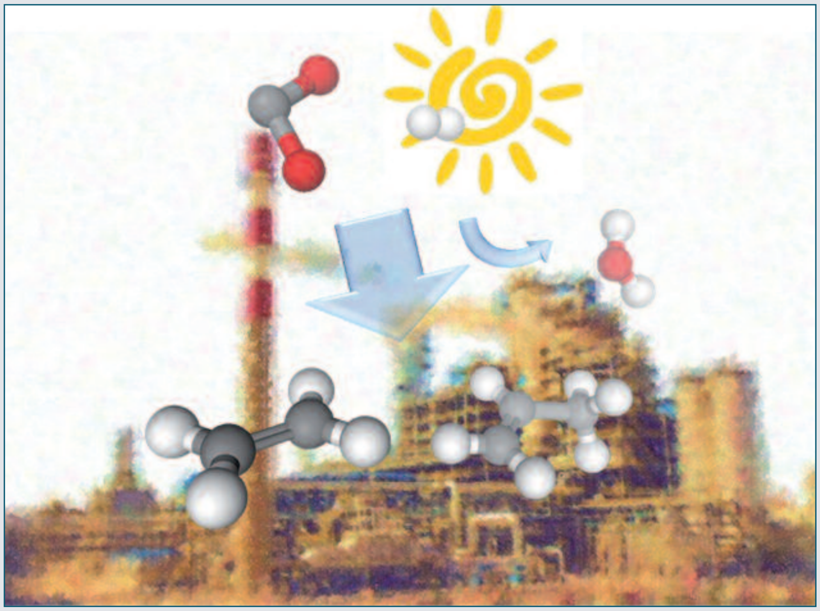

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RESOURCE AND ENERGY EFFICIENCY: THE WINNING STRATEGY FOR CHEMICAL INDUSTRY

Resource and energy efficiency is presented as a winning strategy for a sustainable chemical industry to maintain its competiveness and boost innovation. This contribution discusses this topic from the perspective of reusing CO_2 to produce base chemicals as an effective way to introduce renewable energy in the chemical production chain and to decouple the economic growth from the resource impact.

Resource and energy efficiency is one of the grand challenges defined within EU 2020 Agenda and correlated to various flagship initiatives such as Innovation Union, Resource Efficient Europe, and Industrial Policy for the Globalisation Era. However, before to discuss the role of resource and energy efficiency as the winning strategy for chemical industry and its link to the problem of carbon dioxide, it is necessary to highlight some necessary premises:

- chemical production is a high-tech industry in which the labour cost is a minor component of the overall cost and thus the competitiveness of this sector in a global world derives from the capacity of investment on research and development (R&D), in an integrated synergy between public and private, to maintain high the level of innovation;
- chemical production is the engine for country development, because it is the backbone for the innovation in the entire manufacture sector, providing the materials and solutions to be competitive on quality rather than on cost. Chemical production should be thus at the heart of competitiveness strategies for a developed country. In a global market, chemicals and materials can be buy where are more convenient, but innovation (i.e. the ability of a company to be competitive not on cost bases) requires the produce tailored products in synergy with manufacture needs and social demands. It is a near-sighted policy to think that it is possible to separate production

(in remote areas) from the innovation management. The analysis of the competitiveness factors in chemical production in Europe reveals that chemical industry is winning only when R&D is tightly integrated with the strategic management *and* the production;
- chemical production is different from many other manufacture sectors, because highly integrated up- and down-stream with chemical (or energy, material) production itself, and deals of products addressing an extremely large range of other sectors and being produced from few to million tons. Value chain is thus a key element for all discussions on chemical production.

For the motivations outlined above, chemical industry has a social role and thus is at the core of the sustainable development, but the right balance between economic growth, environmental protection, and social equity is often not well defined. Realizing a sustainable process industry should be thus a primary goal for society, but it is necessary to clearly identify the enabling technologies and solutions along the value chain that are required to reach long term sustainability for Europe in terms of global competiveness, ecology and employment.

This short contribution will analyse what are the critical enabling technologies for this objective, with focus on the key issue of resource and energy efficiency, and with reference to the Public-Private Partnership (PPP) initiative "Sustainable Process Industry through Resource and Energy Efficiency" (SPIRE) promoted from the European Federation of Chemical Industries (Cefic) and the European Platform of Sustainable Chemistry.

Turning the vision on CO_2

The problem of reuse of CO_2 is a central aspect in this strategy on resource and energy efficiency, because a key element to introduce renewable energy in the energy and chemical production chain. There is a clear link between innovation, low carbon economy, resource and energy efficiency, turning around the new vision of green carbon dioxide [1], i.e. to consider CO_2 not more as a waste, neither as a resource for niche applications, but as the key element around which build a new winning strategy for a sustainable process industry. Address the problem of CO_2 in a new perspective can be the pushing factor for the chemical and energy industry as well as the entire society for a winning strategy for sustainability, combining the economic growth with the preservation of the quality of life and environment for the future generations.

If we consider the 2011 UN Climate Change Conference recently made in Durban (South Africa), it is evident a too slow progress in addressing the issue of greenhouse gas (GHG) emission. The reduction of GHG emissions is still considered a cost slowly down the economy, and from this aspect derives the resistances to introduce limits in the emissions of CO_2. By defining the issue in terms of climate change it is shifted the social perception of the consequences to a long term problem. We know that the issue is not the increase in the height of sea due to global warming (a too far problem), but the shorter term upsetting of the local clima. However, by linking the issue of CO_2 to the competiveness of process industry (and related impact on employment, etc.) through the resource and energy efficiency concept, it is possible to sensitize the society on the direct, and not only long-term benefits.

There are many examples of this need of turning the vision on carbon dioxide. Carbon capture and sequestration (CCS) is still considered the only solution for a direct reduction of CO_2 emissions, i.e. not deriving from using non-fossil fuel resources or from an increase in energy efficiency. Not surprisingly, one of the few elements of success in Durban conference is that after years of discussion, stalling and negotiation the Clean Development Mechanism (CDM) is now able to accept Carbon Capture and Storage (CCS) projects. However, this is related to the inability to consider the problem of CO_2 reuse in a different perspective. Still in most of the debate on carbon dioxide the enhanced oil recovery (EOR) is considered the only relevant application in terms of amount. Chemical uses are considered to not giving a significant contribution. However, the problem is related to using a correct methodology of counting the impact on GHG, based on a revised LCA approach. In the case of CCS, each ton of CO_2 sequestered implies that about 0.5 ton CO_2 are emitted by considering the energy cost for the capture and storage of CO_2. Therefore, the effective impact factor on GHG is about 0.5. A value not very different is observed for EOR. On the contrary, if we consider that CO_2 could be converted to a fuel using renewable energy (for example, using excess renewable electrical energy to produce H_2 for the conversion of CO_2 to methanol), and then the fuel is used to produce back energy (concepts of energy vectors and solar fuels), the same molecule of CO_2 is virtually recycled many times introducing renewable energy in the chain at each cycle, while preserving at the same time fossil fuels to be extracted, processed and used. While sequestration is one step process, the production of solar fuels from CO_2 is a cyclic process having thus a GHG impact (over 20 years, for example) orders of magnitude higher than that of the sequestration case. Even with a conservative GHG impact factor between 5 and 10, the potential contribution of CO_2 chemical recycle in the short-medium term will be around the same of CCS.

Decoupling economic growth from the resource impact

From the industrial revolution the economic growth has been dissociated from the impact on resources. For example, the most important measure of the economic activity in a country, the Gross Domestic Product (GDP), is not including this aspect. A substantial efficiency improvement in using resources and energy has been achieved in industry over the past, but mainly because this implies a reduction in the costs or to comply with regulations. The increase in the efficiency in using resources (including energy) has not compensated the upturn in the consumption of the resources due to the increase in the world GDP. We are rapidly reaching the irreversible turning point in using the resources, which will start conflicts to access to these resources to maintain the style of life. The only way to avoid this problem is to make the paradigm shift of decoupling economic growth from resource impact. Is it possible or just a dream? A man on the moon was a dream and for long time considered impossible. However, the research effort to realize this dream is at the basis of many of today developments daily used from all peoples.

Can be thus possible with enough R&D effort to decouple the economic growth from the resource impact, the necessary condition for a sustainable growth? Let me make an example. Light olefins (ethylene and propylene) are the building blocks of petrochemistry and of a large part of the materials daily used from many industrial sectors and consumers. They are currently produced from fossil fuels, mainly oil. Their synthesis process is the single most energy-consuming production in the chemical industry, and the specific emissions of CO_2 per ton of light olefin range between 1.2 and 1.8. There are various alternative raw materials to produce light olefins, from coal to biomass, but all the routes are energy-intensive [3]. To decouple the economic growth of chemical production from the resource impact, and thus make a breakthrough step towards sustainability, it is necessary to use CO_2 as the carbon-source to produce olefins, using H_2 produced from renewable energy sources [3]. Due to their high energy of formation, C2-C3 olefins represent an excellent opportunity to store solar energy and incorporate it in the value chain for chemical production.

The synthesis of light olefins from CO_2 requires the availability of H_2. Ethylene and propylene have a positive standard energy of formation with respect to H_2, but water forms in the reaction and thus the process essentially do not need extra-energy with respect to that required to produce H_2. From the energetic point of view, the energy efficiency of the process is thus related to the energy efficiency of the production of H_2. The process for olefin synthesis from CO_2 may be described as the combination of a stage of reverse water gas shift (RWGS) (eq. 1) and a consecutive stage of Fischer-Tropsch (FT) synthesis (eq. 2):

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad (1)$$

$$CO + H_2 \rightarrow C_nH_{2n} + C_nH_{2n+2} + H_2O + CO_2 \ (n = 1,2,...) \quad (2)$$

The FT catalyst should be modified in order to minimize the formation of alkanes (especially CH_4), and increase selectivity to C2-C3 olefins. The two above stages may be combined together, but water should be preferably removed in-situ to shift the equilibrium, and avoid FT catalyst reversible inhibition. Current catalysts, derived mainly from the doping with alkaline metals of conventional FT catalysts or catalysts combining a zeolite with a methanol or FT catalyst, give at the best selectivities around 70-80% and around 40% of conversion [3]. It is thus necessary a further improvements in catalysts, reactor design and process operations, but it is reasonable to consider possible a further optimization with a target in selective synthesis of light olefins over 80% at higher conversion (>70%). A techno-economic analysis of this synthesis [3] indicates that for a predicted renewable H_2 cost of about 2-3 US$/kg H_2, the process of synthesis of light olefins from CO_2 can be economically valuable. Current renewable H_2 cost is still higher, but not so far to not consider feasible to produce light olefins from CO_2. Important is that this route shows that it is possible reuse CO_2 as a valuable carbon source and an effective way to introduce renewable energy in the chemical industry value chain, improving at the same time resource efficiency and limiting greenhouse gas emissions. By making CO_2 a base raw material for chemical production, and using this process to introduce renewable energy in the entire production chain, it is possible to effectively decouple the growth of chemical industry from the resource impact.

The actual main barrier to this vision is to produce H_2 from renewable sources in a sustainable and economic manner. There is already intense research on this sector, but still the R&D investments are low. It is necessary to intensity research on this strategic area.

By extending the same concept it is possible to produce solar fuels [4, 5] to introduce renewable energy in a form compatible with the actual energy infrastructure system based largely on the use of liquid fuels (still the preferable energy vector in terms of energy density, and easy transport/storage). There are different possible energy-vectors which derive from the hydrogenation of CO_2, either directly or through the intermediate stage of the RWGS reaction (eq. 1) to produce syngas (mixture of CO/H_2) which can be then converted through the already-established and commercially applied routes, although the syngas is produced from hydrocarbons instead that from CO_2 and H_2:

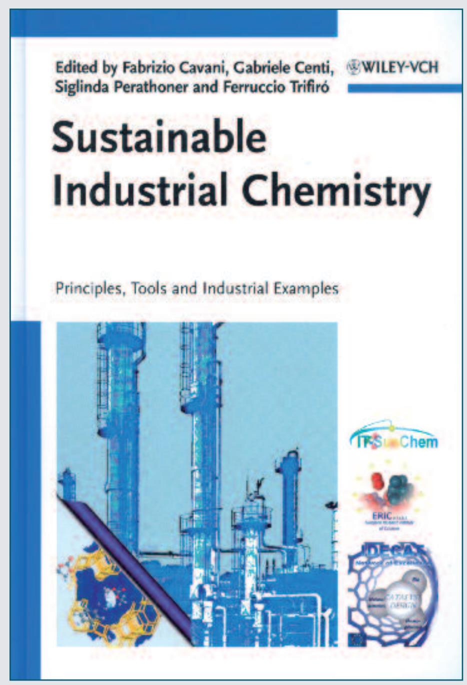
- formic acid, which may be used in formic acid fuel cells or as a vector to store and transport H_2 (the reaction of synthesis is reversible and formic acid can be catalytically decomposed in mild conditions to form back H_2 and CO_2);
- methanol and dimethylether (DME);
- methane (substituted natural gas, SNG);
- >C1 alcohols or hydrocarbons.

Some of these routes are already at a pilot or demonstration scale [2], but also in this case the main critical factor is the production of renewable H_2. However, the concept to highlight here is that there are many routes to create a CO_2-based resource-efficient chemical and energy production which effectively integrates into the existing infrastructure and value chain for a smooth transition from a fossil-fuel to a renewable energy based society.

In a longer term approach, it may be possible a next step, by integrating the function of renewable H_2 generation using sunlight and that of conversion of CO_2 to chemicals or solar fuels in a single nano-device: the artificial leaf [6]. In an artificial leaf it is necessary to mimic the various steps in the hierarchical process present in natural leaves (capture of sunlight photons, electron-hole separation with long lifetimes, energy transduction, etc.), but developing a new functional and robust design which realize two goals: (i) intensify the process, thus allowing a higher productivity and efficiency in converting sunlight (in the plants the quantum yield is typically below 1%); (ii) use solid components which keep functionalities, but are more robust, scalable and cost-effective. It is also necessary to separate the two reactions of water oxidation using sunlight and CO_2 reduction using the electrons/protons generated in the light-illuminated side. They should occur in two different cell compartments separated through a proton-conducting membrane, in order to reduce back reactions, achieve high efficiency and importantly from the practical perspective, have separate production of O_2 and of the products of reduction of CO_2. This is a critical issue both for safety and to avoid the costs of separation. This is the photoelectrocatalytic (PEC) approach [7]. In a longer term perspective, the objective should be thus the direct use of CO_2 in artificial-leaf type PEC cells to fully enable the potential of solar radiation by collecting energy in the same way as natural leaves are making, but in an intensified process producing directly chemicals/fuels. Due to the complexity of the problems, a fundamental understanding is the key for advancing, but taking into consideration the system engineering and integration. The fast advances in the development of nano-tailored materials will be a key to progress in this field, but only when combined to the integration between catalysis and electrode concepts to achieve a real breakthrough in the understanding of the reaction mechanisms of these fast surface processes.

Resource and energy efficiency

Resource and energy efficiency goes clearly beyond the problem of reusing CO_2, but this example is illustrative of how the global requirements for drastically increased resource efficiency can be seen as an opportunity to turn around a decreasing trend in competitiveness of chemical production in countries such as Europe. The foreseen breakthrough developments will stimulate entrepreneurship, create more jobs and improve quality of life. There are a number of critical tools and research areas which have to be further developed as a pre-requisite for a more effective approach to resource and energy efficiency: process intensification, catalysis, membranes, life cycle impact (LCC/LCA) and cradle-to-cradle approach, biotechnologies, waste and by-products valorisation, integrated use of bio-based feedstocks, lean production, supply-chain integration, modular design in process production, whole supply chain analysis, overall water management and water reuse, etc. This list is not exhaustive, but indicative of how cross-sectorial approaches are necessary for research and innovation in resource efficiency. The whole potential of R^3 (Reduce, Reuse, Recycle) has to be investigated and in general terms a new approach for a Sustainable Industrial Chemistry [8] is necessary. The loosing competitiveness of chemical and process industry in Europe, with associated loss in employment, intellectual capacity and economic impact, requires a discontinuity in its approach. Sustainability is the winning strategy to a global crisis.



References

[1] E.A. Quadrelli, G. Centi, *ChemSusChem,* 2011, **4**, 1179.
[2] E.A. Quadrelli *et al., ChemSusChem,* 2011, **4**, 1194.
[3] G. Centi *et al., ChemSusChem,* 2011, **4**, 1265.
[4] G. Centi, S. Perathoner, *Greenhouse Gases: Science and Techn*., 2011, **1**, 21.
[5] G. Centi, S. Perathoner, *ChemSusChem,* 2010, **3**, 195.
[6] S. Bensaid *et al., ChemSusChem,* 2012, accepted.
[7] C. Ampelli *et al., Energy Environ. Sci*., 2010, **3**, 292.
[8] F. Cavani *et al.,* Sustainable Industrial Chemistry, Wiley-VCH, Weinheim, Germany 2009, ISBN: 9783527315529.