PERSPECTIVES IN THE USE OF CARBON DIOXIDE

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The mitigation of carbon dioxide is one of the scientific and technological challenges of the 2000s. Among the technologies that are under assessment, the recovery of carbon dioxide from power plants or industrial flue gases plays a strategic role. Recovered carbon dioxide can be either disposed in natural fields or used. The availability of large amounts of carbon dioxide may open new routes to its utilisation in biological, chemical and innovative technological processes. In this paper, the potential of carbon dioxide utilisation in the short-, medium-term is reviewed.

Keywords: carbon dioxide; supercritical fluids; chemical utilisation; enhanced biological fixation.

It is now quite clear that the world has to use carbon based fossil fuels as the major source of energy for the next twenty years or so. Therefore, the amount of carbon dioxide generated and emitted into the atmosphere may reach a level that is not foreseeable, due to the complexity of the scenario that include: growth of the population, change of central economies to market economies, and increase of the standard of living in expanding economies.

That anthropogenic carbon dioxide (20 Gt per year, that add to ca 8 Gt originated from spontaneous fires) is accumulating into the atmosphere, is clearly demonstrated by the increase of its level: the actual value of 367 ppm should be compared with 275 ppm of the beginning of the industrial era. Such situation could substantially contribute to the enlargement of the 'greenhouse effect", with unknown effects on the average planet temperature. As a matter of facts, CO_2 is unanimously considered as contributing 52% to the potential increase of the temperature of the planet.

In order to prevent that a "non-return point" is approached, the reduction of the emission of carbon dioxide has been agreed at the international level. Such agreement has had a different implementation in various countries so far, also according to the local legislation. A number of Countries have introduced, or are considering the introduction of, the so called "carbon tax", as a regulation tool.

MITIGATION TECHNOLOGIES

Mitigation technologies, that should reduce by 15-20% the emission with respect to the 1990 level, can be separated into two categories, namely: those based on the efficiency of the generation and use of electric energy (that reduce the amount of carbon dioxide produced), and those based on the recovery of carbon dioxide from flue gases (that capture the produced carbon dioxide). The former technologies require either the transformation of existing power plants (that is not always feasible), or the construction of new ones (more realistic approach), based on an innovative production technology. Both approaches demand large financial investments. It is likely that new power stations will adopt innovative technologies for the production of electric energy, with reduction of the carbon dioxide emission.

An alternative approach for reducing the carbon dioxide emission into the atmosphere, is its recovery from power plant flue gases. This technology can be applied also to those plants for which large investments for technological upgrading are not advised.

The recovered carbon dioxide can be either disposed in natural fields or used in several different applications: biological, technological, chemical. Such technology is very interesting as can give a serious contribution to the control of carbon dioxide emission.

RECOVERY OF CARBON DIOXIDE

The recovery of carbon dioxide is now a well known procedure. Either liquid phases or membranes can be used.

Among liquid phases, mono-ethanolamine (MEA) is by far the most used solvent. The procedure is quite simple, as carbon dioxide is adsorbed in MEA under pressure and by simply reducing the pressure and slightly increasing the temperature (60 C) it is released back. The separated carbon dioxide may need further purification, according to its source and use. The cost of this procedure is estimated around 13 USA$/t CO_2, that is not too far from the cost of extracting carbon dioxide from natural wells, a procedure that affords today something like 8-10 Mt per year.

MEA is successfully used in several demonstration plants around the world.

An alternative technology is the use of membranes (organic or inorganic) that are entering the market and already find some practical application. Membrane separation units have the advantage of occupying a reduced space with respect to MEA units, and this may have a considerable importance in many cases. A combination of liquid phases and membranes is an interesting technology: the liquid is used to enrich in carbon dioxide the layer close to the membrane, that is the actual separation means.

Such technology is used with success in the separation of carbon dioxide from natural gas (LNG), that usually contains 35-45% of CO_2. This strategy has been adopted by gas-Companies that operate in those Countries where the carbon tax has been already implemented.

One of the major issues with recovered carbon dioxide is its purity, that drives the use. The grade of recovered carbon dioxide depends on the source: carbon dioxide from combustion processes contains impurities of S-compounds, or other organic pollutants (like non-combusted organic compounds, or else molecules generated in the combustion, dioxins and similar compounds) that may prevent its direct use, for example in the food-industry. Other sources (ammonia synthesis, and sugar-fermentation) may provide quite pure carbon dioxide that, in most cases, can be used as recovered with economic advantage. The fermentation industry is particularly indicated as source of pure carbon dioxide to be used in the food-industry.

DISPOSAL OF RECOVERED CARBON DIOXIDE

The recovered carbon dioxide can be disposed in natural fields: spent gas- or oil-wells, oceans, aquifers, deep geological cavities. The injection of carbon dioxide in oil wells for enhanced oil recovery (EOR) is already practiced in USA and Canada. Half of the total amount of the injected CO_2 remains in the well. Such wells could be used for the permanent storage of carbon dioxide, supposed that they will not be exploited again. Each site may be used for the storage of 25-50 kt of carbon dioxide. A problem that such wells may rise is the leakage of carbon dioxide. In fact, oil wells do not guarantee that they are sealed to gas loss. In the worst of the cases, such storage would correspond to a delayed release of carbon dioxide that avoids peak situations.

The use of spent-gas wells for the storage of CO_2 seems to be an excellent choice as they can be much more effective towards carbon dioxide storage. Field experiments are ongoing for the storage of carbon dioxide separated by LNG. This technology may avoid the emission of huge amounts of carbon dioxide to the atmosphere (equivalent to 70-80% of the extracted methane).

Other storage options are represented by the ocean disposal. This technology has not yet field results. Models show that carbon dioxide can be disposed in several forms, including a solid hydrate (CO_2x5.6H_2O).

More detailed studies are needed before to implementing the ocean disposal that would ensure the elimination of the carbon dioxide produced for centuries from now.

Aquifers are also considered for CO_2 storage. Experiments are in course for terrestrial disposal.

All these options have a regional validity and cannot be implemented everywhere. In fact, gas wells, oil wells or deep oceans are not available in every Country. One of the major issues to address is the localization of power plants with respect to fuel extraction, electric energy utilisation, and carbon dioxide disposal sites. Obviously, the construction of pipelines for transporting carbon dioxide from the production to the storage site could be one solution. The alternate use of existing pipelines for transporting methane and carbon dioxide in opposite directions should be also considered.

The cost of disposal is proportional to the distance to be covered and the depth of the storage site. The total cost for housing carbon dioxide (that has to be added to the recovery cost) can be as high as 100 $/t or more, depending on the factors discussed above.

UTILISATION OF CARBON DIOXIDE

An alternative to disposal in natural fields is the utilisation of carbon dioxide. As a matter of facts, if the recovery technology will be implemented, large amounts of carbon dioxide will become available and ready for use. The recovered carbon dioxide may require further purification, according to the use. This may be necessary if CO_2 has to be used in the food industry.

As we have specified above, several uses of carbon dioxide are possible. With respect to disposal, the utilisation option may represent a lower priority, if the amount is just considered. Anyway, the most correct assessment of the utilisation option is made in terms of innovative clean technologies that would be implemented. In general, the utilisation rises a double beneficial effect, as per each atom of carbon that is recycled, at least one atom is saved as natural resources. The correct evaluation of the carbon dioxide avoided by its utilisation requires a complex analysis that has to be based on the Life Cycle Analysis (LCA) methodology. In this way, is possible to figure out correctly the environmental impact reduction associated with carbon recycling or reuse.

As mentioned above, we can consider three different ways of carbon dioxide utilisation: technological, biological, and chemical. They will be shortly reviewed in the following paragraphs.

TECHNOLOGICAL USE OF CARBON DIOXIDE

As technological (or marchant) use of carbon dioxide, that use of CO_2 that does not convert the molecule is considered. The merchant market of carbon dioxide is roughly 15 Mt/y. The major uses are as: refrigerant fluid, cooling agent, food packaging, soldering and moldering agent, fumigant, anti-fire, additive to beverages. Carbon dioxide is also used for water treatment.

A quite recent use of carbon dioxide is as supercritical (SC) fluid. SC-CO_2 has been used for years for analytical or extraction purposes. An outstanding application of the extraction technology is the caffeine extraction for the production of decaffeinated coffee. The use of SC-CO_2 has the benign side-effect of reducing the environmental impact of organic solvents and produces more pure products for the food-industry. In fact, residual carbon dioxide does not give any effect on the humans, differently from residues of organic solvents.

Moreover, the SC-CO_2 makes very simple the procedure of recovery of the extracted product, that is obtained by simple expansion of the mixture that regenerates carbon dioxide that can be recycled, and affords the pure product or mixture of products.

Much more recent is the application as solvent for industrial processes and as reagent. SC-CO_2 is now used as solvent: in dying processes, in polymerization reactions, for the synthesis of nano-particles, in hydrogenation of unsaturated hydrocarbons and their derivatives, in the synthesis of formic acid.

$$H_2 + CO_2 = HCOOH$$
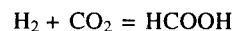
The last application is a rare example of SC-CO_2 acting at the same time as solvent and reagent. Formic acid is receiving a great attention as carboxylating agent and as hydrogen carrier. In fact, it can be converted back to dihydrogen and CO_2 by contact with Pd at room temperature.

The potential of SC-CO_2 is hard to define. The innovation that could be associated to its large introduction in industrial processes is very high. The interesting aspect associated with SC-CO_2 is the easy of recovery and the simple isolation of products from it. SC-CO_2 could be recycled many times, thus contributing to avoid the production of waste organic solvents. This aspect has an important role when assessing the contribution carbon dioxide can give to the reduction of the environmental impact of industrial processes and to avoiding carbon dioxide. It is known that in many cases the wastes produced may be as high as ten to one hundred times the amount of the product, and most of the wastes are solvents. The solvent substitution would greatly improve the quality of the environment and of the chemical industry. It is evident that if such technology is implemented on a large scale the avoided carbon dioxide is much more than the fixed carbon dioxide, as one should consider also the amount of CO_2 that is not produced by the solvents.

The major barrier to such implementation is the cost of the equipment. Should a cheaper technology develop, there may be expected a large expansion of the use of SC-CO_2.

BIOLOGICAL USE OF CARBON DIOXIDE

The fixation of atmospheric carbon dioxide in biomass is, apparently, the most simple technology for carbon dioxide mitigation. It is the less expensive when not-farmed forests are considered, but its cost may become comparable to other mitigation options if the fixation process must respond to specific fixation-rate and uses of the biomass. In particular, one should decide if the biomass has to be used for the sequestration of carbon dioxide or as a fixation strategy for replacing fuels or producing chemicals. In fact, the normal light efficiency of superior plants is very low (1.5-2.3%) for a profitable use as a

fuel substitute and for an efficient capture of carbon dioxide from the atmosphere. The amount of carbon dioxide fixed per time unit would be much lower than the produced one: this means that large extension of land would be necessary to this purpose. The cost of land in industrial countries and the use of land in expanding economies open the discussion "where forests should be located": just where most of CO_2 is produced (that just now means: in the north hemisphere and in industrialized areas), or elsewhere? Or one should consider the areas where the major increase of carbon dioxide production is expected (expanding economies)?

In order to reduce the land requisite (for the fixation of the amount of CO_2 released by a 500 MW power plant ca. 400 sqkm of forestry are necessary!) farming the forest or using fast growing plants with a three years cutting has been considered. Such biomass could be treated for energy production. It must be emphasized, at this point, that the direct burning of biomass is not recommended as several pollutant could be emitted into the atmosphere. The cost of the treatment of biomass must be taken into account when making the balance of the avoided carbon dioxide. For this reason, biomass is not really a "zero emission fuel".

Algae are an alternative to terrestrial plants. They present a much higher fixation efficiency (ca. 4.5-6%) under natural conditions. If grown in bioreactors, micro-algae can fix carbon dioxide with a light efficiency close to 8%. These figures are quite interesting for the amount of carbon dioxide that can be fixed in an algal pond compared to terrestrial plants. Nevertheless, the problem of fresh-water availability remains, coupled with the purity of carbon dioxide, and the algae processing cost. An estimation of the value of the fuel derived from algae fixes its price at ca. 30 $/barrel, that is too high for the actual price of oil. In perspective such approach may be more meaningful.

The fixation of carbon dioxide by halophytes may contribute to reduce the pressure generated by fresh-water use and to expand the area of cultivability.

Interestingly, carbon dioxide recovered from power plants could be used in "greenhouses" or bubbled in algal ponds for its fixation. The use of carbon dioxide in greenhouses has been investigated and demonstrated to increase the rate of growth of plants like flowers or vegetables. Such studies have also shown that the growth-rate is not proportional to the carbon dioxide concentration over a large interval of concentrations. Therefore, such finding does not allow to be optimistic and say that, if the concentration of carbon dioxide increases into the atmosphere, the increased photosynthesis will control the level of CO_2.
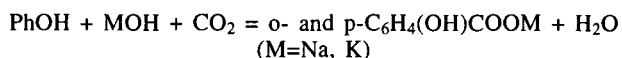
It is common experience that oceans and plants do not control the CO_2 level into the atmosphere as we are measuring a continuous increase of such level.

CHEMICAL FIXATION OF CARBON DIOXIDE

The utilisation of carbon dioxide by the chemical industry is a process implemented since more than one century. The synthesis of urea (50 Mt per year)

$$CO_2 + 2 NH_3 = H_2NCONH_2 + H_2O$$
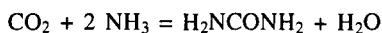
and the Kolbe-Schmitt reaction

$$PhOH + MOH + CO_2 = \text{o- and p-}C_6H_4(OH)COOM + H_2O$$
$$(M=Na, K)$$

are two examples of synthesis of organic molecules. It is worth to recall that the cations Na and K control the o/p isomers distribution. An favours the synthesis of the o-isomer, while K favours the synthesis of the p-isomer. The o-OH-benzoic acid isomer is used for the synthesis of Aspirin.

Inorganic carbonates (Group 1 and 2 elements) are obtained using carbon dioxide (ca. 20 Mt per year) since long time. It is interesting noting that the processes mentioned above do not require any catalyst to go.

Many other reactions based on carbon dioxide for the production of chemicals are known that require a metal catalyst (or an acid-base catalysis). This has expanded in the last few years the investigation of the interaction of carbon dioxide with metal systems and organic substrates.

Most recently CO_2 has been used as additive of CO in the synthesis of methanol. A total amount of ca. 90 Mt/y of carbon dioxide are used for such synthetic purposes, that fixes at ca. 115 Mt/y the amount of carbon dioxide used for industrial purposes (technological and chemical).

Such amount could expand easily, contributing innovative and clean technologies.

In fact the use of carbon dioxide in synthetic chemistry would greatly improve benign syntheses, avoiding the use of toxic products and solvents, and favouring the implementation of more direct synthetic pathways, with energy and atom saving.

A factor that makes the use of carbon dioxide questionable is the energy needed for its conversion. Carbon dioxide lays in a deep potential energy well (ΔG= -96 kcal/mol) and its use is considered as energy requiring. As a matter of facts, we can categorize the use of carbon dioxide in two classes:

A) reactions in which the -COO- moiety is maintained intact [carboxylates: esters, lactones, RCOOR; carbonic acid, ROC(O)OR, and carbamic acid, RR'NCOOR", esters, ureas, RR'NCONRR'].

B) Reactions in which the molecule is reduced to other C1 molecules [HCOOH, CO, CH_3OH, HCN, CH_4].

The energy requirement of Class A and B is quite different. Class A reactions can help to substitute toxic starting compounds like phosgene (that is produced at a rate of ca. 8-10 Mt per year. Due to its toxicity, building new large plants is now forbidden.) and to develop new direct carboxylation reactions of organic substrates.

The synthesis of lactones and carboxylates can represent a new way to develop selective and high yield procedures for the synthesis of high added value products.

A promising area is the functionalisation of polymers that would result an interesting way to fix carbon dioxide in long-lasting materials, that may have new innovative applications.

The synthesis of methanol from carbon dioxide is a challenging area, as it would allow to recycle large amounts of carbon dioxide for energy, and for chemical, purposes. In fact, methanol is a unique species that has a key role as chemical intermediate, hydrogen carrier, and energy vector. When the use of carbon dioxide is compared to the actual synthesis of methanol from carbon monoxide, the question rises about the source of hydrogen.

$$CO + 2 H_2 = CH_3OH$$

$$CO_2 + 3H_2 = CH_3OH + H_2O$$
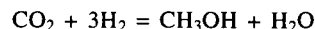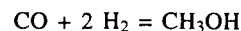
In fact, carbon dioxide requires one extra mol of hydrogen as sink of the excess atom of oxygen with respect to CO. Hydrogen should not be obtained from hydrocarbons (CO_2 recycling and fixation in methanol is intended to avoid the extraction of natural resources), but should more likely come from water.

Coupling the water splitting reaction with carbon dioxide reduction is a very challenging way to go. The use of semiconductors or of homogeneous catalysts has been investigated with alternate success. The actual limit is in the light efficiency of the process. If organic solvents are used, more than water, as electron donors, an efficiency close to 13% has been obtained, that is an absolutely excellent result, also if not practical at all.

Improving the light efficiency using solar light and water is the challenge. Plants and algae use solar energy under natural

conditions with a 1.5-6% efficiency. The artificial photosynthesis in water has now a limit of 0.1% light efficiency, at the best. Will research provide the correct solution for getting better results than Nature?

CONCLUSIONS

The recovery of carbon dioxide is a technology that may find a large application in the short-, medium-term. This would make available large amounts of carbon dioxide, ready for use in innovative technologies, biological and chemical processes. An estimation of the contribution of the chemical utilisation to the total amount of carbon dioxide that should be avoided according to the agreed limits (15-20% reduction with respect to the 1990 emission), sets for the utilisation a share of 7-10% of the total in the short term. This is not the upper limit. Several new applications are possible.

In order to make this option more significant, more basic and oriented research is needed in the area of new catalysts, new technologies, new processes.

This is a challenge that scientists cannot miss. It is the challenge of the years 2000!

ACKNOWLEDGMENTS

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