INCA
Consorzio Interuniversitario Nazionale
“La Chimica per l’Ambiente”
www.incaweb.org

Research plan of the INCA Consortium

Prepared by the Scientific Board in March 2010

The prime mission of the Interuniversity Consortium “Chemistry for the Environment” is to coordinate research activities in the field of environmental chemistry through the gathering of scientific expertises and technical know-how in an organized way. To this end, great attention must be paid to its mid/long-term research plan, in order to get full advantage of its potential, integrating the several skills of its components. Such a research program is presented in this document, in order to prepare it we first took into consideration the Consortium name itself.

Environmental chemistry has deeply changed during the last decades, gaining the ability to couple its heuristic role, based on the major deductive nature of chemical knowledge, with an active part in defending the quality of life. The latter is to be obtained in the framework of a sustainable development, in order to preserve ecosystems and their resources for the future generations.

Presently, the sole collection of analytical data concerning the quality of the environment is not enough. Knowledge surely is the first step of any action, but the capability of utilizing it in order to remediate the environment is based on a more complete and complex approach. We must consider the mechanisms of the natural processes, their interactions with the anthropic systems, the natural diffusion pathways of pollutants and their removal, and we must be able to provide a quantitative evaluation of the environmental impact of our activities. Certainly, alternative industrial technologies, including those for energy production, are fundamental to abate the environmental impact of human activities that are necessary for the wellness of our advanced society. In such a framework, the collection of analytical data must be finalized to a corrective action, followed by definitive remediation and subsequent prevention. In order to do this, we need alternative technologies, services, processes, and materials.

This research program intends to organize all of the abovementioned issues into a limited number of well defined research themes, in order to let the several INCA Research Units act in a coordinated, reliable, and impacting way with respect to the INCA mission. Such program takes into consideration three fundamental research fields: i) alternative methods, processes and technologies, ii) product innovation, iii) on-field applications regarding the most relevant market sectors, also according to the respect of REACH.

Scheme of the present document

Macro-area I – Fundamental methods

- *Fine chemistry for synthesis and extraction*

Macro-area II – Technologies

- *Clean technologies and renewable energy sources*
- *Process intensification*
- *Environmental biotechnologies*
  - *recycling and reuse*
  - *removal of pollutants*
  - *bioremediation*
- *Industrial biotechnologies*
- *Process and product innovation, also with reference to REACH*

Macro-area III – Materials
Innovative materials for the environment

Macro-area IV – Applications

- *Metropolitan/urban areas (to be considered also in terms of general environmental monitoring and of interaction between environment and cultural heritage)*
- *Food ecological footprint*

Macro-area I – Fundamental methods

Green Chemistry for Fine Synthesis

Green chemistry shows a strong industrial connotation, being primarily focused on the abatement of the impact of chemical products, in particular of those manufactured on a large industrial scale.

There are some niche products fabricated in small quantities at academic or industrial research laboratories which are often innovative, but sometimes lack optimization and show a proportionally higher impact. Even if the risk is low due to the limited amounts, it is necessary to assess the environmental performance of these single processes, in accordance with Green Chemistry principles, before performing their optimization prior to their production.

In the abovementioned sectors some new technologies, reagents, and reaction conditions can be applied:

- new catalysts and new catalytic conditions (immobilized catalysts, organic catalysis, etc.);
- non-conventional activation methods, such as photochemistry, use of microwaves and ultrasounds;
- non-conventional reaction conditions, new solvents, use of solvents in supercritical conditions, ionic liquids, new (micro-)reactors.

The boundary existing between pure and applied research must be traversed in order to limit pollution and the waste of resources. This can be achieved through different combined approaches, such as: recovery and reuse of catalysts, minimization of phases and reagent quantities, economic feasibility, toxicological assessment.

Besides these new findings, the importance of the environmental evaluation must be stressed. Namely, this entails the wide use of life cycle assessment (LCA), in order to: i) reveal the actual impact related to each process and to allow its direct comparison with alternative methods; ii) identify critical phases and possible corrective actions.

Such an approach shows an high added didactic value at a university level. It can be profitably used for devising explicative synthetic pathways in advanced laboratory courses for chemistry students. Conversely, the adoption of such approach in industries provides benefits in terms of education and ethics.

Macro-area II - Technologies

A) Clean Technologies and Renewable Energy Sources

A sustainable industrial development must take into consideration issues such as environmental impact, energy consumption, valorisation of raw materials and the quality of end products. To this end, it is necessary to understand the molecular mechanisms which allow chemical transformations. In this way, it is possible to devise new eco-compatible and sustainable processes. Two classical examples are the decreasing use of separation processes based on state passage with heating and the increasing utilization of membrane-based molecular separation.

The use of renewable energy sources such as solar, wind, geothermal, and saline gradients is particularly relevant, along with the net energetic balance and yield of each productive phase. Such alternative energies are well coupled with non-thermal separation processes, which are conducted at room temperature or at just slightly higher ones.

Studies about the integration of new energy sources with separation processes and chemical transformation are really important. Photochemical reactors and submerged membranes reactors (already considered as the best available technologies for the treatment of civil wastewaters) are some of the interesting research fields, with notable potential for development and use in several productive cycles.

Membrane Bio-reactors (MBRs) are an emerging technology for the depuration of waters, they combine the use of suspended biomass, similar to that of activated-sludge plants, with a membrane system. MBRs display several advantages with respect to classical water treatments: wider operational range, high robustness with respect to peaks in the incoming load, smaller dimensions, possible automation for most of the operations, reduced need for manpower and maintenance, reduced sensitivity to changes in hydraulic fluxes, and easy scaling-up for treatments ranging from 1 to 100,000 cubic meters per day.

B) Process Intensification

At present, it is extremely difficult for chemical industries to satisfy the growing need for raw matters, energy, and products in a sustainable development framework, future challenges will concern: i) intensification and multi-scale control of processes, ii) devising of new operations and methodologies, iii) the identification of new procedures to guarantee the high quality standards required for end-products, iv) the implementation of computational applications fit for managing the several phases of a process, from molecular to industrial scale.

The term “Process Intensification” (PI) defines a strategy aiming at achieving tangible benefits for productive cycles, through a significant reduction of the dimensions of the machineries, possibly down to real miniaturization. The conceptual correlation between sustainability and physical dimensions of a productive plant should be the core guideline for the planning and building of new machineries and the design of operative protocols. These would provide more flexibility and safety to industrial processes, along with advanced automation, reduced energy consumption, minimization of wastes, in one word: a major eco-sustainability.

There are two fundamental research sectors on PI: i) the design of new machineries, processes, and plants (hardware) and ii) the implementation of new methods and protocols for already existing unitary operations (software). Research areas of major interest are shown in Fig. 1.

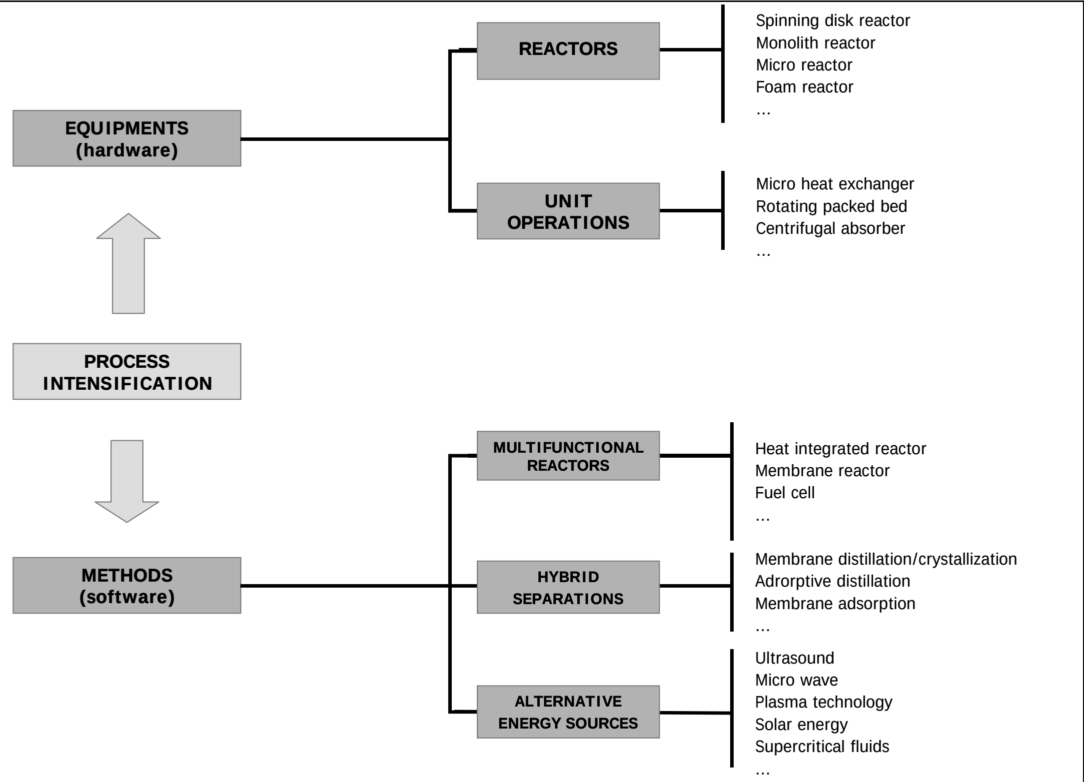

Fig. 1
Research areas related to PI

The recent European Roadmap for Process Intensification (2008) has identified potential benefits in three industrial fields of strategic importance: i) petrochemical, ii) pharmaceutical, and iii) food industry. In the petrochemical sector energy consumption is a fundamental factor for the definition of the price of end products. In this case, an increased energy efficiency would allow for economical and ecological benefits (reduced production of greenhouse gases). Commercial competitiveness is a primary objective of pharmaceutical industries. In this respect PI can provide a valid contribution through an increased reaction selectivity, better yields of the processes, and higher purity of the end products. The processes of food industry are generally characterized by high volumes of diluted spent liquids to be treated according to the low stability of raw matters. In this field, commercial viability is dependent on the costs of product transformation and of the treatment and disposal of liquid wastes. Both these aspects could be improved by the application of PI.

Process Intensification is often based on radically innovative principles (“paradigm shift”). For their application it is necessary to overcome some conceptual and practical barriers; the main ones being:

- insufficient know-how possessed by the process technicians;
- lack of pilot plants and high (technical and financial) risks connected to the implementation of PI devices at an industrial scale for existing productive processes;
- high (technical and financial) risks related to the production of prototypes at an industrial scale;
- lack of specific control systems for innovative PI devices;
- insufficient awareness about the potential benefits of PI at a managerial level.

Some combined actions are needed to overcome the abovementioned barriers, some of these actions have been already implemented:

- a specific financial support to fundamental and applied research is a prerequisite in order to reach the “proof-of-concept” on a lab scale, followed by the scaling-up to pilot plants (such research topics are specifically addressed by FP7 of the EC);
- the development of new analytical and monitoring methods (including *in-situ* ones), allowing a better comprehension of the thermodynamics and kinetics of chemical processes at a molecular level;
- the implementation of faster and more reliable non-linear models for chemical reactions;
- a wider knowledge dissemination.

C) Environmental Biotechnologies

In the future, biotechnologies will be applied more and more frequently for environment protection, since they are generally cheaper and more eco-compatible than chemical and/or physical processes.
The scaling-up from lab to on-field application requires a multi-disciplinary approach, integrating several techniques. It is fundamental to verify the economical feasibility of the process to be scaled-up. The environmental biotechnology sectors characterized by the most intense and innovative R&D activities are:

- Civil and/or industrial wastewater depuration (chemical, biological, and physical methods, bioreactors, photo-degradation, bio-photo-degradation).
- Bio-electrochemical processes: development of MFC (Microbial Fuel Cells) which couple degradation of pollutants with energy production in a very innovative fashion; they use electrodes as direct electron donors for the anaerobic microbial respiration, producing hydrogen, methane and other compounds with an high added value.

D) Industrial Biotechnologies

The state-of-the-art at a national and international level

The term White Biotechnologies collectively indicates industrial and environmental ones, which are of interest to several industrial sectors:

- Pharmaceutical companies are a classic example: (monoclonal) antibodies, vaccines, vitamins, amino acids, excipients and so on.
- Food industry is another productive sector heavily exploiting biotech: microbial starters, enzymes, proteins, organic acids, vitamins, amino acids, etc.
- Biotech is also used for innovative application of the modern chemical and textile industries: fine chemicals, building blocks, biopolymers, bio-lubricants, etc.
- Another innovative application of biotech is in the field of cosmetics: antimicrobials, antioxidants, biopolymers, etc.
- Also energy production can take advantage of biotech: bio-fuels, bio-combustibles, etc.
- Recently, biotechnologies are being used for environmental monitoring and protection: bio-sensors, bio-remediation, bio-decontamination, bio-valorisation of wastes, etc.

Due to the continuous increase in the price of oil, new white biotechnologies are being devised every day, since they are less energy consuming than chemical ones. One of fastest growing field for their application is the production of chemicals. The US market of chemicals grew from 1,200 to 1,600 billion dollars from 2001 to 2010, in the same period the sole market of biologically-produced chemicals grew from 30 to 310 billions. An identical trend is seen in Europe, where the increase over the same period is estimated between 40% and 70% (McKinskey, June 2008).

Unfortunately, the Italian biotech industry is not fully ready to take advantage of this market opportunity. It is weak and fragmented, comprising of small companies which cannot be competitive with the huge multinationals active in this field. Nonetheless, empowering research in some particular areas would allow for an increased competitiveness.

1) New and/or upgraded bio-catalytic processes for chemical synthesis

The first area is that of new and/or upgraded bio-catalytic processes for chemical synthesis, major investigations should concern:

- optimization of the activity of existing microorganisms and enzymes;
- new rapid and effective methods to identify and select new microorganisms and enzymes;
- formulation of efficient and easy-to-use enzymes;
- improvement of the engineering of the process.

2) Innovative and/or upgraded strategies for the valorisation of biomass

A second area to be investigated is that of the innovative and/or upgraded strategies for the valorisation of biomass, production surplus, by-products, residues and spent process waters (including wastewaters) of the national food industry.

Three main specific objectives are related to this area. The first is the valorisation of biomass, residues, and by-products of the Italian food industry, aiming at a more rational use, with particular attention to biomasses alternatives to carbohydrates (such as oils/lipids or oils/fats). Bio-conversion processes should be adapted to such type of biomasses, increasing and improving the activity and stability of the enzymes/microorganisms, possibly looking for synergies with the classical oil chemical processes.

The second objective is to develop the next generation of highly efficient industrial fermentations. This can be achieved by: i) increasing the process yield (metabolic engineering, genetically improved microorganisms, specialized bacteria); ii) suitable scaling-up; iii) process intensification; iv) minimization of wastes and residuals (combined techniques for recycling).

The final objective concerns the eco-efficiency of processes and their integrations through the creation of bio-refineries. In this case, an integrated approach is necessary in order to devise new processes allowing for the use of all the components of the biomass. It is fundamental to analyze the bio-refinery value chain, in order to abate costs, reduce emissions, and integrate production pathways. Critical aspects are: i) costs and eco-efficiency of production; ii) implementation of the bio-refining technologies; iii) identification of the molecules to be produced as bulk chemicals.

3) Improvement of Bioprocesses for the Production of Bio-fuels from Biomasses

a) Hydrolysis processes utilizing low-cost biomasses already available;
b) Fermentation processes for the production of ethanol;
c) Processes for the production of biogas (bio-methane and bio-hydrogen);
d) Integration of biogas processes with systems for their conversion into electric energy, e.g. fuel cells.

4) Innovative and/or Improved Strategies for the Bioremediation of Polluted Sites and Contaminated Waters

It is necessary to investigate and develop novel bioremediation techniques; particular aspects to be examined are:

a) improving knowledge on useful microorganisms (bacteria, fungi);
b) improving process engineering in specific *in situ* conditions;
c) devising and implementing new biotech tools for the characterization of sites, the planning of interventions, and the evaluation of their results.

Macro-area III - Materials

Catalytic Materials

Heterogeneous catalysis is a powerful tool for the invention of synthetic processes with reduced or no environmental impact. Functional material chemistry represents an extremely wide and diversified sector of chemistry. It shows correlations with and overlaps both other thematic research areas of INCA Consortium and those of other national academic consortia.

The preparation and characterization of catalytic materials as well as surface technologies strongly require a deep knowledge of nano-sciences, this is particularly relevant to process optimization.

In the last century the preparation of catalytic materials was essentially based on their activity, meant as the production of the highest number of molecules per area and time units. This was made possible by the low costs for the disposal of by-products at that time. Nowadays, the situation has drastically changed: the high costs for the treatment of by-products, as well as the problems connected to their environmental impact, has shifted the focus on selectivity. The latter is the main objective of chemists who devise new catalyst, even at the expense of activity.

The application on wide scale is the final objective of any investigation on catalysts. Therefore the design of a new catalyst must also consider the type of plant in which it will be used.

According to a supra-molecular approach, a catalytic site supported on a surface is similar to a nano-reactor. Here the chemical transformation is the result of the synergic cooperation between the active site itself and the chemistry of the surrounding region, just like what happens with enzymes.
Trying to imitate natural processes, we can devise sequential pathways which take place in very limited spaces and are structurally connected in a cascade: the product of a reaction is the substrate of the following one, or acts as its catalyst. Such cascaded processes are raising more and more interest, since they represent a valid tool for increasing the efficiency of the scaling-up from the laboratory to the productive plant scale.

A fundamental objective is represented by the realization of combined catalytic systems allowing for cascaded multistep continuous processes in which experimentation and production may take place simultaneously. It is to be stressed that such an approach represents also a primary tool for Process Intensification (see Macro-area II).

One of the most recent research topics about catalytic materials concerns the construction of multifunctional catalysts able to promote processes which need the coexistence of active sites with opposite characteristics (e.g. acid/base or reduction/oxidation), with high efficiency and selectivity. The technical problem is to build them in such a way to inhibit the reciprocal neutralization of the diverse active sites. Such sophisticated catalytic materials are becoming more and more similar to enzymes. Therefore, their preparation and characterization requires strict collaboration among experts from different disciplines.

Thematic research areas concern heterogeneous catalysis for :

- eco-sustainable processes;
- processes in eco-compatible media;
- solvent-free processes;
- multi-step and multi-component processes;
- continuous flow processes
- preparation and use of multi-functional catalysts.

Macro-area IV - Applications

A) Environment and Cultural Heritage

Although currently technicians and researchers often focus their attention on organic pollutants (down to those present at trace level), historically inorganic contaminants were first studied and many monitoring stations of inorganic pollutants in urban environments detect molecules such as CO, NO_X, and SO_2. The first environmental traffic emergency ever detected was due to inorganic pollutants, namely to lead compounds previously used as anti-detonation agents in gasoline (petrol).

Besides their direct impact on environment and health, inorganic pollutants also act indirectly by reacting with each other, or with other natural or anthropogenic atmospheric compounds. In this way they alter the cycles of relevant chemical species in the atmosphere (radicals, ozone, halogenated compounds). Furthermore, they have an impact on environmental protection and preservation and can influence the quality of habitats and of the whole ecosystem.

Another important issue it the effect of inorganic pollutants on cultural heritage. They can damage materials of artistic manufactures in different ways, such as: the reaction between SO_x and calcareous materials, the corrosion of metals, the hydrolysis of cellulose and lignin. So, it is obvious that the defence of cultural heritage depends primarily on the protection of the environment in which they are located. This can be achieved only with a multidisciplinary approach.

Acid atmospheric depositions (rain, snow, dew, and, in particular, fog), commonly tagged as “acid rains”: they are the major threat to cultural heritage. Sulphur oxides transform into acids which can react with marble turning it into gypsum, less valuable and stable. The acidity of the atmosphere can corrode metallic materials both in dry and wet conditions and it can hydrolyze lignin and cellulose, damaging their mechanical properties. This last phenomenon is particularly relevant to paper historical documents.

Besides acidity in the atmosphere, we can find further noxious compounds, such as radicals deriving from incomplete combustions of fuels for energy production, including engines of vehicles. Radicals are instable and reactive species, due to their nature they can interact and damage several biological and non-biological matrices.

Knowledge, prevention, restoration, consolidation, and stabilization are the phases of a proper program to remediate damages to the cultural heritage provoked by environmental pollution.

B) Urban Pollution Monitoring

The term monitoring indicates the observation of the destiny of a xenobiotic from its detection in the environment to its action in our body. The monitoring aim is that of providing data for the adoption of proper prevention systems, through a continuous or periodic evaluation of the exposure and of the effects, along with a correct interpretation of collected data.

Excluding the sanitary surveillance, we find two types of monitoring: i) environmental and ii) biological. The goal of the first one is the evaluation of the exposition levels by the analysis of matrices such as air, water, soils and food. Conversely, in biological monitoring we analyze biomarkers (also called biological indicators), they can be chemical compounds or their metabolites. Biochemical effects produced by both can also be investigated. A wide variety of biological samples can be tested: blood, urine, exhalants.

The emission of aromatic carcinogens, such as benzene and analogous molecules, into the urban environment has increased as a consequence of the elimination of lead from gasoline. Unleaded gasoline shows an high concentration of such compounds, in order to reach a proper octane rating. Its approximate composition is:

- n-paraffins, 15%
- iso-paraffins, 30%
- cycle-paraffins, 12%
- aromatics, 35%
- olefins, 8%
- oxygenated compounds, *in traces*.

When using such a fuel, emissions greatly depend also on the efficiency of the catalytic converter, which in its turn depends on the degree of wearing and on the running conditions.

About 17-19% of the benzene found in urban atmosphere comes from its evaporation during storage (including the vehicles tanks), transportation, and fuelling. The remaining part comes from exhaust gases according to the equation:

“benzene weight % = 0.5 + 0.44 bz + 0.04 ar”

where

bz = percent weight of benzene in gasoline
ar = percent weight of other aromatics in gasoline

Part of the other aromatics can be converted into benzene during the combustion.

Monitoring is presently evolving into increasingly selective methods, with reduced separation phases for mixtures and a higher accuracy of measurements. They should possibly provide real-time results (in order to identify possible health risks immediately), show a linear response and be performed by automated small-sized instruments, in order to be located into urban monitoring stations. At preset time, great attention is given to the contribution of single chemical species to total concentration of a class of atmospheric pollutants.

C) Ecological Footprint of Food

Irrespective of its actual causes and fine mechanisms, global warming forces our society to strive for the reduction of CO_2 emissions. In our time a dietary regime does not represent just a way to intake a proper amount of nutrients and energy, it is also important for prevention and wellness with a minimum use of medicines. In such a context, it is important to understand the environmental impact of food production in terms of CO_2 equivalent emissions.

The ecological footprint of food industry is represented by the result of the life cycle assessment (LCA) analysis of a food considered as an end-product (or a process) reported in terms of emitted CO_2-eq. The proper evaluation of such footprint still requires further research, in order to upgrade and optimize the available LCA methods.