  - Non-inflammable and non-toxic
  - Odourless and colourless
- Highly polar reaction medium
  - Novel reactivity of organometallic complexes
  - Facile product separation/catalyst recycling
  - Reduced product contamination

*Growing interest, but still limited industrial examples*
An ionic liquid is a liquid that contains essentially only ions. The melting point is usually below 100°C and they have negligible vapour pressure, excellent solvents for many compounds.
Solvent Replacement

$\text{scCO}_2$ is inexpensive, non-flammable and non-toxic.

Current applications include:

- Decaffeination of coffee - replacing dichloromethane
- Dry Cleaning - replacing perchloroethylene.
Supercritical CO$_2$ as a Reaction Medium

- $T_c$ 31.0 °C, pc 73.8 bar, dc 0.477 kg L$^{-1}$
- Low viscosity (more like a gas than like a liquid); hence, fast mass transfer
- Cheap and abundantly available
- Easy to remove (N.B. no net production of CO$_2$)
- Non-toxic, non-inflammable, inert

$H_2$ and scCO$_2$ Completely Miscible
Membrane Technology

Aqueous Phase
Whole cells or enzymes as biocatalysts

Organic Phase
R = Reactant
P = Product
Nonporous membrane

Membrane Bioreactor for Biotransformations
Reactor miniaturization

- Low viscosity (more like a gas than like a liquid); hence, fast mass transfer
- Cheap and abundantly available
- Easy to remove (N.B. no net production of CO₂)
- Non-toxic, non-inflammable, inert

Diagram showing a microreactor with single phase, gas-liquid-solid, and immiscible liquids. Stages include isocyanate, alcohol, and nitrogen gas for liquid-liquid separation. Microseparator for aq waste.
Microreactor

Benefits: Surface to Volume

Surface to Volume Ratio

Heat Management
Surface Reaction
Explosion-Safe
Microreactor for GTL production

Primary source of value is reduced size with same output

- Microchannel Reformer
- Same capacity
- 90% size reduction
- 33% capital cost reduction
- 100% increase in profit margin
Sustainability

4-E problem
Energy, Environment, Economy, & Education

Innovation through R&D

Maintain the eco-balance in a world with increasing nr. peoples accessing to resources