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Product review

The contribution of the utilization option to reducing the CO_2 atmospheric loading: research needed to overcome existing barriers for a full exploitation of the potential of the CO_2 use

Abstract

The use of CO_2 (biological/chemical/technological) is the only technology that may contribute to reducing the atmospheric loading while generating a profit. In this paper some options that may find an early industrial application are considered, and barriers that need to be overcome for their full implementation are analyzed. Options that may produce a reduction of the immission into the atmosphere of the order of 1 Mt/y of CO_2 are considered. The estimate of the atmospheric reduced loading, in case the various options are implemented, ranges at 300 Mt/y in the short-medium term, with an upper limit of 700 Mt/y in the long term.

Keywords: CO_2 atmospheric loading; Re-use of CO_2; Carboxylation reactions; Selective processes; Supercritical carbon dioxide

1. Introduction

The reduction of CO_2 atmospheric loading has been agreed at the international level for preventing a reinforcement of the greenhouse effect that may increase the earth average temperature to such a value that may cause catastrophic events. In a 'business as usual' frame, it has been estimated that during the 21st century an amount of CO_2 ranging from 3480 to 8050 Gt will be emitted [1], compared to 1100 Gt CO_2 emitted since 1850 until 2000. The corresponding yearly CO_2 emission by 2100, according to the above scenarios, ranges from 73 to 128 Gt/y, while the 1990 baseline is 20.2 Gt/y. [3] To keep at 550 ppm the threshold limit [2] for 2100, is becoming quite impossible. A debate is ongoing on how to move towards the 1990 baseline. Two approaches, namely: (i) reducing the production of CO_2, or (ii) implementing innovative technologies for the capture of produced CO_2, are under discussion. The confrontation is on which is the best strategy for meeting the urgent need of reducing the C-immission into the atmosphere without a deployment of the economic growth. On a shorter time-scale, the forecast is that, following a BAU scenario, 6000 TWh of electric energy will have to be made available in the next 30 years or so. Considering the actual energy sources (75% from fossil carbon) and the fact that they will not experience a sensible change over the period considered above (as the use of nuclear power and renewables for the production of electric energy will not expand that great during the next two or three decades) the need to implement a reduction of the immission into the atmosphere of CO_2 raises serious worries if it should occur only through the reduced use of fossil carbon (coal, oil, LNG). This might have negative consequences on the economy and development. As a matter of fact, the reduction of the emission of CO_2 can be conjugated with an increased production of energy from fossil fuels only if the efficiency of the conversion of chemical into electrical or mechanical energy is increased and if the produced excess CO_2 is captured. The efficiency of production of electricity from fossil carbon currently averages 30%, a very low value. Consequently, more than the double of the electric energy produced is wasted as heat, and transferred to the atmosphere with a large impact on the atmospheric energy structure. Technologies are ready that may improve the efficiency of production of electric energy to 42 or 52% (Pulverized coal or combined cycle gas turbine), with higher investment and management costs than actual. As a matter of fact, both improving the efficiency of existing plants and building new efficient power plants require huge investments and capital costs [4]. Also, increasing the efficiency of the existing plants, will not cover the energy demand for next

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thirty years, that means that will not meet the need of reduction of CO_2 emission to the required limits. This brings to the conclusion that efficiency alone is not the technology that may give an answer to the need of reducing the emission of carbon dioxide: it should be coupled with a technology that may prevent that the produced CO_2 enters the atmosphere. Such technology is the capture of CO_2, that appears a winning strategy that may cope the need of reducing the CO_2 atmospheric loading with the expectation of a growing development that requires an increased use of fossil fuels over coming decades.

CO_2 separation technologies are already marketed, available for large-scale application and, thus, ready to be implemented. The question arises: what to do with captured CO_2? Two options are on the market with further possible development: the utilization or the storage in confined environments. The latter include 'storage in oceans or geological cavities, such as spent LNG or oil wells'. The geological storage is already practiced and may find a larger exploitation. The ocean disposal is far away from implementation. Either option has a large potential, with the ocean storage being the one with the largest capacity. Both options require energy for transporting (or pumping) to the storage site and housing CO_2. Depending on the separation technique, the distance, and depths the amount of energy varies and may reach the value of 263 MJ/t of housed CO_2 [5]. By burning fossil carbon for the production of electric energy, CO_2 is generated at an approximate rate between 1 and 0.5 t/MWh depending on if coal or LNG is used (with oil sitting in an intermediate position), this means that per each ton of CO_2 stored, ca. 0.3 t of CO_2 are generated. A study has set at 21.8% the loss of power of a 549 MW station with CO_2 underground storage [6]. In conclusion, the effect of storage is that the extraction of fossil fuel will increase by 20–35%, with an effect on the future availability of fossil fuels and continuous growth of the emission. An emerging technology is the fixation of CO_2 in basic oxides-rich natural silicates, which also demands energy for mining, milling, processing the mineral, and housing the formed carbonate. The energy required is not easily quantifiable as such process is still at a very preliminary stage of development. Use of carbon dioxide, instead, represents a net reduction of both the use of carbon resources and CO_2 atmospheric loading, with a benefit in terms of less extracted carbon and carbon dioxide immitted into the atmosphere. In this paper, the possible uses of CO_2 as source of carbon for chemicals will be described, the relevant potential for reducing the atmospheric loading will be defined, and the existing barriers to a full implementation of the utilization technologies will be identified.

2. Discussion

Use of CO_2 can be classified as either biological, chemical or technological [7,8]. In all cases, it brings about the reduction of the atmospheric loading, which can be correctly estimated by application of the life cycle assessment-LCA methodology for comparing the use with the non-use scenario. At a glance, the overall benefit associated with the use of CO_2 can be perceived considering that should it be used either as a source of carbon for the synthesis of chemicals or as an anti-fire agent, it substitutes compounds that, in general, will require the extraction and use of reduced carbon (coal, oil, LNG) and other natural resources for their synthesis. The production processes for such chemicals usually have low yield and selectivity, with generation of waste which amount depends on the molecular complexity of the product. This is true whether such species do or do not contain carbon. Consequently, one can say that in the less positive case the use of CO_2 will save an equivalent amount of carbon. As a matter of fact, the reduction of the atmospheric loading is higher than the quantity of used CO_2 and in some cases can be five to ten times as much, if CO_2 substitutes chemicals with a high-molecular complexity. Also, the use of CO_2 may improve the safety and health conditions if toxic chemicals are avoided, with a multiplying effect in respect of greening the chemical industry. Additionally, several chemicals can be obtained via biomass conversion as discussed below, with the implementation of a quasi-zero-emission technology.

3. Enhanced CO_2 fixation into biomass for the production of chemicals

The enhanced fixation of carbon dioxide into either terrestrial or marine biomass has a different exploitation potential. In fact, the former application is limited to cultures in greenhouses that include cut flowers and some vegetables. The potential market is limited, being 0.2 kg/person and year in northern Europe [7,8], and close to zero for southern Europe, and Asian and African countries. Conversely, the fixation in aquatic biomass has a much larger use as both micro- and macro-algae can be used as either food or source of chemicals. Micro-algae have been extensively investigated [9] as source of fuels. They can be grown in ponds or in a bio-reactor and the production cost varies accordingly, ranging from a few hundred to 5000 US\$ per t_{dw} micro-algae, depending on the production scale and technology and the algal species. Bio-diesel can be extracted from both micro- and macro-algae, which cost ranges around US\$ 100 per barrel, too high for an earlier exploitation. The scale optimisation and the use of nutrient-rich waste water may reduce the cost to an affordable value for commercialisation.

A general set of reference data is categorized below:

One kilogram of bio-fuel is obtained from 5/10 kg of dry matter, corresponding to the fixation of 1/1.3 mass ratio of CO_2 with respect to the algae.

Macro-algae have had a less consideration so far as source of fuels, but the pond production of some species is well established as they are used as food for humans and animals [10]. They can be converted into various fuels, by using several technologies, depending on whether wet or dry masses are treated. Wet macro-algae can conveniently be converted into biogas by anaerobic fermentation or into Syngas by gasification or supercritical water treatment, or can be pyrolysed in presence of metal catalysts to afford a mixture of chemicals [11]. Dry macroalgae can be either extracted using supercritical CO_2 or organic solvents to produce bio-fuels and other chemicals [11], or used in a direct combustion. The latter is the less valuable technology, being the biomass characterised by a low heat value [12]. The cost of production of some species of macro-algae is well established [13], and research is ongoing in order to select species that can be grown at various latitudes and longitudes with low investment and management costs and produce fair amounts of fuels. Macro-algae, nevertheless, are used as source of a number of other chemicals as reported in Table 1.

The potential fixation of CO_2 in macro- and micro-algae, should their production cost become affordable, may scale up from actual ~2 Mt/y [14] as food to Tens Mt/y for use as fuels. However, the fixation of carbon dioxide in biomass may reach the 10–50 Mt/y scale within a short term.

4. Utilisation as a source of carbon in the synthesis of chemicals

Carbon dioxide can be used as a source of carbon, as a co-reagent or as a solvent in a variety of synthetic processes. In the last years, thousands of patents appeared that emphasize the potential of such application together with many reviews [15–18]. The International Conference on CO_2 Utilization has been hold biannually, since 1993. In a frame of reduction of the CO_2 atmospheric loading, there are a few constraints to the use of CO_2, mainly from the point of view of the reaction energy. Obviously, if CO_2 replaces other carbon sources, its use cannot produce more CO_2 than is stored. Therefore, the reaction based on carbon dioxide must have a reaction energy lower than that of the substituted reaction, better yield, and selectivity. The latter can be achieved by using a more direct synthetic pathway with respect to existing methodologies: for example, substituting the hydrolysis of cyanides or the oxidation of aliphatic or aromatic groups with the direct catalytic incorporation of the –COO group into an organic substrate. Actually, the waste factor (defined as the ratio of the amount of waste produced to the amount of product) ranges for bulk chemicals from two to five, for fine chemicals from 5 to 10 and for pharmaceuticals from 25 to 100. It is obvious that there is a relation between the molecular complexity and, thus, the number of reaction steps necessary for the synthesis of a compound, and the waste produced. Consequently, the synthesis of carboxylates *via* the introduction of the –COO moiety into a molecule responds to the waste reduction because: (i) carbon is recycled, (ii) reduced carbon is not used for producing oxidized carbon, (iii) a single step is used instead of many. In this case, the CO_2 atmospheric loading is reduced by an amount that may easily be two to ten times higher than the amount of used CO_2. A further advantage occurs if supercritical CO_2 is used as solvent, substituting organic solvents. A net reduction of the atmospheric loading equal to 3.3 times the amount of the substituted solvent is achieved, considered that waste solvents are mostly combusted with production of CO_2. The reactions that, if exploited, will produce a net reduction of the CO_2 atmospheric loading can be categorized as:

- Direct carboxylation reactions (generation of the moieties C–COOH, C–COOR, N–COOR, N–CO–N, –NCO).
- Use of CO_2 as oxidant in selective processes.
- Use of CO_2 as additive to CO for the synthesis of methanol.
- Direct on site LNG to liquid (GTL) conversion.
- Use of supercritical CO_2 as solvent, or as solvent and reagent.

Such cases will briefly be discussed, emphasizing the need for new catalysts and processes so that their potential can be fully exploited.

Table 1
Classes of compounds obtained from macro-algae and their uses

Class of products	Chemicals	Extraction technology	Commercial use
Proteins		Folin reagent	Pharmacology
Amino acids		Phenol–acetic acid–water	Food industry
Lipids		$ScCO_2$, organic solvent, liquefaction, pyrolysis	Biofuels, food industry, pharmaceutical industry
Essential oils	Geraniol, geranyl formate or acetate, cytronellol, nonanol, eucalyptol	Distillation	
Alcaloids		Solvent extraction	
Sterols	Cholesterol	Smith method	
Pigments: chlorophylls, carotenoids, xantophylls, phycobiliproteins	Isoprenoids	Solvent extraction	
Amines	Methylamine, dimethylamine, trimethylamine, ethylamine, propylamine, isobutylamine		Pharmaceutical industry
Inorganic compounds	Iodides, bromides, sulphates, nitrates, etc		Pharmaceutical industry

4.1. Direct carboxylation reactions (generation of the moieties C–COOH, C–COOR, N–COOR, ROCOOR, N–CO–N, –NCO)

The direct carboxylation of organic substrates is, in general, an exothermic reaction (Eq. (1)).

$$CH_4(g) + CO_2(g) \rightarrow CH_3COOH(l),\ \Delta H = -16.6\,kJ\,mol^{-1} \quad (1a)$$

$$C_6H_6(l) + CO_2(g) \rightarrow C_6H_5COOH(s),\ \Delta H = -40.7\,kJ\,mol^{-1} \quad (1b)$$

$$C_6H_5OH(s) + CO_2(g) \rightarrow (o-OH){-}C_6H_4COOH(s),\ \Delta H = -31.4\,kJ\,mol^{-1} \quad (1c)$$

$$CH_2{=}CH_2(g) + CO_2(g) \rightarrow CH_2{=}CHCOOH(l),\ \Delta H = -42.8\,kJ\,mol^{-1} \quad (1d)$$

This is also true if ammonia and amines are considered (Eq. (2)).

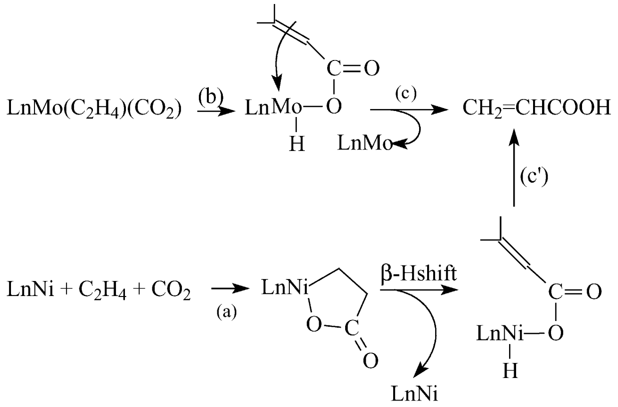
$$NH_3 + CO_2 \rightarrow H_2NCOOH \quad (2a)$$

$$RNH_2 + CO_2 \rightarrow RHNCOOH \quad (2b)$$

Reactions (1) and (2) release energy when occurring. Nevertheless, only reaction (1c) is industrially exploited, others are in a quite early stage of investigation.

Reaction (1a) has been seen to occur either in a cold plasma [19–21] or catalysed by transition metal systems [22]. The addition of starch to a CH_4/CO_2 mixture seems to improve the selectivity towards oxygenates under plasma conversion [23], but the yield needs to be improved for practical applications. The barrier to a full exploitation is the controlled activation of the C–H bond [20]. Reaction (1b) is not known, while reaction (1c) is industrially exploited since 1890 as the Kolbe–Schmitt reaction for the synthesis of salicylic acid [24], and known to afford also the para isomer *p*-OH–C_6H_4COOH. There is an actual interest to find a most effective route to such products, avoiding the use of one mole of sodium or potassium salt per mole of product, as it occurs right now [25]. Reaction (1d) has been attempted and is shown to occur following different paths according to the catalyst used. Nickel promotes the formation of a metalla-carboxylate (Scheme 1a), while Mo affords a hydrido acrylate (Scheme 1b).

The formation of a M–O bond prevents in both cases to have a turn-over-number (TON) for the C–C coupling higher than 1 [26]. The formation of acrylic acid (via elimination from the metallacycle (c′) or the acrylate (c) as depicted in Scheme 1) would be of great interest, as it would represent a clean and easy way to the synthesis of acrylic acid and the relevant polymers. Also, the coupling of ethene (or propene) with CO_2 might produce polyesters. Governing the insertion of the olefin and the cumulene may produce polymers with different oxygen content. Both polyacrylates and polyesters have a market higher than 1 Mt/y, so that the exploitation of such reactions would represent the storage of large amounts of CO_2, reducing the CO_2 atmospheric loading by an amount close to 10 Mt/y considering the market of the products and the effects of implementing a clean technology.



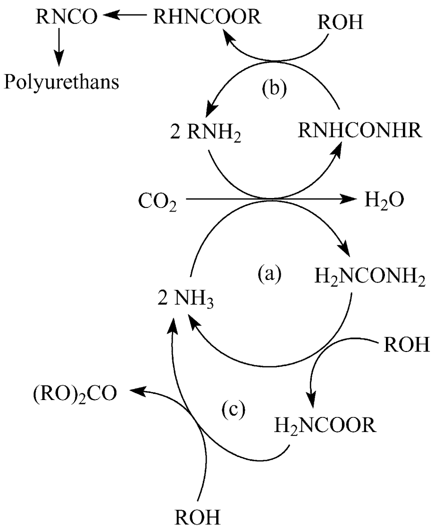
Scheme 1. (a–c) Transition metal catalysis in the synthesis of acrylic acid from CO_2 and ethylene.

Reactions (2a) and (2b) have been shown to occur [27], but have no application as the acids are quite instable and release CO_2 upon shift of the equilibria to the left. Conversely, the organic esters of such acids (H_2NCOOR, urethanes or $RHNCOOR'$, carbamates) have a large market (several Mt/y) and the use of CO_2 for their synthesis would avoid the utilization of phosgene, a toxic species [28]. The synthesis of urethanes is conveniently performed starting from urea that is produced by thermal treatment of ammonia with CO_2 (Scheme 2a).

Such reaction has a great potential as it represents the route to use urea as a bulk chemical instead of only as a soil additive, enlarging, thus, its market beyond the actual 90 Mt/y. The synthesis of urea represents, indeed, the largest single use of carbon dioxide as source of carbon for chemicals. If primary amines were used instead of ammonia, the resulting carbamates would convert easily into isocyanates that are used as co-monomer for the synthesis of polyurethans (Scheme 2b). Urethans could also be converted into carbonates by a further alcoholysis reaction (Scheme 2c), making urea a phosgene substitute and a very useful starting material for chemicals that have a strongly expanding market [29]. A TEXACO study has evaluated that, if dimethylcarbonate were used as gasoline additive, it would have a market higher than 30 Mt/y, which cannot be reached with existing synthetic technologies. This makes the synthesis of carbonates from routes alternative to phosgene a priority theme in innovative research. The direct carboxylation of alcohols (Eq. (3)) is under investigation to this end.

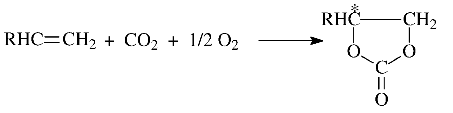
$$2ROH + CO_2 \rightarrow (RO)_2CO + H_2O \quad (3)$$

In order to fully exploit such reaction, it is necessary to discover new active catalysts and an efficient way of trapping the water formed in the reaction. Metallorganic $R_2Sn(OR)_2$ species are active as catalysts, but have a short



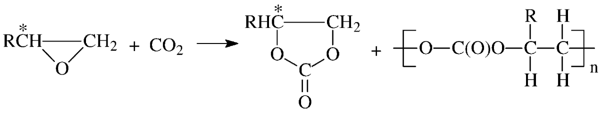
Scheme 2. (a–c) Urea as substitute of phosgene and starting material for chemicals.

life-time as they are converted into R_2SnO [30,31], an inactive species. Both Zr- and Ti-supported catalysts [32,33] show an interesting activity, but the low equilibrium concentration of the carbonate (1.2%) does not make them ready for practical application. Nb-alkoxides have been shown to maintain a quite constant catalytic activity over several runs [34] with still a thermodynamic limitation. The elimination of water, either using chemical traps [35] or designing new processes, and the development of new active and water resistant catalysts are the key issues to address in order to foster this technology that may have a prominent role in the future in the synthesis of carbonates. It is worth to mention that linear carbonates can be converted into other carbonates through the *trans*-esterification reaction that uses transition metal oxides as catalysts [36]. An interesting route to cyclic carbonates is the oxidative carboxylation (Eq. (4)) that converts olefins, dioxygen, and CO_2 into valuable products [37].



(4)

New more selective catalysts must be found, that may also selectively convert prochiral olefins into optically active carbonates [38]. This direct route could substitute the reaction of epoxides with CO_2 (Eq. (5)) that may be more conveniently used for the production of polymers [39,40].



(5)

Although Zn-catalysts are quite active, new catalysts need to be developed in order to produce polymers with high molecular mass, and low molecular mass dispersion, using various olefins that may contribute different properties to the polymers.

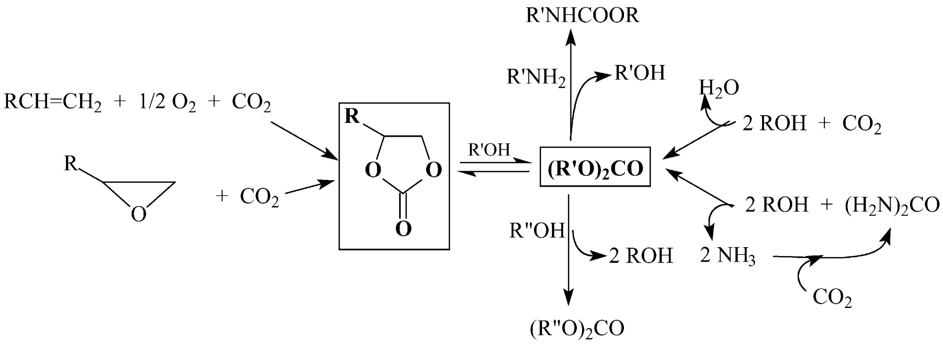
All the carbonation and carbamation reactions are networked as shown in Scheme 3.

However, whatever synthetic technology is found to be convenient for the synthesis of either product it can be used for the synthesis of the other. The potential atmospheric loading reduction in the short term linked to the full implementation of the reactions discussed above, should all existing barriers be overcome, is estimated at around 120 Mt/y, 100 of which as CO_2 fixed in products and 20 as reduced emissions due to technology innovation.

4.2. *Use of CO_2 as oxidant in selective processes*

A very promising field of use of carbon dioxide is as mild and selective oxidant. CO_2 has been shown to produce much more selective processes [41] when used instead of dioxygen in 'dehydrogenation reactions' such as that represented in Eq. (6).

$$C_6H_5CH_2CH_3 + CO_2 \rightarrow C_6H_5CH{=}CH_2 + CO + H_2O \qquad (6)$$



Scheme 3. Network of carbonation and carbamation reactions based on CO_2.

This utilization has a great relevance to the issue of alkanes valorisation with reduction of waste production. The reaction can be applied to many different low-value hydrocarbons that can be transformed into more valuable products. Metals supported over alumina are used as catalysts. Having this reaction been investigated only very recently, there is room for new research for developing new catalysts, more active and selective that may promote the reaction under milder conditions with respect to those in use. Although there is not direct fixation of carbon dioxide, the CO_2 atmospheric loading reduction potential is assessed in terms of less energy used (lower temperature of operation) and lower waste production (higher selectivity) with respect to the thermal processes used nowadays (1100 K, 30–50% selectivity).

It can be calculated that per each ton of converted product, two to three ton of CO_2 are not discharged into the atmosphere, also considering that the used CO_2 is converted into CO that can be recovered and re-used either as a chemical or as an energy product.

A particular case of use of CO_2 as oxidant is its photochemical conversion into CO, C_1 or C_n molecules. This technology is not exploit as catalysts are not enough efficient so that the of light conversion is around 0.1%, too low for any practical application [8].

4.3. Use of CO_2 as additive to CO for the synthesis of methanol

This practice is well understood today and CO_2 is already used as additive to CO in the molar ratio CO/CO_2 = 3:1. Under these conditions the utilisation of dihydrogen is optimised [42]. CO_2 can also be directly converted into methanol with dihydrogen with a higher selectivity than CO and working at lower temperatures [43]. Right now, the market of CO_2 used for such practice is around 5–10 Mt/y with a potential net increase in the short term.

4.4. Direct on site LNG to liquid (GTL) conversion

The direct conversion of LNG into Syngas first, and then into methanol or gasoline (GTL) would represent a great achievement in terms of carbon management. In fact, LNG contains methane and CO_2 in a rough 3:1 ratio: CO_2 is actually separated and vented. Attempts are made to dispose the separated CO_2 into spent LNG wells. LNG could be converted at the site of extraction into Syngas according to reactions (7), and the latter used for the synthesis of liquid fuels such as methanol or gasoline that are much easier to transport.

$$CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g) \tag{7a}$$

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \tag{7b}$$

$$CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CO(g) + 2H_2(g) \tag{7c}$$

The combined set of reactions (7a)–(7c) uses 1 mol of CO_2 per 3 mol of methane, producing 4 mol of CO, and 7 mol of H_2, with a H_2/CO ratio equal to 1.75 that is quite good for methanol or gasoline formation. This process is known as 'tri-reforming' [44]. As a matter of fact, it couples the dry- (Eq. (7a)) with wet-reforming (Eq. (7b)), and the partial oxidation of methane. (Eq. (7c)) The first two processes are strongly endothermic ($\Delta H^{\circ}_{298\,K} = 247$ and 206 kJ mol^{-1}, respectively), while reaction (7c) is exothermic ($\Delta H^{\circ}_{298\,K} = -35.5$ kJ mol^{-1}) and partially compensates the energy demand of the other two processes. In this way, CO_2 must not be separated from methane, saving its capture costs that are estimated at US$ 13–25 per t CO_2, and disposal costs, which are spread over a wide range (up to US$ 200), depending on the technology and the location of the host geological cavity [45]. Based on the content of CO_2 in the natural gas, reactions (7a)–(7c) can be modulated one with respect to the other, so that H_2 is obtained in the correct ratio with respect to CO. Interestingly, a low temperature plasma technology is under experiment for the direct conversion of LNG into valuable products on site [46]. Should this technology be implemented, the very large amounts of CO_2 extracted as LNG could be re-used with a great economic benefit.

4.5. Use of supercritical CO_2 as solvent and reagent

Carbon dioxide can be used in a number of applications that use the physical properties of the gas, more than its reactivity. The total amount of CO_2 used in this way is at the moment 15 Mt/y plus 45 Mt/y specifically used in enhanced oil recovery (EOR). The latter application has used so far CO_2 extracted from natural wells but could utilise captured CO_2 from flue gases. Enhanced oil recovery can allow to store in spent oil wells large volumes of CO_2. In EOR, supercritical carbon dioxide (scCO_2) is used that also finds application as a solvent in several chemical reactions, as shown in Table 2.

Supercritical carbon dioxide physical properties can be tuned with pressure and temperature, remaining close to those of a non-polar organic solvent like hexane or dichloromethane. Either homogeneous- or heterogeneous-metal catalysts can be used in scCO_2. The former are most effective, their solubility being improved by using particular ligands that usually bear either long aliphatic chains or perfluorinated moieties.

A particular use of scCO_2 is as solvent and reagent that may bring a net innovation in the chemical industry. Examples of such reactions are:

- The synthesis of formic acid from CO_2 and H_2 [47].
- The synthesis of DMC from ortho-formates [48] or acetals [49].
- The synthesis of ethylene carbonate from a ketal [50].
- The synthesis of organic carbonates from alcohols [51,52].

The use of scCO_2 in continuous processes is improved by using biphasic systems in which the catalyst is dissolved in a phase (like ionic liquids) immiscible with scCO_2 that extracts the product. This approach may bring to a substantial innovation in chemical processes with elimination of organic solvents substituted with scCO_2. Noteworthy, in this

Table 2
Uses of $scCO_2$

Applied chemistry	
	Dendritic micelles
	Dyeing processes
	Impregnation and extraction of residual impurities by swelling of the polymer matrix
	Micro-encapsulation
	Drug-formulation
	Waste stream detoxificaion – removal of plutonium and uranium waste in the nuclear industry
Analytical chemistry	
	Use as separation fluid in pressure-chromatography
Catalysis	
	Cationic polymerizations
	Free radical polymerizations
	Heterogeneous catalysis
	Homogeneous catalysis
	Metal complex promoted polymerization reactions
	Modification of polymers
	Oligomer processing
	Reactive modifier, complexing agents
	Step-growth polymerizations

case the amount of ionic liquid necessary is quite small, as it serves for dissolving the catalyst that is not lost with the gas stream. Good results have been obtained with this technique in hydroformylation reactions that have been shown to proceed with a higher selectivity [53] in sc-CO_2 than in organic solvents, using the appropriate catalyst. The potential of the use of $scCO_2$ as solvent and reagent has not yet been completely explored. The reduction of the atmospheric loading is much higher than the amount of CO_2 fixed in a compound, as one must consider the amount of CO_2 not released because of solvent shift: the latter may be much larger than the former considered that per each ton of organic solvent not used, at least 3.3 t of CO_2 are not released. The reduced atmospheric loading can be quantified in ca. 30–50 Mt/y, according to the intensity of the solvent substitution.

5. Conclusions

Carbon dioxide use as source of carbon for the synthesis of chemicals or as selective oxidant or else as a solvent for chemical reactions, may greatly expand from actual 115 Mt/y to ca 300 Mt/y in the short term, and to higher levels in the following decades if all possible approaches to its use are implemented. Both new catalysts and new processes need to be developed for a full exploitation of the potential of CO_2 use. As a result of the development of a CO_2 based chemistry, a reduction of the use of toxic products in the chemical industry can be foreseen, with an improvement of health and safety conditions. A further benefit will derive from the use of sc-CO_2 instead of organic solvents that avoids the production of waste organics with a net reduction of the released amount of CO_2 to the atmosphere. Should new photochemical catalysts be developed that allow the reduction of CO_2 to occur with the appropriate reaction rate under solar irradiation in water as source of hydrogen, the amount of use CO_2 may grow to unexpected levels (an upper limit of 700 Mt/y has been estimated [54]), as fuels will be obtained in this way. New catalysts are needed and new processes must be developed that are more efficient and selective than existing ones.

An alternative, indirect way to use CO_2 for the synthesis of chemicals, is its enhanced fixation into biomass (essentially marine biomass), and the conversion of the latter into Syngas or its use for a direct extraction of chemicals. Fuels, bulk- and fine-chemicals can be advantageously produced in this way with a large reduction of the CO_2 emission.

However, the chemical and biological utilization of carbon dioxide can contribute in the short-term to reduce the industrial carbon dioxide emission and immission into the atmosphere both in a direct (CO_2 conversion) and indirect way (waste reduction) with a further benefit coming from toxic chemicals substitution. The utilization option may contribute to reduce the CO2 immission into the atmosphre by 5–7% of the total, without expansion of the fossil fuel extraction and generating a profit.

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