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Conditions for the Use of CO_2

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Abstract: This review presents several aspects of the utilization of carbon dioxide. In particular, it will consider the conditions for its correct utilization in order to reduce its emission into atmosphere and to size the demand of CO_2 that may be used within several different industrial sectors, spanning from fine chemicals to bulk chemicals, intermediates and fuels.

Keywords: Carbon dioxide utilization · Catalysis · Chemicals and fuels · Fixation into biomass

Introduction

As reported by the Emission Database for Global Atmospheric Research,[1] in 2011 the global emission of CO_2 was 48% higher than two decades ago (33.4 billion tons) reaching the record atmospheric concentration high level of 400 ppm in May 2013, with a corresponding increase in global surface temperature of about 0.8 °C.[2] Without climate change mitigation policies it is estimated that global greenhouse gas (GHG) emissions in 2030 will increase by 25–90% over the level in 2000, with CO_2-equivalent concentrations in the atmosphere growing to as much as 600–1550 ppm.[3]

The use of CO_2 in chemical synthesis will be boosted by its capture from industrial and power sources. When it has the correct purity, CO_2 can be used as building block for chemicals or carbon source for fuels, an approach that also meets the need of developing new clean processes.

So, in order to develop a 'carbon dioxide-based industry', it is necessary to set up new catalytic processes. Therefore, it is important to know the interaction of CO_2 with metal centers that may catalyze the new reactions. The chemistry based on carbon dioxide is very young, the first evidence on the interaction of CO_2 with a metal center was highlighted by Aresta *et al.* in 1975.[4]

From an energetic point of view the reactions involving carbon dioxide can be divided into two main classes, namely: *Class 1,* when CO_2 is used in its entirety as in the carboxylation reactions where C–C or C–heteroatom bonds (C–E; E=O, N, P, other element) are formed, and *Class 2* where a reduction reaction occurs. In the latter case a source of energy is necessary, such as dihydrogen, electrons, or heat. *Class 1* reactions can be considered as an example of sustainability as they make possible the synthesis of carboxylates using diversified starting materials, recycling carbon, reducing waste. It is possible that, under the appropriate reaction conditions, the direct carboxylation of organic substrates may produce a lower energy consumption with respect to processes on stream. New processes must be developed that: i) reduce the overall CO_2 emission compared to relevant processes on stream, ii) are safer and more eco-sustainable than the present ones, iii) are economically viable.

Sources of Carbon Dioxide and Reduction Technologies

CO_2 is emitted in several human activities:

- combustion of coal, natural gas, and oil to produce energy (>30% of the emission).
- transportation (*ca.* 30%).
- heating, other industrial processes and land-use changes.

The sources can be differentiated into point-continuous (power stations, industries) and mobile-discontinuous sources (transportation, heating). Table 1 shows some approximate energy content of natural gas, oil and coal, and the amount (mg/kJ) of CO_2 produced during their combustion.

As shown in Table 1 coal represents the lowest source of energy but also the highest producer of carbon dioxide.

The need to reduce CO_2 emissions has been agreed on a global level and implemented by a number of countries that have adopted a variety of technologies to reach their target, including:

i) Improvement of energy efficiency and promotion of energy conservation;
ii) Increased usage of low carbon fuels, including natural gas, hydrogen or nuclear power;
iii) Deployment of renewable energy, such as solar, wind, geo, hydropower and bioenergy;
iv) Implementation of geo-engineering approaches, *e.g.* afforestation and reforestation;
v) CO_2 capture and storage (CCS);
vi) CO_2 capture and utilization (CCU).

Strategies (i)-(iii) reduce the emission of CO_2 at source, while (iv)-(vi) capture emitted CO_2.

Preliminary to the exploitation of strategies (v) and (vi) is, thus, the 'capture' of CO_2 from gas streams (including the atmosphere) in which it is present. Rich streams will require less energy, the atmosphere is a most diluted source (400 ppm or 0.4% by volume) and is not the best source of CO_2, unless carbon-free energy is used for the separation.

Table 1. Energy values of fuel.

Fuel	energy content [kJ/g]	mg of carbon dioxide produced per kJ
Natural gas	52	53
Oil	43	71
Coal	24	93

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We deal here with the utilization option (CCU) and shall consider the constraints to such technology. The exploitation of the conversion of CO_2 must be coupled with implementing safer and eco-compatible processes. Avoiding toxic reagents and by-products will reduce the cost of processing, while producing a lower environmental impact, in terms of end-of-pipe treatments, storage and disposal costs. CO_2 is not a toxic substance (it may become an asphyxiating agent at concentrations above 10%), therefore, under controlled conditions of utilization, it does not give rise to serious concerns and safe conditions are easily implemented. Usually, there is no need to work at very high pressure, the highest (10–40 MPa) being used when CO_2 is used as supercritical fluid.

Quality of Anthropogenic Carbon Dioxide and its Use

Today, *ca.* 200 Mt/y of CO_2 are used in various industrial applications, of which 180 are used in chemical processes and *ca.* 20 in technological uses where CO_2 is used as a fluid, and not converted into other chemicals. Surprisingly, until recently, almost 80% of CO_2 used in technological applications is extracted as quite pure CO_2 (>99%) from natural reservoirs with no poisonous contaminants. Such a practice should be dismissed in favor of the use of anthropogenic CO_2. The latter has a variable purity, depending on the process in which it is generated. CO_2 produced in power plants is the most abundant, but the most polluted and costly to purify as it is a diluted stream and mixed with NOx, SOy, CO and other contaminants that must be removed. In fact, NOx, SOy may poison catalysts or can be tolerated by bio-systems only below 100 ppm. Industrial processes (Table 2) may be a more convenient source of CO_2. Fermentation processes produce quite pure CO_2 that has only moisture as co-product (and some alcohols or other minor organics).

Table 2. Industrial sources of CO_2 (not including power plants)

Source	**Amount/Mty^{-1}**
Oil refineries	850–900
LNG sweetening	20–25
Ammonia	160
Ethene and other petrochemical processes	155
Ethene oxide	10
Fermentation (bioethanol, breweries, *etc.*)	> 100
Cement production	> 1000
Iron and steel	870

However, industry produces *ca.* 3300 Mt/y of CO_2, representing 10% of the total amount.

Although the direct use of recovered CO_2 is not in general possible due to contaminants present in the stream, and CO_2 recovered from industrial plants cannot be directly used in the food industry, nevertheless part of such industrial CO_2 has long been recovered and used in industrial syntheses: for example, CO_2 generated in the ammonia synthesis is used for the production of urea, and CO_2 produced from $CaCO_3$ in the Solvay process is used for the synthesis of Na-carbonates. In the following paragraphs the current uses of CO_2 are analyzed.

Non-chemical Uses of CO_2

Carbon dioxide can be used in non-chemical applications, such as the food industry (production of carbonated beverages: mineral water, beer, *etc.*, or as a source of cooling in storing and transporting food, or as an inert atmosphere in order to prevent the proliferation of micro-organisms, insect larvae, bacteria, fungi, *etc.* in foodstuffs. It can be also used as an industrial gas, in the pulp and paper industry to control pH levels, enhance pulp yield, and wash brownstock and bleached stock. It finds application as an alternative to strong acids such as H_2SO_4, assuring the decrease of costs, improving plant safety and flexibility and reducing the environmental impact.

Carbon dioxide is, most often, mixed with argon as a shielding gas used to prevent atmospheric contamination of molten metal in electric arc welding processes.

Several other uses have to be cited, namely the emerging industrial uses of CO_2 such as enhanced coal bed methane recovery and enhanced oil recovery, algal bio-fixation and bio-fuel and chemicals production, enhanced geothermal systems (using CO_2 as a working fluid), bauxite residue processing, power generation with CO_2 as a working fluid, carbonate mineralization (aggregate production), polymer processing, CO_2 concrete curing, renewable methanol and formic acid production.

Moreover, carbon dioxide can be used as a fire extinguisher with good performance since it reduces or completely deprives fire of oxygen. It is also used as liquid in washing processes, in which it substitutes ammonia or halogenated solvents, and could also be used as a cooling fluid in air-conditioners.

In all the above uses CO_2 substitutes chemicals (such as CFC) which have a much higher climate impact than CO_2 itself with high environmental benefit. In such applications, CO_2 has a variable value depending also on the geographical areas where it is used (up to >600 US$/t as dry ice in some countries) that pays for its separation from industrial gas-streams (average separation costs 30–50 US$/t).

CO_2 Conversion (CC)

CC can play a key role in saving fossil resources, while reducing the CO_2 emission to the atmosphere, despite some thermodynamic and kinetic barriers. It is common to say that carbon dioxide is a stable molecule under both thermodynamic and chemical point of view under standard conditions, which requires energy for its conversion. Noteworthy, under certain conditions it can react with low energy demand (carboxylation reactions), with some energy-rich (olefins, anions, amines, similar compounds) substrates.[5,6] Conversely, it requires energy and proper catalysts if it has to be converted into fuels,[7] which have a much larger market than chemicals. In general, we can say that if the oxidation state of the carbon atom remains equal to four in the product (inorganic and organic carbonates, carbamates, ureas, similar products) the conversion of CO_2 will not require energy, and the process may even be exoergonic (Fig. 1).

If the oxidation state of C is reduced below 3, then energy is required in the form of heat, electrons, hydrogen, radiations, *etc.*

However, CC might present limitations that affect its implementation. To convert more CO_2, it is necessary to develop new capture agents with higher efficiency and lower energy requirements and to identify innovative and effective catalytic processes, to reduce the capture-conversion cost and its environmental impact.

CO_2 as a Source of Intermediates

With C-based fossil fuels being the main (>85%) energy source, only low-energy processes based on simple chemistry have made sense so far: thermal reactions

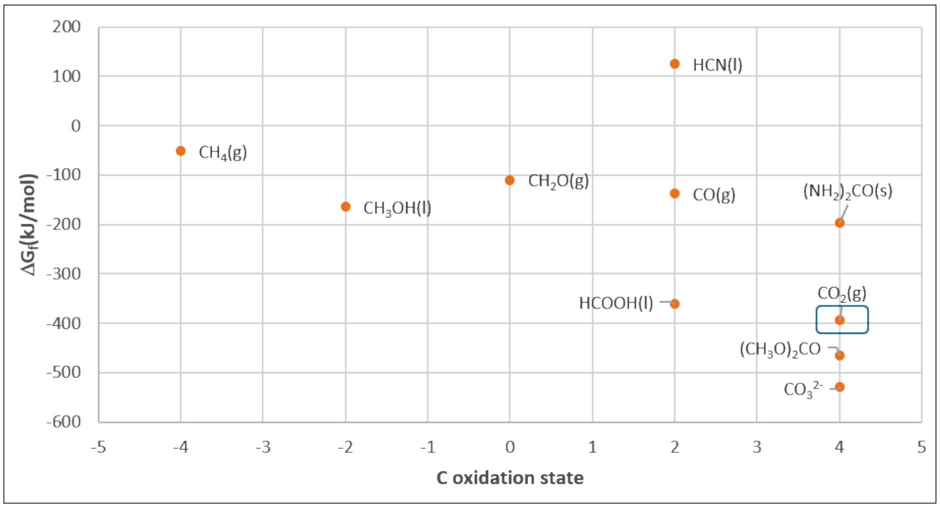


Fig. 1. Free energy of formation of C1 species versus oxidation state of carbon.

that do not require catalysts such as those forming urea, salicylic acid, inorganic carbonates. In the short term carbon dioxide could be largely used to produce carbamates, organic carbonates, carboxylates, new ureas, polymers. In following paragraphs, an analysis of selected applications is made to highlight the barriers that have to be overcome and conditions to be met.

Synthesis of Urea

Urea, H_2NCONH_2, is synthesized under thermal conditions (>400 K) by reacting NH_3 with CO_2. The price of urea depends essentially on the price of LNG (liquid natural gas) from which the H_2 needed for NH_3 synthesis is produced. Urea is used essentially as urea-ammonium-nitrate which is one of the most common forms of liquid fertilizers. Its production (around 155 Mt/y) is set to grow over the next twenty years by 5–7%/y.[8] Today half of the production is located in China, with a plant capacity of 1 Mt/y or 3500 t/d. The forecast of its capacity is around 240 Mt/y (Table 3) by 2016.[9]

So far, urea has been used essentially as fertilizer, but recently it has been considered as 'an active form of CO_2' and used as reagent or as monomer for polymers, resulting in an increasing demand. Such trends may result in a price increase that will soon require a clear distinction between the price of urea for croplands and that for industrial synthetic applications. The above process is not catalytic: efforts must be done to reduce energy consumption, *e.g.* by recycling heat as the reaction is carried out at >400 K. New technologies should also be developed to improve the energy balance.

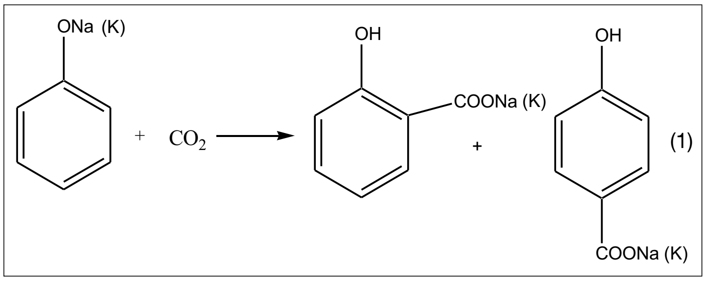
Synthesis of Salicylic Acid

Salicylic acid synthesis has been produced since the second half of the 1800s by reacting phenol salts of Na and K (Eqn. (1), Scheme 1) with CO_2 under pressure at a temperature of 370–430 K.[11,12]

This process is characterized by a mol ratio of salt:product = 1:1, which means that there is a loss of metal and it is necessary to develop a direct process starting from the free acid, avoiding the use of bases. Moreover, the reaction is not characterized by high selectivity as both the *o*- and *p*-isomer of the salt are formed. Both find applications; the *o*-isomer being used for the synthesis of Aspirin (*ca.* 20 kt/y), and the *p*-isomer being a monomer for specialty optical polymers. Although this process was developed several years ago, there is the need for further investigation, in particular it is necessary to develop catalytic systems to avoid the metal loss[13a] or by using enzymes as catalysts.[13b]

Table 3. Worldwide use of urea and CO_2 in the short term (*according to ref. [10])

Year	Mt urea	Mt CO_2
2012	155	114
2013	160	117.3
2014	165 (187)*	121 (137)*
2015	170	125
2016	180	132



Scheme 1. Salicylic acid synthesis.

Carbonation: Inorganic Carbonates

Among inorganic carbonates that have a global market of almost 200 Mt/y, calcium carbonate ($CaCO_3$) is the most used and has a market around 114 Mt/y. It finds application in several fields as commercial functional filler in paper, rubber, plastic, architectural materials, coatings and light chemicals, as additive for thermoplastics and in PVC production. It can be also used in non-metal mineral applications especially when mixed with talc and kaolin. Asia is the area where Precipitated Calcium Carbonate (PCC) is largely used and the largest production capacity (more than 70% of the total) is concentrated in China.

Sodium carbonate has also a large market with 50 Mt/y produced worldwide and 15 Mt/y in Europe due to its use in the manufacture of glass, as a strong base to regulate pH and maintain stable alkaline condition, in chemistry as electrolyte or as primary standard for acid–base titrations. It is produced using an old technology developed by Solvay[14] in 1882.

Potassium carbonate today is produced by electrolysis of potassium chloride to give potassium hydroxide which is then reacted with CO_2 to afford potassium carbonate. Its market is quite large as it is used in soil additives, special glasses and other fields (drying and buffering agent, fire suppressant). Carbonates of other elements (Ba, Sr, Cu, Fe, others) have more limited markets.

Due to their intensive use, the inorganic carbonate market is expected to grow and this means that more CO_2 from the actual *ca.* 90 Mt/y will be consumed. The development of new processes useful to carbonate new substrates will represent a very new approach in this area.

The concept of mineral carbonation[15] has been developed as an alternative to geological storage and where CO_2 cannot be confined underground: CO_2 is stored as calcium and/or magnesium carbonate, harmless materials with a low solubility in pure water. In particular, in mineral carbonation, (captured) CO_2 is proposed to be reacted with minerals (such as olivine-Mg_2SiO_4 and wollastonite-$CaSiO_3$) to form Mg- or Ca-carbonates providing storage on a geological time scale. This process is very interesting as it duplicates the *rock weathering* process that has been naturally reducing the amount of CO_2 from the atmosphere since the creation of the earth. Of course, as all natural processes, the natural carbonation reaction is very slow, so in order to find industrial application on a large-scale, the process has to be accelerated using heat, pressure, mechanical and chemical pre-treatment of the mineral. In principle, the carbonation process is exothermic, which means that no net energy is required for the reactions to occur; also, energy, in the form of heat, could be recovered and used, even if at low temperature and a thermal efficiency around 60–70%. The technology of accelerated carbonation has the advantage of stabilizing toxic compounds, so it is used in the treatment of basic solid waste that, after treatment, can be utilized in the building sector instead of concrete. The latter has a market of 32 000 Mt/y nowadays, and will grow at rate of 0.8–1.2%/y until 2030.[10] This application, if exploited, opens up a very large use of CO_2.

Recently, sodium carbonate has been produced through a low-voltage electrochemical process starting from halides,[16,17] *e.g.* NaCl is converted into hydrogen carbonate ($NaHCO_3$) or carbonate (Na_2CO_3). Demo plants are under construction, as this process seems to be very appealing from the economic and energetic point of view. For example, by using this new methodology the large amount of $CaCl_2$ produced by the Solvay process could be converted back into $CaCO_3$.

Synthesis of Formic Acid

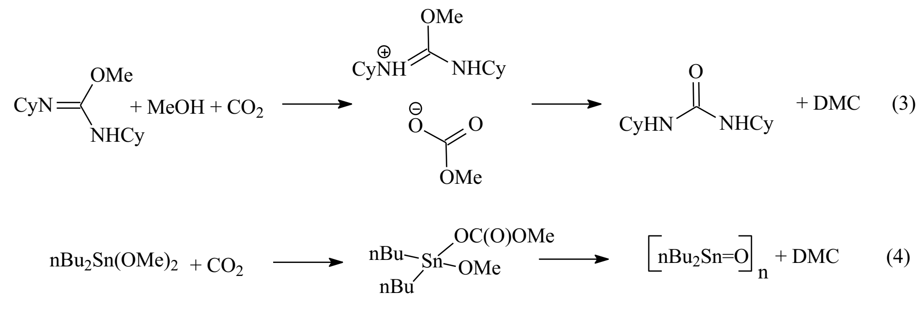
One way to store CO_2 in a liquid form is its conversion into formic acid (HCO_2H) by reaction with hydrogen in a ratio H_2:CO_2 = 1:1. The reaction is a sustainable process as no by-products are formed and it has very high atom efficiency. Formic acid (HCO_2H) can be considered also a good material for hydrogen storage as it has a volumetric hydrogen density of 53 g/L of H_2, low toxicity and is a liquid under ambient conditions.[18,19] Formic acid is easily decomposed to release hydrogen (by using a variety of homogeneous and heterogeneous catalysts)[20,21] with subsequent release of CO_2.

The conversion of carbon dioxide into formic acid is not easy especially in the gas phase ($\Delta G^0 = +33$ kJ mol^{-1}) due to the high kinetic and thermodynamic stability of CO_2, while the reaction is more favorable in aqueous solution ($\Delta G^0 = -4$ kJ mol^{-1})[22] and in the presence of bases such as amines. This means that direct synthesis requires additional investigation for its exploitation. HCO_2H can be recovered by reacting salts with strong acids (H_2SO_4) with the generation of solid waste. A new perspective is open by recent results[23] by the Laurenczy group which demonstrate that appreciable concentrations of free formic acid can be produced in acid solutions.

Synthesis of Linear and Cyclic Organic Carbonates

Linear and cyclic organic carbonates can be used as solvents and chemical intermediates due to their characteristics of low toxicity, good biodegradability and high boiling point. In particular, dimethyl carbonate (DMC) finds utilization in several fields such as production of polymers, as additive to fuels, or in organic syntheses. Its industrial synthesis by conventional methods uses toxic phosgene or carbon monoxide. An innovative process for its synthesis is the direct carboxylation of methanol, a very promising method[24,25] (Eqn. (2), Scheme 2). Its exploitation would represent an alternative to the use of phosgene, a very toxic compound, banned in several EU countries, with great benefit from the point of view of risk reduction, safer working conditions, reduction of chlorinated wastes.

$$2CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O \qquad (2)$$



Scheme 2. Synthesis of dimethylcarbonate. Eqn. (2): Innovative processes based on CO_2 use; Eqn. (3): Use of organic promoter as catalyst; Eqn. (4): Use of Sn-catalyst.

Reaction (2) is quite clean as under controlled conditions only water is formed as co-product. However water may deteriorate the catalyst and prevent the equilibrium to be shifted to the right. Homogeneous and heterogeneous catalysts have been used so far and also organic promoters (such as carbodiimides)[26] which were shown to be very active (Eqn. (3), Scheme 2).

Under homogeneous conditions, Sn-catalysts have also been used[27] (Eqn. (4), Scheme 2) for the synthesis of DMC through an intra- or inter-molecular methyl transfer[28] with conversion of the catalyst into a metallorganic tin-oxide that has an oligomeric structure which is inactive.

In order to avoid the formation of oligomeric tin-oxo-complexes, Sn catalysts were supported to keep the Sn centers separated. With this different structure a different reaction mechanism occurs that prevents the formation of inactive oligomers. So in order to verify this idea metallorganic Sn species or niobium methoxide were grafted on a polystyrene-PS matrix (Fig. 2a,b).[24,29]

By using mesoporous materials such as SBA-15, anion exchange resins and various functionalized MCM-41s,[30] and inorganic oxides,[31–36] the conversion yields are not very high.

Using ZrO_2-based materials or modified Nb and Ce catalysts,[37] at temperatures in the range of 403–443 K, DMC is obtained with a conversion yield around 2% and a selectivity to DMC close to 100%.[31] To increase the DMC yield, ZrO_2 was modified with H_3PO_4,[38] which reduces the operation temperature, improving, thus, the conversion yield, but also lowering the selectivity. Other mixed oxides such as $Ce_{0.2}Zr_{0.8}O_2$[39] or CeO_2-Al_2O_3[37b] have been used.

The elimination of water has been attempted in several ways: use of chemical

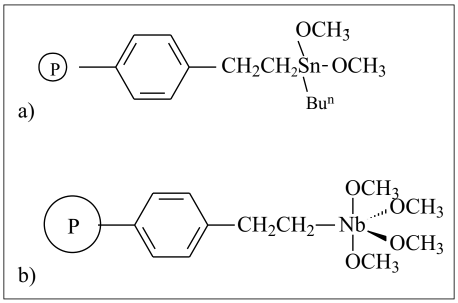


Fig. 2. a) Metallorganic Sn species and b) niobium methoxide supported on a polystyrene matrix.

traps (zeolites,[40a] nonrecyclable organic agents like orthoesters[40b] or nitriles,[40c–e] and recyclable organic agents like acetals or ketals[40f,g]) and physical means (pervaporation membranes[37a]) which still require more intensive investigation for practical application. To increase the yield and selectivity urea can be used instead of CO_2 giving interesting results.[41]

The necessary breakthrough is the equilibrium shift that would generate a concentration of carbonate that could be easily separated at a low energy cost.

Cyclic carbonates find utilization in several fields. In particular ethene carbonate (EC), propene carbonate (PC) and styrene carbonate (SC) are used as polar solvents, as monomers for polymer synthesis, electrolytes in lithium secondary batteries, in pharmaceutical and chemical industry.[42,43] The synthetic process mainly used is the carboxylation of epoxides (Eqn. (5), Scheme 3)[44,45] that represents a very interesting example of implementation of 'green chemistry' and 'atom economy' as no by-products are formed.

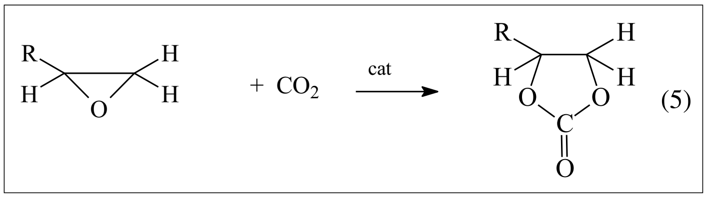
Different catalysts have been described[46–51] as active species for their production. Organometallic species and metal complexes,[52] classic Lewis acids[53] and metal phthalocyanines[54] have also been used with good results.

Heterogeneous and supported catalysts have been used[55–62] that are more stable. Increasing the reaction rate is the key issue in this application, avoiding concomitant formation of monomers and polymers. In fact, the copolymerization of CO_2 and epoxides is a quite attractive route to polycarbonates (chemical storage of CO_2) which properties depend on the epoxide used and on the regularity of the sequence of insertion.[63]

Interesting is the role of the solvent that may promote the carboxylation process (amides such as dimethylformamides (DMF) or dialkylacetamides (DAA[55]). By using DMF as solvent and starting from a pure enantiomer of the epoxide, a total retention of configuration has been observed and the formation of optically active carbonate.[56]

Cyclic carbonate can be obtained by reacting CO_2 with cyclic ketals, propargylic alcohols, diols and through the direct oxidative carboxylation of olefins. The latter approach is an interesting synthetic process of cyclic carbonates starting from CO_2 and O_2, both cheap and easily available reagents (Eqn. (6), Scheme 4).

The barrier here is the concomitant addition of O_2 to the double bond of the olefin that can be cleaved with consequent loss of olefin.[64–66] The reaction has been studied under homogeneous and heterogeneous conditions and the mechanism has been completely elucidated.[67] When a homogeneous catalyst is used the reaction has a short lifetime and low TON as the homogeneous catalysts (Rh-complexes) are converted into different species which are inactive. Under heterogeneous conditions, by using metal oxides[55–57,64–67] as catalysts, the process is characterized by a longer life and is able to reduce the radical oxidation of the olefin affording up to 50% conversion of the olefin into the carbonate.



Scheme 3. Carboxylation of epoxide.

High rates and selectivities are the target in this reaction, with reduction of loss of olefin and repression of the radical addition to the double bond of the olefin in order to reduce its loss.

Synthesis of Carbamates

The field of application of carbamate esters is very large: i) pharmacology (pro-drugs, drugs),[68] ii) agrochemistry, iii) synthetic chemistry (intermediates for protecting amino-group,[69] linkers in combinatorial chemistry, isocyanates and polymers,[70] precursors of ureas,[71–73] substitution of phosgene in organic synthesis[68,74,75]). Carbamate esters are usually prepared from $COCl_2$. Alternatively, the 'RR'NCO_2' moiety can be synthetized by interaction of CO_2 with amines, mediated or not by metal or non-metal species.[76,77] The reaction of primary or secondary amines alone (Eqn. (7), Scheme 5) or in presence of metals, metal salts or metal-complexes (Eqn. (8), Scheme 5) with carbon dioxide affords ammonium carbamates that can be used as building blocks for the production of pesticides and for other purposes.

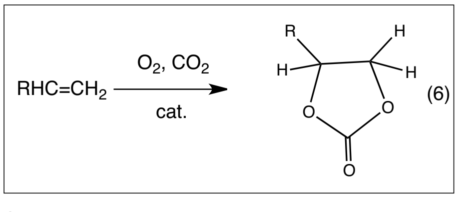
Quaranta and Aresta[5] have published a complete review of N-carbonyl compounds from CO_2 including the urea derivatives discussed above.

The development of CO_2-based routes to carbamates is challenging as the carbamate anion, $^{+}RR'NCO_2^{-}$, easily generated from the direct reaction of amines and CO_2, is an '*ambident nucleophile*', at the oxygen- and nitrogen atom. To be converted into an organic ester it needs to be alkylated at the oxygen atom. The selective attack of an electrophile (R^+) to one of the two O-atoms of the carbamic group is not a trivial step and plays a key role for the selectivity of the process. In fact, an attack at the N-atom is quite common with alkylation of the amine.

Carbamate esters can be prepared very easily and under mild conditions, using suitable sterically hindered and strong organic bases.[78,79] In particular, very often DBU (1,8-diazabicyclo [5.4.0] undec-7-ene),[80] and pentaalkylguanidine superbases, such as CyTMG[79] are used together with tetraethylammonium superoxide,[81] basic resins,[82] triton-B (benzyltrimethylammonium hydroxide),[83] and K_2CO_3 in presence of catalytic amounts of $(Bu_4N)I$[84] and alkyltosylates.[82–84]

Electrochemistry has been also used to develop systems where the base is obtained by cathodic reduction of O_2 to superoxide.[85] Interesting are also the results obtained using the radical anion $CO_2^{\cdot-}$ obtained by electrochemical activation of CO_2. The reaction is carried out in conventional solvents[86] or in ionic liquids to obtain carbamate esters starting from aromatic or aliphatic amines and alkyl halides under mild conditions.[85,87]

Organic carbonates, produced from carbon dioxide as already discussed above, can be used as carbonylating agents (Eqn. (9), Scheme 5) to obtain carbamates from aliphatic and aromatic amines.[88]



Scheme 4. Direct oxidative carboxylation of olefins.

$$2RR'NH + CO_2 \rightarrow (RR'NH_2)O_2CNRR' \qquad (7)$$

$$RR'NH + L + MBPh_4 + CO_2 \rightarrow M(O_2CNRR') + [HL]BPh_4 \qquad (8)$$

R' = H, alkyl, L = RR'NH; R = aryl, R' = H, L = NR''$_3$ (R'' = alkyl); M= Li, Na, K

$$RNH_2 + (R'O)_2CO \rightarrow RHN\text{-}C(O)OR' + R'OH \qquad (9)$$

Scheme 5. Ammonium carbamate synthesis.

One interesting direct way to produce organic carbamates from amines, CO_2 and alcohols is through the one-pot synthesis proposed by Tomishige *et al.*[89] where CeO_2 was used as recyclable catalyst and methylbenzylcarbamate was obtained with a yield of 92%. The exploitation of the direct carboxylation of amines is a process of great relevance to the polymer chemistry and developing efficient processes would be of great economic value.

CO_2 as Source of Fuels

Depending on the catalytic system and on the reaction conditions used, CO_2 can be converted into a number of interesting high-energy chemicals (Eqns (10a–c), Scheme 6) that can be used as fuels.

The use of methanol as fuel is expected to increase in comparison to previous years, when the amount of methanol used directly was very small. Nowadays in China gasoline is mixed with 15% methanol and used directly in cars without causing problems for engines. To increase the amount of methanol up to 85% it would be necessary to make some changes to engines. Nowadays the amount of methanol used as fuel is almost 9 million t/y (14% of total production) but it is expected to increase to 16% by 2016.

The production of methanol has been based, for a long time, on the use of fossil fuels, essentially coal *via* conventional syngas chemistry.[90–95] In order to improve hydrogen utilization, since 1970s the production of methanol has been performed by using CO_2 instead of CO.

Nowadays, due to fossil fuel depletion, methanol is also produced by renewable feedstock,[15] including CO_2 (Eqn. (10a)): a plant of 5000 t/y has been built in Iceland in which natural CO_2 is converted into methanol using renewable H_2 generated with geothermal energy.[96] With respect to syngas, CO_2 requires an excess mol of H_2 but if the latter is obtained from water, the process is viable. Today the cost of such methanol is still higher than that produced from LNG reforming, but the lower cost of renewable energy may ultimately reduce the cost of production of renewable methanol. Noteworthy, methanol can be converted into DME, or a single reactor technology can be used that converts CO_2 and H_2 into DME, used in China as a diesel substitute (a few hundred thousand Mt/y capacity).

Recently, synthetic liquid hydrocarbon fuels have become increasingly targeted for CCU.[7]

Development of Catalytic Systems and Use of Solar Energy

In order to convert carbon dioxide into valuable products it is necessary to develop effective and cheap catalysts that can be applied on a large scale. They should also be stable under the reaction conditions, robust and eventually supported on solid matrix so that they can be easily recovered by simple filtration from the reaction mixture and reused.

Biological systems and processes can inspire new ideas as a lot of effort has been made to mimic such systems. Under mild conditions Nature has developed methods to capture CO_2 and to convert (reduce) it into high-energy molecules. However, the biological processes are multi-catalyst and multi-reaction steps that are not easy to reproduce *in vitro*.

Photocatalysis may be considered an interesting approach to convert carbon dioxide into valuable chemicals where sunlight can be used as source of energy.[97]

Energy from waste plants is a potential source of heat for chemical plants. Power at off-peak times is also another option to make profit. Synthetic fuels represent a way of storing energy when there is a peak of production that would otherwise not be used.

Photocatalysis and photoelectrocatalysis may represent in the long term an ideal solution to the conversion of large volumes of CO_2.

Fixation of CO_2 into Aquatic Biomass

Another aspect to tackle is the use of CO_2 for an industrial growth of biomass. Implementing the concept of biorefinery, aquatic biomass may represent a source of energy (fuels), chemicals and new materials. Very interesting is the possibility to grow aquatic biomass (microalgae) in air enriched with carbon dioxide (concentration of CO_2 in the gaseous phase up to 150 times higher than natural conditions) and this makes the production of biomass quite attractive for CO_2 enhanced fixation.

Biomass, in general, is considered a substitute of fossil fuels as a 'quasi-zero emission' option in the production of fuels for the transport sector. In fact, in the future it is expected that more than 20% of the global energy may derive from biomass[98] and this means that an additional amount of biomass should be specifically grown and used for energy purposes in addition to the quantity (terrestrial or residual biomass) used today. To this end aquatic biomass can be considered a good option as it has a very high photosynthetic efficiency, having, thus, a higher (6–8%) solar energy utilization efficiency with respect to terrestrial biomass (1.5–2.2%). To date, microalgae[99,100] have been intensely studied, and very recently the interest has been extended also to marine macro-algae.[101] What is worth to emphasize is that CO_2 derived from power plants or recovered from industrial flue gases could be pumped into a photobioreactor or into ponds under controlled conditions as a source of carbon.

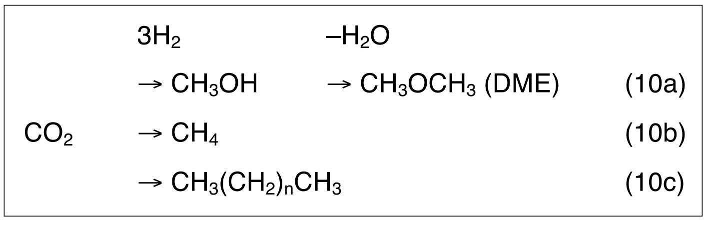
Several options can be used to grow micro-algae. Fig. 3 shows the most common cultivation techniques.[102,103]

Using bioreactors micro-algae can be cultivated under conditions more controlled than those used in ponds. In a photobioreactor a constant light-irradiation can be used (either through walls or *via* fibers or tubes) and the optimal temperature can be maintained, with carbon dioxide bubbled through the culture medium at a constant rate, implementing an enhanced fixation of carbon. For a good gas exchange and in order to assure the best exposition to light it is necessary to have dynamic systems where a continuous mixing of the algal culture occurs. For large-scale production the most common methodology is the use of raceway ponds.

The direct use of carbon dioxide derived from power plants or industrial flue gases may have some limitations due to the high content of NO_x and SO_x. Some algal species[104] are able to grow in the presence of such contaminants. In the literature it has been reported that some algae are resistant to 150 ppm of NO_2 and 200 ppm of SO_2.[104]

Almost a double amount in mass of CO_2 is necessary to grow algal biomass (1.8–2 g of CO_2 per 1 g of algal biomass). Therefore, to grow algae in a *ca.* 6000 m^2 pond (single algal pond), that produces a total amount of 300 kg algal biomass per day, almost 600 kg CO_2 per day are used, which means only 0.006% of CO_2 produced by a 500 MW power station.[105,106]

The cultivation techniques have a key importance: semi-closed photobioreactors (Fig. 3a,b) allow the cultivation of algal species that are difficult to grow in open



$$\begin{array}{lll} & CO_2 \xrightarrow{3H_2} CH_3OH \xrightarrow{-H_2O} CH_3OCH_3\ (DME) & (10a) \\ & CO_2 \rightarrow CH_4 & (10b) \\ & CO_2 \rightarrow CH_3(CH_2)_nCH_3 & (10c) \end{array}$$

Scheme 6. Production of high-energy chemicals from CO_2.

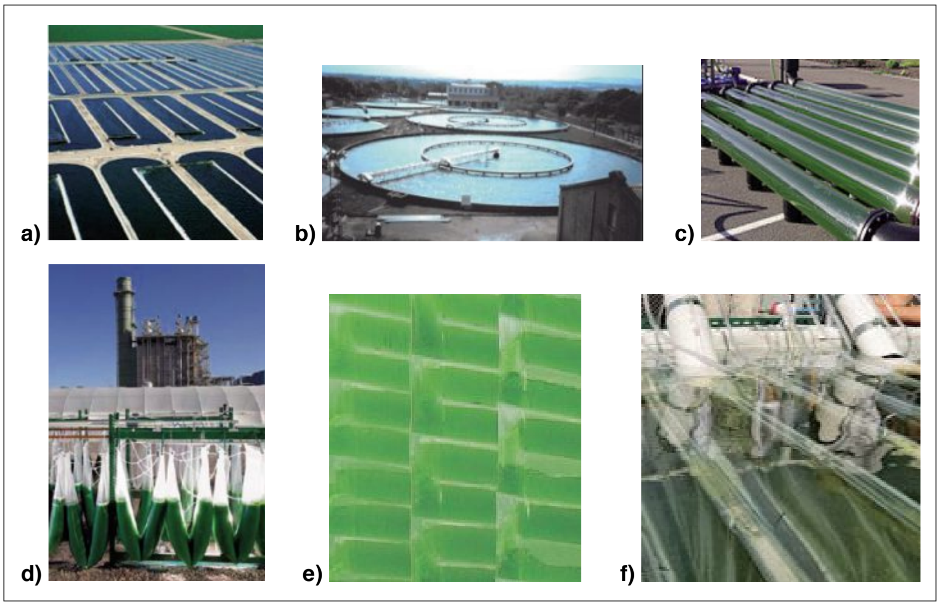


Fig. 3. a) Raceway pond; b) circular pond; c) horizontal glass tube; d-f) plastic bags.

ponds with a high productivity as they enable the cultivation conditions to be kept under control.[107] On the other hand, photobioreactors require high investment costs (>USD 100/m^2) up to 10 times that of open systems. Also scale-up is not straightforward, as it requires engineering solutions that may assure the gas/liquid mass transfer, to prevent the wall-growth of cells, and guarantee energy efficient mixing and cooling.

In order to reduce the investment costs, alternative methodologies have been developed such as vertical flat-panel reactors (Fig. 3e) made from thin polyethylene film. The development of such systems is expected to expand especially with improvement in material lifetime (and thus cost reduction) and energy requirement for cooling and mixing.[108,109]

As already stated, macro-algae (seaweeds) have recently been investigated since they present different properties with respect to microalgae, either for productivity (1–20 kg m^{-2} y^{-1} dry weight (10–150 t_{dw} ha^{-1} y^{-1}) for a 7–8 month culture) or for nutrient requirements. Concerning the latter aspect, as algae are able to uptake nutrients (N, P) from sewage and industrial waste water (estimated at 16 kg ha^{-1} d^{-1})[110] they find utilization either in Europe or in Japan for cleaning municipal wastewater,[111,112] reducing the content of N and P in fishery effluents[112,113] and recycling nutrients. Macro-algae, such as *Ulva lactuca* or *Enteromorpha intestinalis,* adapted to non-natural basins, grown on nets or lines, or seeded onto thin light-weight lines suspended over a larger horizontal rope[114] have been tested in the north-western Mediterranean Sea, along the French coast.[115]

It is possible to extract several chemicals present at different concentrations from aquatic biomass, depending on the site where they grow.[116] Different kinds of non-destructive technologies can be used to extract chemicals[117,118] that allow the recovery of all components with the original molecular structures without change.

In general micro- and macro-algae can be used for the production of: i) energy-products, such as hydrocarbons, hydrogen, methane, methanol, ethanol, others; ii) food and chemicals, such as proteins, oils and fats, sterols, carbohydrates, sugars, alcohols; iii) other chemicals, such as dyes, perfumes, vitamins/supplements, enzymes, *etc.*

Microalgae are rich in essential vitamins[119] and rich in omega-3 fatty acids. Very interestingly, some species can be engineered to produce a specific product. For examples *Botryococcus braunii* has been modify genetically to produce the terpenoid C30 botryococcene, a hydrocarbon with a structure very similar to squalene.[120,121]

If the biomass is rich in lipids (30–70% dry weight) it will be useful to produce chemicals, biooil and biodiesel; if the biomass is rich in sugars, it will be more suited to produce bioethanol. Biogas will be also produced from anaerobic fermentation of biomass (sugars, proteins, organic acids).

In contrast to microalgae, macro-algae, in general, are poor in lipids and present a larger variability[122] that depends on the cultivation conditions (technique, period of the year they are collected, temperature and light).[123,124]

The condition for extensive use of such an approach is the use of process water that may contain nutrients for the growth of the biomass: the addition of nutrients (micro and macro) out-balances both the economics and carbon balance, making this technology less useful for CO_2 reduction.

Conclusions

Carbon Capture and Utilization (CCU) may find several options for its exploitation such as a useful process to convert carbon dioxide into chemicals and fuels. Any process we consider must be a net CO_2 consumer, also reducing the overall emission with respect to processes on stream. It also needs to be economically viable for the industry that has to apply the technology. Post combustion capture is today the most common technology for CO_2 recovery from industrial or power station flue gases. Such CO_2 has variable purity and can be used in different applications, by trying to match purity with process requirements, so as to avoid costly separation technologies. It may also be possible to use the available CO_2 to produce a variety of chemical products with high added value. The production of fuels from carbon dioxide is a way to increase public opinion positively. In fact, if one perceives that the use and conversion of a waste into chemicals represents a benefit, the new technology is more likely to be accepted. And the visibility of fuels is, maybe, higher than that of chemicals, at least due to the different volume.

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