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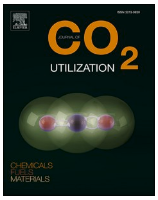

Review article

Merging the Green-H_2 production with Carbon Recycling for stepping towards the Carbon Cyclic Economy

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ABSTRACT

Hydrogen Economy and Cyclic Economy are advocated, together with the use of perennial (solar, wind, hydro, geo-power, SWHG) and renewable (biomass) energy sources, for defossilizing anthropic activities and mitigating climate change. Each option has intrinsic limits that prevent a stand-alone success in reaching the target. Humans have recycled goods (metals, water, paper, and now plastics) to a different extent since very long time. Recycling carbon (which is already performed at the industrial level in the form of CO_2 utilization and with recycling paper and plastics) is a key point for the future. The conversion of CO_2 into chemicals and materials is carried out since the late 1800s (Solvay process) and is today performed at scale of 230 Mt/y. It is time to implement on a scale of several Gt/y the conversion of CO_2 into energy products, possibly mimicking Nature which does not use hydrogen.

In the short term, a few conditions must be met to make operative on a large scale the production of fuels from recycled-C, namely the availability of low-cost: i. abundant, pure concentrated streams of CO_2, ii. non-fossil primary energy sources, and iii. non-fossil-hydrogen. The large-scale production of hydrogen by Methane Steam Reforming with CO_2 capture (Blue-H_2) seems to be a realistic and sustainable solution. Green-H_2 could in principle be produced on a large scale through the electrolysis of water powered by perennial primary sources, but hurdles such as the availability of materials for the construction of long-living, robust electrochemical cells (membranes, electrodes) must be abated for a substantial scale-up with respect to existing capacity. The actual political situation makes difficult to rely on external supplies.

Supposed that cheap hydrogen will be available, its direct use in energy production can be confronted with the indirect use that implies the hydrogenation of CO_2 into fuels (E-fuels), an almost ready technology. The two strategies have both pros and cons and can be integrated. E-Fuels can also represent an option for storing the energy of intermittent sources.

In the medium-long term, the direct co-processing of CO_2 and water *via* co-electrolysis may avoid the production/transport/ use of hydrogen.

In the long term, coprocessing of CO_2 and H_2O to fuels *via* photochemical or photoelectrochemical processes can become a strategic technology.

1. Introduction

1.1. Transition from the Linear to the Cyclic Economy

Transitioning away from fossil carbon (coal, oil and natural gas), stated with some defections at COP21, has found the unanimous agreement of 197 Countries plus the European Union at recent COP28 [1]. The deadline for reaching the Net-Zero-Emission (NZE) is set at 2050, nevertheless, due to the complexity of the subject, it is urgent to identify operative solutions that may implement the transition. For over 200 years our society has based its growth on the Linear Economy, assuming that natural C-based resources were infinite and their use was safe. As for today, 82 % of the energy consumed by humans is derived from fossil-C: which is also used as feed for the Chemical Industry. (*vide infra*) Despite the call to reduce the use of fossil-C was launched some two decades ago and alternative energy sources (solar, wind, hydro, geo-thermal, biomass) have seen a growing deployment since the beginning of this century, the use of coal has touched the new maximum of 8.93 Gt_C used in 2022 due to the demand of energy of developing

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Nomenclature

AWE	Alkaline Water Electrolysis.
CCE	Carbon Cyclic Economy.
CCS	Carbon Capture and Storage.
CCU	Carbon Capture and Utilization.
CE	Circular Economy.
CI	Chemical Industry.
COP	Conference Of the Parties, United Nations.
CR	Carbon Recycling.
DAC	Direct Air Capture (of CO_2).
HTWE	High-Temperature Water Electrolysis.
MSR	Methane Steam Reforming (high-temperature treatment with water).
Nimby	Not In My Backyard.
NZE	Net Zero Emission (of CO_2).
PEM	Proton-Exchange Membrane.
RFNBO	Renewable Fuels of Non-Bio Origin.
RuBisCO	Ribulose Bisphosphate Carboxylation Oxidation.
RWGSR	Reverse Water Gas Shift Reaction.
SotA	State of the Art.
SWHG	Solar Wind Hydro Geoi.
TRL	Technology Readiness Level.

economies. Coupled with the increased use of oil and natural gas, CO_2 emission has touched a record level of 36.8 Gt [2]. Such a trend is worrying for several reasons: rises questions about the future availability of fossil resources, reinforces the impact on climate of the continued emission of CO_2, makes evident the existing difficulty to get away from fossil-C. Fig. 1 gives the estimated duration of fossil-C reserves [3] left for use at the actual rate of consumption.

Obviously, a more efficient use of fossil-C (today used with an average efficiency equal to 33–35 %) would prolong the availability of resources and reduce the environmental burden. Increasing the efficiency of industrial processes is actually under serious consideration by several manufacturing sectors and process innovation and integration contribute to reducing the emissions. New regulations and directives (national and international, see for example the cited COP actions) push in the direction of reducing emissions by increasing the efficiency in the use of fossil-C in particular and energy in general, and the selectivity of synthetic processes. Some results clearly show that the Industry is moving in the correct direction, nevertheless, the rate of change is producing lower than wished impacts. Economic constraints (higher production cost) also slow down innovation and demand for careful evaluation of public support for green innovative products.

On the biology side, efforts have been made for four decades now to improve the efficiency of Ribulose Bisphosphate Carboxylation Oxidation (RuBisCO), the most abundant enzyme in Nature that has a key role in photosynthesis. It has an average 55 % selectivity towards carboxylation and 45 % towards oxidation of the C_5 substrate that is converted into C_6 (glucose): increasing by >5 points the carboxylation activity would most likely allow to fix the excess anthropogenic CO_2 not buffered by the natural Carbon-Cycle which runs some 200 Gt_C per year. As for today, results are still very modest and far away from exploitation.

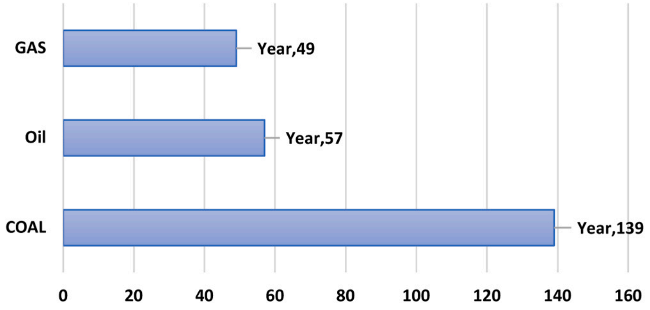


Fig. 1. Years of fossil reserves left worldwide at actual consumption.

Despite the continuous expansion of the use of fossil-C, the discovery of new natural reserves or the access to fields not reached before has made that during the last 50 years or so the reserves/consumption ratio has not collapsed. The fact that reserves of fossil-C may be more abundant than we estimate is not a sufficient guarantee for continuing the Linear Economy model. Since a couple of decades International Organizations (see the above-mentioned COP28 and the EU), policymakers and decision-makers claimed that the Linear Economy model based on fossil-C uncontrolled exploitation, cannot be continued and call not only for a more efficient and less intensive use of carbon but more urgently for a shift to a more conservative economic model. The Circular Economy-CE, in which natural resources are used with higher efficiency and have more than a single life is the model for the future of our Society. CE can assure a reduction of the emission of CO_2, avoiding the rising of the average planet temperature and worsening of climate change. *Carbon Recycling-CR* is at the heart of the CE and demands for a new concept organization of the production and use of energy and goods, deploying technological innovation coupled with system integration, inspired to natural *cooperative-systemic-cyclic* concepts. The ultimate goal is a *"Man-made C-cycle"* that may enhance the rate of CO_2 conversion into target compounds with respect to natural processes. Recovery and reuse of carbon is a new paradigm in CO_2-emission reduction made possible by the availability of non-fossil-energy sources [4] that must be framed in the CE by exploitation of Carbon Capture and Utilization-CCU as a strategic technology for the future. The Carbon Capture and Storage-CCS remains, thus, more suited for the Linear Economy and does not contribute to circularity. CCS should have been already operative on a large-scale since a decade or so, but its large-scale exploitation has been slowed down not only by our scarce knowledge of the storage sites but also by the Nimby attitude.

Noteworthy, our society cannot be decarbonized: humans live on carbon, the chemical industry needs carbon, even the energy sector needs carbon in some specific areas (avio-, maritime-transport) that will not be easy to convert to hydrogen or solar power as energy supplies.

1.2. Defossilization of the energy and chemicals sectors

The progressive shift-away from fossil-C (defossilization) as main source of energy and chemicals is, thus, dictated by environmental constraints, more urgently than from the strategic choice of saving natural resources for next generations. As for today, not only 82+ % of the consumed energy comes from fossil-C but also *ca.* 90 % of used goods are made *via* catalytic conversion of fossil carbon (mostly oil or methane). Such figures demonstrate how deeply our society relies on fossil-C and how complex is the change: we need to find at the same time new sources of energy and carbon for the chemical industry that should be used at the same intensity we use fossil-C. The amount of energy globally used by our society in 2021 was estimated at 13 865 Mt_{oileq} (*oileq= oil equivalent, counting as oil all sources of energy used*) [5] equivalent to 580 MTJ *(million terajoules)*. The electric energy consumption was in 2021 equal to 25 343 TWh, or 91.23 MTJ (15.7 % of the total energy). The fossil-C used by the Chemical Industry (CI) was *ca.* 300 Mt/y with an emission of 925 Mt_{CO2}. Interestingly, some 230 Mt of CO_2 are converted into useful chemicals in a variety of processes, with a record carbon recycling of 24.9 % [6]. Therefore, concurrently with the implementation of the defossilization strategy, it will be necessary to find alternative C-sources for the CI [7–9]. They are identified into: biomass (waste and expressly grown), used plastics and CO_2. The latter is the most abundant and easy-to-reach source of carbon, yet used by Nature for making all the available biomass.

The use of hydrogen as an energy vector has been proposed as an alternative to fossil-C for over four decades now [10]. Nevertheless, both the deployment of the application of hydrogen in new fields (energy vector) and the increase in the production of Green-H_2, obtained *via* electrolysis of water using non-fossil energy, have been only marginal so far.

2. Hydrogen Economy: hydrogen production and uses

Very recently, worldwide campaigns in favor of hydrogen as energy vector are generating a momentum about large-scale low-carbon (Green-H_2 or Blue-H_2) hydrogen production, [11] while a number of issues remain to be solved and uncertainties overcome certainties.

Hydrogen is produced today at a rate of *ca.* 90 Mt/y [12] (with some 8 Mt/y lost in flue gases), mostly *via* methane steam reforming-MSR (*ca.* 50 %), and only <2 % is obtained *via* electrolysis of water, using electric energy mostly produced from fossil-C. MSR causes the emission of CO_2 (5.5 t_{CO2}/t_{H2}). Therefore, to use such technology in a NZE frame, MSR must be coupled to CCS or CCU [13]. Hydrogen produced *via* MSR with CO_2-capture is labeled as Blue-H_2 and its cost would be dictated by the cost of the CO_2-capture technology. The latter depends on the purity of the source. As for today, the cost of production of Green-H_2 using photovoltaic electric energy (PV) or wind energy is some 3–4 times (depending on the location) higher than that of MSR-H_2 without carbon capture. Implementing the CO_2-capture and storage would rise the cost of H_2 by *ca.* 50 %, making Blue-H_2 economically more convenient than Green-H_2. But infrastructures for CO_2 storage on a scale of tens Mt/y are not available everywhere. Therefore, for either Green-H_2 or Blue-H_2 may be produced on a large scale, a huge investment in research and infrastructure is necessary at various levels. The large-scale production of Green-H_2 requires that the electrolysis of water is powered with either perennial energies (solar-, wind-, hydro-power) or even clean and safe nuclear (fusion). Moreover, large-stable-durable electrolyzers are necessary, which, in turn, require special materials on a large scale. In addition, electrolyzers are not very suited for continuous switch on-off, therefore the intermittency of solar and wind energy demands buffers so that electrolyzers can work continuously. Batteries are the direct candidates to store electric energy for feeding electrolyzers, chemical bonds (fuels obtained from CO_2 hydrogenation or ammonia) represent an alternative strategy to store solar or wind energy. Hydro-power (or nuclear) electricity would represent a better option for its continuity. Hydrogen is mainly used in industrial applications (hydrogenation reactions, as the main one) and its use as an energy vector has not seen a substantial increase during the last ten years [14] despite all the campaigns for its use. It must be emphasized that water electrolysis will produce molecular oxygen as the water-oxidation product at a rate equal to half volume than hydrogen. Such pure oxygen can be sold on the market (price varying with purity [eight purity grades, 15] and use -from industrial to medical- with an average price of 20 €/kg for pure O_2 in 20 L cylinders at 20 MPa [16]) and represents a revenue that may mitigate the cost of production of hydrogen.

2.1. *Electrolysis of water powered by perennial energies*

Three technologies are used today for making electrolytic-hydrogen (*Green-H_2*) from water, namely: i. alkaline water electrolysis (AWE), ii. proton-exchange water electrolysis (PEM), and iii. high-temperature water electrolysis (HTWE). Table 1 shows their operative conditions [17].

The diaphragm membrane [18] is the crucial point of AWE, as it requires low gas permeability and high ion (OH^-) conductivity, which are affected by the operative conditions. White asbestos, $Mg_3Si_2O_5(OH)_4$ [19], used for long time, due to health risks and fast corrosion by the hot caustic environment is being substituted by composites such as polytetrafluoroethene (PTFE) or polysulfones, integrated with zirconia, ZrO_2, or potassium titanate, K_2TiO_3. The cathode [20] is made of perforated steel with a surface Ni-treatment, and mixed oxides containing Ni are elected materials for the anode [21]. Nickel alloyed with metals such as Zn, Fe, Co and V is used to protect electrodes from deactivation, especially at the cathode side, due to nickel hydroxide, $Ni(OH)_2$, and hydride, NiH_x, formation in on/off cycles. Intermittent energy sources such as solar and wind are, thus, not much suited for AWE: integrated sources such as PV-wind-towers-accumulators of energy are best suited for assuring feed continuity to electrolyzers.

Table 1
Working conditions of main electrolytic technologies and their demand for improvement.

	AWE	PEM	HTWE
Cathode	Steel covered with Ni	Platinum-black	Ni on ceramics
Anode	Ni-based mixed oxides	RuO_2, IrO_2, $Ir_xRu_{1-x}O_2$	Mixed oxides, Perovskite-like
Operative Conditions	P: ambient T = 353 K	5 Mpa	973–1273 K
Compartment Separation	OH^--permeable membrane	A solid electrolytic membrane separates cathode and anode	
Strong Points	Mature technology	Efficiency >80 % Very high H_2 purity >99 %.	Production of H_2 under high-T/high-P with potential direct feeding to chemical processes
Weak Points	Low H_2-purity. Electrodes corrosion. Long switch-off switch-on delay	High CAPEX and OPEX. Short life of the solid electrolytic-membrane.	Poor lifetime of components due to the harsh operative conditions.

PEM cells [22] are now finding their own space as a mature technology even if with a still limited market. The advantages are *represented* by H_2 being produced at high pressure (*ca.* 5.0 MPa, which allows a direct feeding into most chemical processes without further pressurization) and high purity (99.99 %, almost meeting fuel-cells requirements) at 80 % efficiency, and by fast activation times, that makes these cells suitable for intermittent power-feed. Disadvantages are the request for special materials, meaning high CAPEX and OPEX. In PEM, a solid membrane capable of efficient H^+ ions transport is the electrolyte: it represents the most fragile part (low thermal, mechanical, and chemical stability) and cost-rising in the system because of thinning due to degradation. Membranes are made of perfluorosulfonic acid polymers, among which Nafion® shows superior performance. Noteworthy, such material is under careful check and its use is under debate within the EU [23]. Electrocatalysts for HER and OER are deposited onto the two membrane sides (membrane electrode assembly, MEA). Platinum black (even supported on graphite nanofibers and multi-walled carbon nanotubes doped with N or B) is used as the standard element for cathodes. Open challenges are the carbon-support corrosion and the reduction of the Pt-loading.

The anode is made of RuO_2 or the more stable IrO_2, or even mixtures of them, $Ir_xRu_{1-x}O_2$. Addition of a third oxide such as Ta_2O_5 or MoO_3, results in better OER performance, but lower stability. The high cost (as for 2022) of Pt (33.5 €/g), Ru (12.9 €/g) and Ir (34 €/g) and the quite expensive components, current collectors and bipolar plates represent a limitation to scale-up such cells.

High Temperature (973–1273 K) *Water Elecrolysis-HTWE* [24] (even known as *Solid Oxide Electrolysis-SOE*) is the third option, characterized by high reaction kinetics. HTWE would represent the best option whenever coupled to industrial processes that release high-temperature heat that would be used to vaporize water to be fed to the solid electrolyte made of metal oxides. Pros in such cells are the fast on/off cycling and long-term stability of key components. Conductive oxide electrolyte is made of yttria-stabilized zirconia-YSZ, Y_2O_3-ZrO_2, often added with Sc_2O_3. Anodes are made of composite ceramic materials, perovskite-like structures, such as: $La_xSr_{1-x}MnO_3$, $La_xSr_{1-x}Co_yFe_{1-y}O_3$, $Ce_xY_{1-x}O_{1.95}$,

$La_xNd_yPr_{2-x-y}NiO_{4+z}$. The cathode is made of ceramics such as YSZ or $Ce_{0.9}Gd_{0.1}O_{1.95}$ coupled with metallic nickel. Structural and electrical connections require materials with appropriate resistance (excellent expansion coefficient) to high temperature and temperature swing and are usually made of steel or chromium-enriched alloys.

2.2. *Constraints to up-scale the Green-H_2 production*

Up-scaling the production of electrolytic equipment for the production of large volumes of Green-H_2 is not an easy task and will require investment in innovation and infrastructure. New PV materials must be used with respect to those used today to increase the solar-to-PV conversion efficiency (today 20 %, expected to rise to 40 % in the future decade) [25] and lower the cost of materials (organic materials are expected to half the cost with respect to Si). This is a necessary step, for bringing the cost of PV-H_2 or wind-H_2 closer to that of MSR-H_2.

Therefore, the key issues are to scale-up the electrolytic-H_2 production from an actual 1.2 Mt/y over a total amount of *ca.* 90 Mt/y, to >65 % of future foreseen >240 Mt/y within 2050 [26] and less than half the price of production of Green-H_2 at zero CO_2 emission: three hard tasks if the actual international political situation is considered, that may delay the deadline of 2030 for substantial availability of H_2. That either Green-H_2 will be largely available at a cost comparable with that of MSR-H_2 and/or sustainable Blue-H_2 will be available on a large scale, are considered as enough realistic options: in fact, the question of whether the direct use of H_2 as an energy vector must be preferred to its use for the conversion of CO_2 into fuels (E-fuels or Renewable Fuels) is also under serious consideration at the international level. The use of H_2 for the production of fuels by CO_2 hydrogenation may cause the loss of efficiency 20–25 % of H_2 due to the chemical processes but could result in a wiser option as existing infrastructures would be continued to be used and costly materials required for H_2 safe handling, storing and transporting would not be necessary. This is a matter of large debate today [27] and the Hydrogen-Economy strategy sees a waving trend, even for the bottlenecks to a rapid upscale of the production discussed above.

3. Cyclic Carbon Economy

3.1. *The need for carbon for our society and the Carbon Cyclic Economy*

As mentioned above, carbon cannot be eliminated from our life, but the use of fossil-C must be deeply reduced. Most likely, by 2050 we shall be able to use fossil-C at 20 % of the actual rate [8] with a deep cut of the emission of CO_2 to the atmosphere. Although one can foresee a deep change in the CI for what concerns either non-fossil-C used as an energy source, or processes and even the use of solvents, anyway the CI will need carbon. Pharmaceuticals, polymers, solvents, food, clothes, specialty materials, *etc.* will all require carbon sources different from fossil-C. As mentioned above, Recycled- (plastics and CO_2) and Renewable-Carbon (biomass) will replace fossil-C [27]. Consequently, a considerable change will occur in the area of catalysis, which is involved in the production of *ca.* 90 % of goods we use today [28]. Mainly, a shift towards raw materials richer in oxygen will occur (from hydrocarbons to carbohydrates and from CO to CO_2), and this will require new catalysts or even combined technologies such as hybrid catalysis (combination of thermal-enzymatic catalysis, or thermal-electro catalysis, or electro-enzymatic catalysis or even of the three technologies) [29]. The Carbon Cyclic Economy will reduce the fossil-C extraction, stepping toward a NZE. The use of biomass rises the issue that the rate of the combustion [30] or digestion of C-based materials (in which CO_2 is generated) is higher (some 1000 times) than the rate of natural photosynthetic processes [6]. Interestingly, industrial catalytic processes can be much faster and more intensive than natural processes and even much more selective towards a target product. Natural systems produce what they need for functional and structural purposes and even energy storage of the organism, without any specific energy optimization towards a single product (there is plenty of energy in the form of solar energy). Such a high-entropy product-system makes also energy intensive the isolation of target molecules from biomass. Therefore, a Man-Made C-Cycle may result winning over the natural photosynthetic system in terms of optimized energy use towards target molecules and shorter time of production.

3.2. *Capture of CO_2*

Most of anthropogenic CO_2 has either a:

* *fossil-origin.* Power- and industrial-plants, including cement and stainless-steel manufacture, are point continuous sources; conversely, transport is a mobile-discontinuous source and heating-conditioning are seasonal-intermittent sources.

* *bio-origin* (sugars-fermentation and waste-digestion, either anaerobic or aerobic).

In the natural Carbon Cycle, over 200 Gt/y of carbon are cycled among the various compartments: atmosphere, biosphere, and inorganic materials [31].

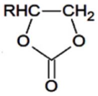
Anthropogenic CO_2 can be conveniently captured from continuous, concentrated (5–90 %) fixed sources such as power plants, industrial processes, fermentation and digestion plants at a variable cost (80–120 US$/t, depending on the source). Its capture from mobile sources has been attempted but is not very convenient and of general use due to the fact that the vehicle should transport large masses of sorbents (suitable for trucks or boats, not for cars). Discontinuous sources (heating-conditioning) are not convenient either. The atmosphere is a potential and the largest source of CO_2 (over 800 Gt_C are available there) [31]. Direct air capture (DAC) is also possible, but due to the low concentration (440 ppm and anti-entropic work, the cost of capture is now at least four times that of capture from concentrated sources. All the above-listed sources differ mainly for two factors: the concentration of CO_2 and the presence of contaminants, both dictating the cost of production of CO_2. The CO_2 source determines the nature of contaminants, such as nitrogen- and/or sulphur-oxides in flue gases, or hydrocarbons in some industrial streams, or even water and O_2 that need to be removed for most applications [32]. Different applications demand a specific purity of CO_2. Food grade CO_2 is the purest (>99.999 %) and the one that requires the elimination of contaminants at ppb level, increasing the cost of production. The standards for CO_2 purity *versus* application are internationally defined by ISBT, CGA, and EIGA.

3.3. *Energy issues in CO_2 utilization as a building block for chemicals and materials or source of carbon for energy products*

CO_2 is a stable molecule ($\Delta G_f^0 = -396$ kJ/mol). The conversion of CO_2 into other chemicals will require an amount of energy that depends on the downward steps of the oxidation state of carbon from +4 in CO_2 to that of the target product. The reactions in which CO_2 is involved can be divided into three main classes [33] namely: i. *low-energy processes* in which the oxidation state of C remains equal to +4, essentially relevant to chemicals' production (carbonates, carbamates, or their derived polymers); ii. *average energy processes* in which C-C bonds are formed (by either reacting CO_2 with olefins and dienes or by insertion into a C-H bond, a more problematic process as C-H activation is required); and iii. *high-energy processes* (synthesis of fuels, which also need hydrogen). It is worth mentioning that fuels have a market that is *ca.* 16 times larger than that of chemicals and the manufacture of fuels would convert significantly larger volumes of CO_2 (Gt/y) than that of chemicals (Table 2).

Conversely, the production of chemicals from CO_2 would reduce the C-footprint of synthetic processes by a factor up to 2.8.

Table 2
Actual and Perspective use of CO_2 to chemicals and materials.

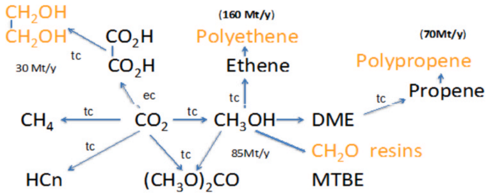
Compound	Formula	$C_{oxstate}$	Market (Actual) Mt/y	CO_2 Use Mt/y	Market (2030) Mt/y	CO_2 Use Mt/y
Urea	$(H_2N)_2CO$	+4	180	132	210	154
Linear carbonates	$OC(OR)_2$	+4	>2	0.5	10	5
Cyclic carbonates		+4	*ca.* 1.5 mostly for captive use	*ca.* 0.3		
Polycarbonates	$-[OC(O)OCH_2CHR]-n$	+4	5	1	9–10	2–3
Carbamates	RHN-COOR	+4	>6	1	11	*ca.* 4
Acrylates	$CH_2 =CHCOOH$	+3	5	(0.5)?	8	5
Formic acid	HCO_2H	+2	1	(0.9)?	>10	>9
Inorganic carbonates	M_2CO_3	+4	$CaCO_3$ **250**	70	**400**	100
Methanol	CH_3OH	–2	60	10	**120**	**>100**
Total				207		**>370**

3.4. *Conversion of CO_2 into chemicals*

Processes of CO_2 catalytic conversion into chemicals span in the 3–9 TRL range, with the synthesis of urea, carbonates and methanol leading the application. Table 2 presents the SotA and perspective use of a number of chemicals that have a market of at least 1 Mt/y. Several other specialty chemicals can be advantageously synthesized using CO_2 as a building block, mainly carboxylated and carbonylated products, reducing the CO_2 emission not only by the amount of used CO_2 but for being more direct syntheses, producing less waste. As an example, the direct carboxylation of an organic substrate by CO_2 insertion into a C-H bond would have a much lower C-footprint than the actual method based on the oxidation of aromatic or aliphatic moieties [6] that causes loss of carbon as CO_2. The deployment of innovative technologies should be assessed *via* LCA from the techno-economic-environmental point of view, so to exclude that more CO_2 is produced than is converted [6].

The use of CO_2 as a building block for added-value chemicals and materials (polymers and inorganic carbonates) does not require hydrogen. CO_2 added-value derivatives have *short-* (months, for fuels), *medium-* (years, for chemicals), *long*-life (decades, organic polymers; or centuries, inorganic carbonates). The market of such products may expand from actual *ca.* 207 Mt/y CO_2 to over 350–400 Mt/y within 2030 (Table 2). At glance, such use of CO_2 will not contribute significantly to controlling the CO_2 atmospheric level. Nevertheless, if the *avoided* more than the *used* CO_2 is considered, assuming an average *avoided/used* ratio of *2.8* [34], one can conclude that close to *1 Gt/y* of *CO_2* will be *avoided by 2030*, that represents a more significant contribution, which is coupled to a cut of 200–300 Mt/y of fossil-C. The chemistry relevant to the conversion of CO_2 into added value organics has been extensively investigated since the first example of activation of CO_2 by co-ordination to Ni was reported by Aresta et al. in 1975 [35]. In an energy frame based for 82+ % on fossil-C it had no sense to develop reductive processes of CO_2 that would have emitted more CO_2 than converted. The electrochemical coupling of CO_2 and organics was also investigated as a new clean route to developing an efficient synthetic CO_2-based methodology with the use of PV.

Co-processing CO_2 and water is an innovative approach that may serve to produce large-scale chemicals such as olefins that may find multiple applications. Of interest is the case of the synthesis of C_2 (ethene) [36] and C_3 (propene) olefins from CO_2 *via* electrolysis in water that would *per se* convert close to 0.8 Gt/y of CO_2. Olefins can be used for making polymers or molecular chemicals that would result to be produced from bio-carbon as CO_2. Scheme 1 shows an example of a value chain based on CO_2 conversion into methanol, olefins and polymers that, if fully implemented, would convert some 800–1000 Mt of CO_2 per year into added-value chemicals and materials. The production of fuels is not counted in this value-chain: it would potentially require one order of magnitude larger amount of CO_2.



Scheme 1. Value-chain for the conversion of CO_2 into methanol, olefins and polymers.

3.5. *Energy products from CO_2*

In the longer term, let us say by 2040, a different perspective can be built [37] for CO_2 conversion as by then large volumes of PV-H_2 at a cost close to MSR-H_2 may be available. The conversion of CO_2 into fuels may grow to levels of 2–3.5 Gt/y using technologies on stream today. The hydrogenation of CO_2 to methane or methanol is established, and the conversion of CO_2 into C_n hydrocarbons is gaining TRL grades and may be ready for exploitation in a decade or so.

However, in the long term (15 years), Carbon Capture and Utilization technologies may mitigate climate change [38] by using industrial off-gases captured directly at point sources so that they do not enter the atmosphere. In December 2021, the European Commission adopted the Sustainable Carbon Cycles [39] communication, which sets out an action plan on: (i) how to develop sustainable industrial solutions to increase carbon removals (using direct air capture and bio-based products with long lifetimes); and (ii) key actions to support the industrial capture, use and storage of CO_2 (CCU and CCS). CCU is a strategic technology for the defossilization of energy-intensive industries, including the chemical industry. Its application potential has been identified as particularly high for the chemical sector [40].

4. Crossing area: Green-H_2 (Blue-H_2) and CCE

4.1. *Short term options and benefits*

CO_2 in combination with hydrogen, can be in the short term used to produce fuels such as methane [41] and methanol [42], easier to handle than H_2. Pilot and demonstration plants are on-stream that convert CO_2 at a scale 100–5000 t/y. Perennial energy sources (SWHG) and Green-H_2 must be used in the conversion of CO_2 into sustainable E-fuels. Such option requires a short time (mainly dictated by the scale-up of Green-H_2 production) to be scaled to a large volume. Even if such conversion will cause the loss of 20–25 % efficiency with respect to the direct use of H_2, it will bear several benefits in terms of reduced CAPEX and OPEX, lower demand of specialty materials necessary for storing, transporting and using H_2, assuring higher safety and continued use of existing infrastructures that will eventually compensate the loss of efficiency. Using Green-H_2 (Blue-H_2) for the reduction of CO_2 to E-fuels is one of the beneficial uses of H_2. Both CCU and Green-H_2 will contribute to move towards the net zero emission in a shorter term. The use of Blue-H_2 (produced *via* MR with CO_2 capture, so to reach the target of 70 % emission reduction) is gathering much attention as a short- to medium-term option to large scale H_2-producion using on-stream technologies [43]. CCS looks as a more ready technology than water electrolysis for scaling up. This expectation needs to be confirmed on field and by storage of tens of Mt_{CO2}/y.

4.2. Direct use of solar energy in CO_2-reduction

The use of solar energy for driving reactions in which CO_2 and water are converted into energy-rich products can be considered a sustainable approach alternative to the production of H_2 from water. Solar energy is an inexhaustible resource, which provides about 100 000–120 000 terawatts (TW) of solar irradiation to the Earth's surface, 20 000 times more than the whole world's energy demand [44].

To convert carbon dioxide into fuels, two different approaches can be deployed in addition to electrolysis of water that generates hydrogen used for the hydrogenation of CO_2 to fuels. Such technologies are: 1. use of concentrated solar power for splitting CO_2 and H_2O at high temperature (>1000 °C) and making Syngas [45] used in turn for making hydrocarbons through the F-T process on stream since decades; 2. the direct co-processing of water and CO_2 to energy-rich products under solar irradiation [46].

The former option needs some further improvement of both the technology for concentrating solar energy and the performance of catalysts for H_2O and CO_2 splitting and may be applied in the medium term (10 y); the latter will most likely be exploited more likely in the long term (15 y) as new, effective and stable photocatalysts and photo-electro-catalysts must be discovered and new advanced photo- photo-electro-reactors need to be developed [46,47]. The deployment of the latter technology would run-off the need to produce hydrogen for CO_2 reduction, representing a really big step in the direction of a Man-Made C-Cycle. As for today, the photochemical/photoelectrochemical conversion of CO_2 and water into C1 molecules such as methanol or methane has been developed at a TRL 3–4, and the production of C_{2+} molecules is at TRL< 3. Investment in Research and Innovation is necessary for boosting the development of such technology that may contribute to deploying the Carbon Cyclic Economy without crossing the H_2-production.

5. Conclusions

The integration of the Carbon Cyclic Economy with Green-H_2 or Blue-H_2 may represent a strategic combination of technologies for an efficient moving away from fossil-C, in the short-medium term, taking the benefit of the change without a huge economic investment. The known hydrogenation of CO_2 to fuels may allow to continue to use existing infrastructures, avoiding the investment in special materials required by the diffused use of H_2. Noteworthy, non-marginal amounts of CO_2 are used since a few decades in the ICI process for the synthesis of methanol and the direct conversion of CO_2 and hydrogen into methanol is demonstrated at a demo-scale. The conversion of CO_2 into fuels with Green-H_2 would not require a huge change in chemical plants as it would be enough a minor modification of FT-processes for its implementation. Balanced mixtures of CO_2 and H_2 could be converted into Syngas ($CO+H_2$) through the known Reverse Water Gas Shift Reaction (RWGSR) and Syngas would be fed to existing FT-plants for their conversion into hydrocarbons. Possibly, the RWGSR could be coupled with FT into a single plant [48] by adding a preliminary catalytic step for the production of Syngas from CO_2 and hydrogen. In the medium term, the electrochemical C-C coupling of CO_2 and organics may represent a sustainable route to chemicals and co-electrolysis of H_2O and CO_2 may bring to fuels. In the long-term co-processing of H_2O and CO_2 under solar irradiation may produce hydrocarbons without the need to produce hydrogen: a substantial change. Shifting away from fossil-C in a sustainable way and without major economic efforts is possible, but requires investment in R&I and clear political choices. The EU-Trilogue (Parliament-Council-Commission) is intensively working at a common reading of the regulations about low carbon hydrogen and low carbon fuels that will regulate the production of Green-H_2, Blue-H_2, E-Fuels and Renewable Fuels of Non-Bio Origin (RFNBO) [49]. This will help to clarify the conditions for large scale implementation of CCU.

CRediT authorship contribution statement

Aresta Michele: Conceptualization, Writing – original draft, Writing – review & editing. **Dibenedetto Angela:** Conceptualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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