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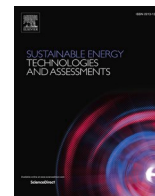
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Review article

Perspectives of CO₂ utilization as a negative emission technology

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ABSTRACT

In the race to net zero, attention is turning to solutions that remove carbon dioxide from the atmosphere. Among them, technologies for the capture and geological storage of atmospheric CO₂ are promising, while the capture and utilization of CO₂ is a more uncertain way to significantly mitigate climate change. In this review, we aim at examining solutions to utilize and store CO₂ in products in order to identify those eligible for negative emissions and quantify their potentials. First, we review the scientific literature and point out that CO₂ utilization could both enable the production of goods and suck CO₂ out of the atmosphere if employed for solvents, refrigerants or working fluids, or converted into carbonates and plastics. Then, we review energy models that explore the future potential of CO₂ utilization to understand whether negative emissions are envisioned through CO₂ utilization routes. We note that only a few models represent the negative emissions value chains through CO₂ utilization, and even fewer report them in the results of their exercise. Finally, we discuss the feasibility and impacts of CO₂ utilization deployment as well as its representation in energy models, considering the complexity of this value chain.

Introduction

It is acknowledged by the scientific community that anthropogenic greenhouse gas (GHG) emissions are responsible for global warming and climate change, CO₂ being the largest contributor. Although methane is 28 times more potent, CO₂ is emitted in such high quantities that its related emissions accounted for roughly 76 % of global warming in 2010 [1]. To tackle these emissions, global agreements have been ratified, such as with the Kyoto Protocol, which engaged the signatories to constrain their GHG emissions, up to the more ambitious and binding Paris Agreement [2]. Since its ratification in 2016 by 195 of the 197 countries recognized by the United Nations, companies and governments around the world have announced a series of novel climate commitments. These commitments aim at mitigating the climate impacts due to anthropological activities, referred to as a *net zero emissions* (NZE) ambition - or carbon neutrality.

Global carbon neutrality can be defined as a balance between anthropogenic CO₂ emissions and anthropogenic CO₂ removals [3]. Removing as much CO₂ as that emitted by human activity each year is necessary to stop the build-up of CO₂ in the atmosphere, and thus stabilize mean temperatures. In order to meet the 1.5 °C objective of the Paris Agreement, the NZE target must be achieved by the middle of the

21st century [4,5], and it requires action now.

Given the challenge, organizations must rely on two means: reducing emissions and increasing carbon sinks [6]. On the one hand, reducing emissions relies on four major levers: energy efficiency [7]; demand reduction [8] – which lowers emissions but cannot eliminate them; the replacement of fossil fuels with clean renewable energy carriers for energy generation [9]; and Carbon Capture Utilization and Storage (CCUS) [10]. On the other hand, carbon sinks represent natural or unnatural options that absorb and remove CO₂ from the atmosphere, which is possible via natural-based carbon sinks (afforestation, reforestation, biochar and enhanced weathering), or via industrial techniques (Bioenergy with Carbon Capture and Storage (BECCS), Direct Air Capture with Storage (DACs) and Carbon Capture and Utilization (CCU)) [11]. Therefore, CCUS is a set of technologies that can both reduce emissions and remove CO₂ from the atmosphere.

To be more specific, Carbon Capture and Storage (CCS) consists in capturing CO₂ emissions from human activities (e.g. fossil-based power generation plants) and storing them underground to phase out a facility's emissions [12]. If fossil fuel is the origin of CO₂, then this technology cannot perform negative emissions and is thus not considered as a carbon sink technology. However, if the CO₂ comes from biomass combustion (BECCS) or directly from the atmosphere (DACs), then the

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storage results in negative emissions because atmospheric CO₂ has been absorbed during the growing of biomass, and therefore its combustion is considered as CO₂-neutral. The potential of CCS to generate negative emissions has been widely studied and is now fully recognized as inevitable to achieve net-zero commitment [4,13,14]. However, CCS is much more expensive than conventional processes [12,15], raising concerns on its economic viability and its deployment. With CCU, the captured CO₂ is not destined for geological storage but may be utilized to run processes or transformed into another valuable product in which it will be sequestered subsequently for a certain period. Because CO₂ can be used and enhanced, CCU technologies have been recognized to stimulate the economic viability of CCS technologies [13,16]. In some cases, CCU can be considered as a *negative emission technology* (NET) - that we call CCUNET¹ - if and only if the CO₂ captured is climate neutral and sequestered for long enough. Some CO₂-based products, such as fuels, have great deployment potential in future markets, but cannot contribute as a NET option because the CO₂ is released during their utilization (e.g. through combustion). In contrast, CO₂-based plastics or building materials could sequester CO₂ for decades or even centuries [17,18] but this opportunity has received much less attention. To tackle economic and climate mitigation concerns, it would be extremely interesting to capture CO₂ not only to generate negative emissions, but also to produce goods, as a combination of CCU and NETs, thus bridging the gap between CCS and CCU.

In the literature, several researchers have reviewed and estimated the prospects for CCU as a whole, i.e. not focusing on CCUNET. The International Energy Agency (IEA) envisions in its Sustainable Development Scenario (SDS) that CCUS will contribute to reducing cumulative CO₂ emissions by 15 % until 2070 [13]. This represents the cumulative storage of 240 GtCO₂, of which 20 % is captured from the atmosphere through BECCS (94 %) and DAC (6 %). 92 % of the captured CO₂ is sent underground and the remaining 8 % is used. Although the targeted capture sources and industrial sectors are known, there is little insight into what the CO₂ is used for, with the IEA recognizing that 'the prospects for CO₂-based products are very difficult to assess'. In 2013, Aresta et al. mapped the current state of CO₂ use in terms of the tonnage employed worldwide to produce a range of industrial goods, also called CO₂-based products [19]. They estimated the global amount at 200 MtCO₂ of which 15 kt could generate negative emissions by producing carbonates or polycarbonates. The Global CCS Institute also performed an assessment of the current and future markets with more details on the CO₂-based products options [20]. Their estimation for future negative emissions generated with CCU is in the range of 335 to 630 Mtpa from the manufacture of carbonates, concrete or aluminum. Armstrong and Styring focused on the specific use of CO₂ to recover hydrocarbons, i.e. CO₂ Enhanced Oil Recovery (EOR). As some of the CO₂ is buried to pressurize the reservoir and recover the remaining oil in the bottom of the well, the authors estimated that the net CO₂ sequestered to enhance recovery is not enough to compensate the emissions due to oil combustion, which means it is not a CCUNET option. The authors have produced different scenarios consistent with 2030 reduction targets worldwide that result in a potential for negative emissions through CCU including waste mineralization and polymers between 0.1 and 0.8 GtCO₂ used. Rather than estimating the current market and its development, Huang and Tan estimated the CO₂ reduction potentials per ton of CO₂-based microalgae, urea, polycarbonate, methanol, dimethyl ether, and dimethyl ethylene [21]. The authors also reported the global demand, with an estimated potential CO₂ emission reduction of 269 MtCO₂ per year, of which only 2.15 MtCO₂ can be turned into negative emissions if climate-neutral CO₂ is used to manufacture polycarbonates and dimethyl carbonates. Finally, one study concentrates on the prospects of CO₂ utilization and removal considering the variety of CCU

options, in an aggregated manner [22]. The authors estimate a range of removal and utilization potential of CCU in 2050. In terms of negative emissions, their estimates show that 100 to 1,400 MtCO₂ per year could be utilized and removed in 2050 through CO₂ mineralization in building materials. The review of existing studies assessing the current and future potential of CO₂ utilization shows that little attention has been paid to CO₂ removal with CCU techniques – or CCUNETs. Moreover, none of the aforementioned studies include all CCUNET possibilities. The literature assesses different indicators that express the potential roll-out of CO₂ utilization:

- 1) The quantity of CO₂ utilized, now or in the future, useful to reflect the scale of capture needs.
- 2) The quantity of CO₂ reduced or removed through CCU routes in the future, useful to reflect the effectiveness of CO₂ utilization.

Considering the aforementioned review articles, scientists have concentrated their research on the estimation of CCU potentials without worrying about CO₂ removal. In the present paper, we only focus on technological pathways of CO₂ utilization as a NET by defining the concept and assessing in detail its perspectives. An additional novelty of this paper is that perspectives for CCUNET are assessed and discussed in light of the results of prospective models in the literature. We start with a review of the different alternatives that CO₂ utilization has to offer and then identify those that are eligible for negative emissions (Section 2). In this section, we aim at defining what we call CCUNET and at estimating the global potential of CO₂ that could be utilized for negative emission purposes, considering the current markets. Thirdly, we review prospective energy models that project the future of the energy systems around the world, including CCU technologies as a mitigation technology alternative (Section 3). For these models, we select only those that include CO₂ utilization processes capable of generating negative emissions that we have identified and discussed in Section 2. We analyze the results the models deliver in terms of the quantity of CO₂ utilized. This allows us to give a critical viewpoint of what the future utilization of CO₂ might be and to what extent we might need it to achieve carbon neutrality. In the last section, we discuss the role of CCU as a NET (Section 4) to clarify the implications of CCUNET roll-out as well as the commonly used CCUS acronym, which confuses the debate on CO₂ utilization.

CCU for negative emissions: state-of-the-art

For a CCU route to be qualified as a NET, capturing climate-neutral CO₂ is a prerequisite. This can be achieved by capturing atmospheric CO₂ directly from the air (DAC), or by capturing biogenic CO₂, i.e. CO₂ that has been emitted from the combustion or gasification of biomass. We explicit these technologies in subsection 2.1.

Two technological pathways of CO₂ utilization can be differentiated: the direct utilization of CO₂ (DUC) and the conversion of CO₂ into a valuable product in which CO₂ is a co-reactant. In this section, the respective benefits of DUC and CO₂ conversion to reach the NZE target are discussed based on an analysis of the market they supply, the type of product they deliver, and their potential to substitute current products and sequester CO₂. These elements are essential to determine in which cases CCU is a promising NET.

The combination of climate-neutral CO₂ capture and use in goods or processes that sequester CO₂ for a long period can be qualified as a negative emissions technology, or CCUNET.

Capture of climate-neutral CO₂

Climate-neutral CO₂ denotes carbon dioxide molecules that do not contribute to the build-up of CO₂ in the atmosphere when emitted. This property is attributable only if the CO₂ has been extracted from the atmosphere in the first place – and not generated from the use of fossil fuel

¹ Carbon Capture and Utilization as a Negative Emission Technology (CCUNET).

resources. This category includes two types i.e. atmospheric CO₂ which is extracted directly from the atmosphere, and biogenic CO₂, which denotes atmospheric CO₂ that has been absorbed by the photosynthesis of biomass and then released when combusted or fermented. For both types, emissions are considered as neutral from a climate perspective because the CO₂ is recycled from the atmosphere. Using climate-neutral CO₂ is fundamental for generating negative emissions. However, fossil CO₂ emissions can occur during the process of capturing these CO₂ molecules, which compromises their neutral property. This aspect is discussed in section 4. In terms of technology, DAC processes and BECC processes have been proven feasible to generate respectively pure atmospheric CO₂ [23,24] and pure biogenic CO₂ [12,25] to be stored or used.

Direct utilization of CO₂ to run processes

The direct utilization of CO₂ aims at employing the chemical properties of the carbon dioxide molecule in industrial processes as a utility, thus participating in the manufacture of a final product that does not contain CO₂. Many minor applications of DUC are currently commercialized, while some others could be developed in the future and be potentially helpful to reach NZE targets [20]. To be carbon negative, the amount A_{atm} of climate-neutral CO used in a DUC system should not exceed the emissions associated with the energy required to capture atmospheric CO₂ E_{energy} plus the leaks within the process $E_{process}$ in a cradle-to-gate approach – see Fig. 1.

The specificity of a DUC process is that the CO₂ emitted by the final product is not the CO₂ that was used to manufacture it, which makes allocation of the emitted CO₂ difficult [26]. A wide range of products are – and can be – manufactured from CO₂ [27]. Enhanced oil recovery (EOR) currently utilizes about 70 to 80 Mt of CO₂ annually [33], making it the most widespread DUC process. The principle of EOR is to inject supercritical CO₂ into an oil reservoir, reducing its viscosity and draining it to the surface [12]. EOR accounts for about 5 % of US crude oil production [29]. Part of the injected CO₂ is sequestered inside the rocks' pores, and another part is brought to the surface together with oil before being separated. However, the quantification of the fraction vented, and the fraction stored is difficult to assess and depends on the properties of the rocks. An estimation is that 296 kg of CO₂ are utilized to recover one barrel of oil [12] while the combustion of one barrel emits 430 kg of CO₂ [30]. It should be noted that the IEA argues that EOR could produce carbon-negative oil [31]. As these values can vary from one EOR project to another, Life-Cycle Assessments (LCAs) are essential [12,32,33] and should be systematically performed for each new EOR project. Although this is the only commercialized and viable option for DUC, the technique is often considered to be an unreliable climate mitigation option because it encourages the consumption of fossil fuels [34,35]. A similar application is the recovery of methane from coal mines. Enhanced coal-bed methane (ECBM) recovery consists in injecting CO₂ into coal seams to

extract natural gas that is partly trapped in the porous coal grains while imprisoning CO₂ in the ground [36]. ECBM recovery is not currently commercialized but appears to be environmentally beneficial. Indeed, in 2017, Oudinot et al. estimated a potential recovery in coal beds of 80 kg of sequestered CO₂ per thousand cubic feet of natural gas [37], whose combustion emits 55 kg of CO₂ [30].

CO₂ molecules are non-flammable, non-toxic [38] and inert [39], making them suitable for preserving organic products, as for instance, in winemaking [40]. Minor direct uses of CO₂ also include fire extinguishers and pneumatics [41]. Other current utilizations of CO₂ concern the iron and steel industry [42], coffee decaffeination (448 kg of CO₂ to decaffeinate 1 kg of coffee) [43], pharmaceutical processes [44], and electronics manufacturing [45]. In these processes, the CO₂ is used to manufacture final products, and in some cases, it is recycled to be used again, depending on the production site and process. As long as the CO₂ employed in the process is recycled and kept away from the atmosphere, the process itself could serve as an artificial sink. CO₂ used as a refrigerant and solvent (for perfumery and textile industries) is a good candidate for this purpose. 'A green solvent would be non-flammable, nontoxic, nonecotoxic, abundant, renewable, easy to prepare, easy to remove from product, non-eutrophying, and would not contribute to global warming' [46]. Except for the global warming aspect, "CO₂ meets these criteria" whilst conventional solvents are either toxic and/or flammable. Obtained under high pressures and temperatures, supercritical CO₂ solvent has a global use of less than 1 Mt per year [20], while the global annual demand for solvents was estimated at 28.5 Mt in 2020 [47]. Additionally, most of the refrigerants used today are harmful to the environment due to their huge global warming potential (GWP) [48], whereas CO₂ has a much lower GWP (roughly 1,000 times less). Therefore, replacing conventional refrigerants with CO₂ seems attractive to avoid the leakage of noxious refrigerants and to sequester CO₂ into heat pumps and pipes. However, technical challenges related to the use of CO₂ as a refrigerant cannot be ignored. The process requires liquefying CO₂ at very high pressure, which raises safety and feasibility concerns if used in residential or commercial environments.

An emerging DUC technology is the recovery of geothermal energy enhanced by injecting supercritical CO₂. Enhanced geothermal systems (EGS) consist in extracting geothermal energy by fracturing the rocks with water, which is subsequently heated and transformed into steam run through a turbine in a closed-loop system. Instead of injecting water, in 2006, the Lawrence Berkeley Laboratory proposed to inject CO₂ as a novel working medium supposed to be "superior to water in its ability to mine the heat stored in a geothermal reservoir". Although the technology faces major as-yet unsolved technical challenges [49], it is nonetheless a unique process that enables the extraction of renewable resources while sequestering CO₂. In theory, there is no doubt that LCA studies would demonstrate that EGS removes CO₂ while producing heat and power. However, the suitability of geothermal reservoirs for permanent CO₂ storage is uncertain [20].

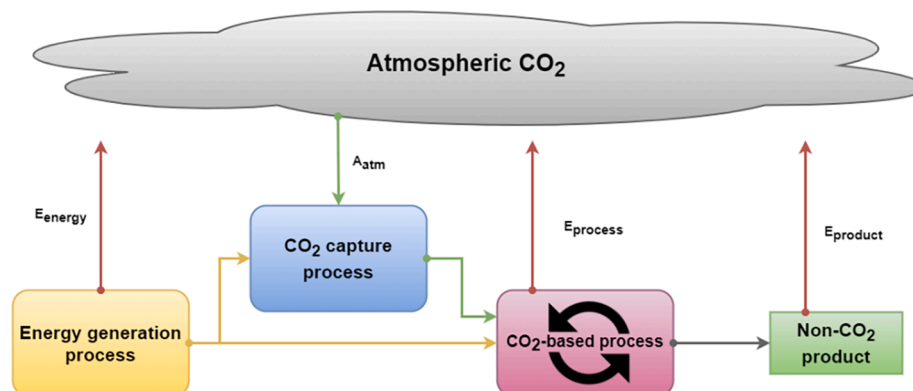


Fig. 1. . Simplified block-flow diagram of a DUC chain [Source: author] {color image, single column fitting image}.

Globally, current DUC represents roughly 97 MtCO₂/y, mostly driven by EOR demand [20]. However, no DUC processes have yet demonstrated their ability to deliver negative emissions at a commercial scale. Some applications, namely CO₂ as solvents and refrigerants, could act as carbon sinks. In other words, DUC processes could behave just like geological storage, and the storage system would be the process itself. The advantage is that, unlike DACS or BECCS, DUC carbon-sequestering processes produce a valuable product at the end.

For any DUC process aiming to bring negative emissions, the following requisites must be verified:

- 1) Ensure that the captured CO₂ is atmospheric.
- 2) Provide sufficiently low-carbon energy to capture CO₂.
- 3) Prevent the DUC process from CO₂ leakages so that CO₂ is trapped in the process, recycled, and kept away from the atmosphere for a long time.
- 4) Ensure that the final products do not generate CO₂ emissions.

Among the DUC options, only the use of supercritical CO₂ as a solvent, refrigerant, and working fluid (respectively to produce perfumes, cooling, and heat and power) seems to be attractive for policymakers seeking to achieve negative emissions while enhancing CO₂. LCAs still lack in this field, making decisions hazardous. Another barrier is that the volume of CO₂ that can be stored in DUC processes is somewhat limited: as the CO₂ involved in the process must be recycled, the end-product is manufactured without the need to inject additional CO₂, i.e. CO₂ is not a feedstock, but a utility.

Conversion of CO₂ into value-added products

The concept of CO₂ conversion is not to run a process but to utilize CO₂ as a feedstock – a reactant or a co-reactant – in order to transform it into a valuable product (Fig. 2). Ultimately, CO₂ is retained in the final product, which is not the case for DUC processes. The conversion of CO₂ offers a wide range of possibilities and product options including chemicals, fuels, plastics, fertilizers, and building materials, all of which are essential in our daily lives. However, their contribution to addressing climate change is uncertain [13,50–52] and their ability to deliver negative emissions even more so. It is hard to assert the capability of the final product to retain the converted CO₂, which itself depends on its usage and life. The European Commission considers the sequestration of CO₂ to be long term if the CO₂ is trapped in the product for more than 100 years; normal CO₂ emissions are inventoried if CO₂ is released before that time, and sequestration is permanent if the CO₂ is not emitted for at least 100,000 years [53].

A milestone to obtain negative emissions through CO₂ conversion is

that conversion processes must be emission-free. This challenge is even greater given that CO₂ conversion processes are energy-intensive [28] because of the high stability of the carbon dioxide molecule, thus high amounts of energy are required to break the two double bonds between C and O atoms [54]. This natural property represents the main technical barrier of CO₂ conversion, a technique that is currently restricted to the laboratory [21,54,55]. Although CO₂ is currently converted into urea at large scales, CO₂ can be turned into many other valuable products through various conversion techniques, namely thermochemically [56–59], electrochemically [60–62], photochemically [56,63,64], by carbonation [65–67], plasma [68–70] or bioconversion [71–73].

The heat and power feeding these conversion processes must be sufficiently CO₂-clean to guarantee negative emissions at the end. The power sector will probably be the first sector to be decarbonized in the near future with the help of renewables [74]. Assuming that both energy-related emissions and co-reactant emissions are phased out (Fig. 2), the final step to achieve negative emissions through CO₂ conversion processes is to ensure that the CO₂ bound in the final product is not released subsequently during its utilization. This requires understanding the uses and the markets of CO₂-based products, which are outlined in the following subsections.

CO₂ to fuels

The best known of the CO₂ conversion pathways, also called Power-to-Liquids and Power-to-Gas [56,57,75], produce methane [76], methanol [77], dimethyl ether [78] and biofuels [79].

Intrinsically, the CO₂-to-fuel value chain is not suited to perform negative emissions. Due to the combustion reaction, the carbon stored in the fuel is bound to be reemitted eventually as CO₂. Thus, the sequestration of CO₂ in fuels is very short term (from days to months), which is not enough to offer durable negative emissions. At best, the CO₂-to-fuel pathway can produce carbon-neutral fuels under the strong requisites that the processes of the value chain must be emission-free, and the CO₂ utilized must come from the atmosphere by any means [80]. Nevertheless, recent techno-economic assessment (TEA) and LCA studies highlight that CO₂ conversion processes reduce the emissions of conventional processes, although they are less economical [77,81–83].

CO₂ to chemicals

To date, only two chemical products are currently made from CO₂ conversion, i.e. methanol and salicylic acid. CO₂-to-methanol is commercialized by Carbon Recycling International, which uses 5,500 tCO₂/y emitted from volcano activity [84]. The company has achieved the production of methanol at a 4,000 t/y rate since 2012 [85,86]. The process runs on cheap geothermal-based electricity and heat, which is then emission-free and recovers native CO₂ from hot waters containing

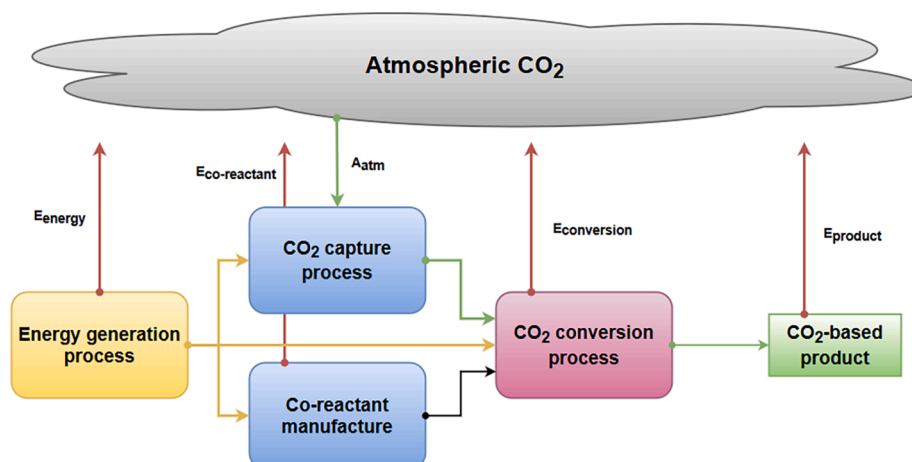


Fig. 2. . Simplified bloc-flow diagram of CO₂ conversion chain.

10 % CO₂ [80] that would have been emitted into the atmosphere anyway. It achieves the production of methanol with 90 % emission reduction compared to the conventional process [86]. In addition, salicylic acid is currently made of CO₂, but its value chain is unable to deliver negative emissions because the final product, namely aspirin, emits CO₂ back into the atmosphere during its consumption when it reacts with water.

Other opportunities for CCU include olefins (i.e. ethylene and propylene) that are chemicals used essentially for their derivatives (e.g. ethylene oxide) and polymerization (e.g. polyethylene or polycarbonates). They represent the biggest market for chemical products that can be made from CO₂, and the end-use products can offer long-term sequestration. The largest demand sector for ethylene and propylene is the plastics sector producing food packaging, plastic bags, window frames, textiles, bottles and insulation materials, which can be recycled. Fig. 3 depicts the breakdown of ethylene and propylene demand, showing that the derivation of olefins can lead to many stable products capable of retaining CO₂ for long periods.

Concerning methanol, when not used as a fuel, this chemical is the basis of numerous chemical products (Fig. 4) which could ultimately lead to long-term sequestration products. The main product, formaldehyde, is a chemical used as a pharmaceutical (resins, adhesives and paints) [88], which are uses that do not release the converted CO₂. However, its interest is limited due to its carcinogenic property [89]. Acetic acid is another basic chemical used for its derivatives to supply the food additive, pharmaceutical, and pigment sectors.

Due to the complex, large value chains of chemicals, it is difficult to assert that CO₂ sequestration into chemicals would be long term. Given the final products resulting from CO₂-to-chemicals, CO₂ can potentially be trapped in a product until the end of its life, which could be decades or centuries for plastics, insulation foams and other materials [12]. Ultimately, it all depends on the products' end-of-life (i.e. the recycling choice made). However, the sequestration of CO₂-to-chemicals pathways exhibits typical lifetimes of days to months [90].

CO₂ to plastics

Rather than producing polymers from olefins or methanol, CO₂ can

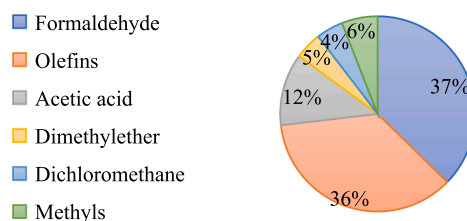


Fig. 4. . Methanol utilization and chemical products [Source: Methanex].

be transformed directly into polymers, namely polycarbonates [91], ethylene carbonates [92], dimethyl carbonates [93] and polyols [94]. Polycarbonates (PC) are polymers containing a carbonate group, taking the form of a transparent solid material, namely thermoplastic. Due to their excellent resistance against heat and impacts [95], polycarbonates have applications in data storage, electronics, building insulation and the automotive industry. Furthermore, this type of plastic could replace many existing petrochemicals derived from polymers and polyols, whose production exceeds 10 Mt per year [96]. Currently, global production of polycarbonates amounts to five million tons per year [94], part of which is already produced by ten thousand tons of CO₂ [19]. The plastic industry emits 360 MtCO₂ per year globally [97] and, assuming that polycarbonates could replace a considerable part, PC represents quite a promising CO₂-based product regarding its market size [98]. Besides, annual growth rates for polycarbonate production in China are set to increase by an estimated 10 % [20] with global sales of 3,000 to 4,000 USD/t ([94,99]), making CO₂-to-PC the most valuable process to enhance CO₂.

CO₂ conversion appears to be a relevant alternative to the conventional pathways producing PC and polyols. For PC, it consists in reacting phosgene (highly toxic) with other chemicals. In 2010, Fukuoka et al. counted 12 advantages of the CO₂ route compared to the phosgene one, including no wastewater, fewer material requirements, and smaller amounts of catalysts required [100]. Thus, the petrochemical industry is progressively abandoning the phosgene route in favor of CO₂. Roughly 0.132 Mt/y are estimated to be currently bound into polycarbonates

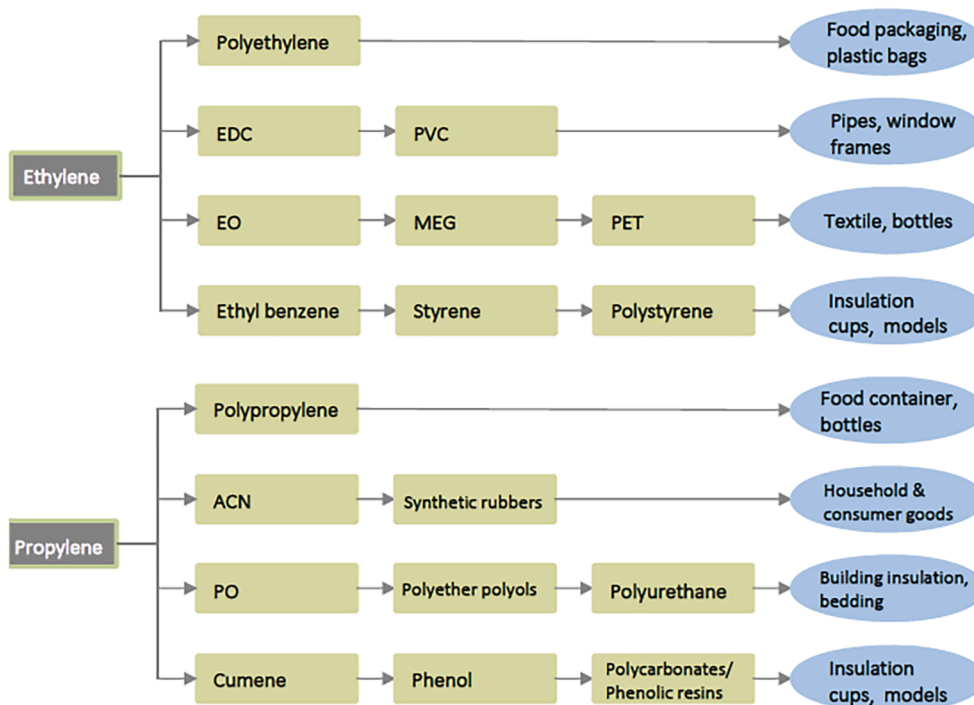


Fig. 3. . Product outputs of ethylene and propylene [87].

[101]. An LCA assuming a 20 % carbon content in polyethercarbonates estimates that the CCU route would reduce the global warming impact by 15 %, and could therefore use up to 1.6 Mt CO₂ per year [102], in line with the findings in 2019 of Kapetaki et al., who estimated that the CCU pathway in plastic production would reduce CO₂ emissions by 20 % compared to the conventional pathway [103].

Polyols – or glycols – are essential feedstock for polymer production such as polyester and polyurethane. Polyurethane foam was estimated to be the largest consumer of polyols in 2019 at 65 % [104] and the global production of polyol is estimated at 6.7 Mt per year. Polyol industrial production appears to be a niche market with a small volume for a high price in the range of €1,700/t [105]. A TEA and LCA study performed for a CO₂ pathway utilizing 232 kgCO₂ per ton of polyol produced [105] concludes that a CCU pathway enables a 70 % reduction in CO₂ emissions at the expense of five times more primary energy. Other studies show a rate of 0.31 kgCO₂ per ton of polyol [102].

Given the place of plastics in our society, the CO₂ routes seem attractive, since they enable at least a reduction in emissions from conventional processes. At best, the CO₂ can remain trapped in plastics for decades or centuries, depending on their end-of-life. The American Chemistry Council considers plastics as durable if their useful life exceeds three years, otherwise, they are considered non-durable. For instance, durable plastics are used in electronics, building materials and automobiles, while non-durable plastics are typically used for packaging [106]. The National Petroleum Council (NPC) states that “the possibility of using CO₂ as feedstock for polymers, followed by circular management practices (e.g., increased recycling), provides the potential to keep the CO₂ out of the atmosphere for longer periods compared to chemicals or fuels” [70].

CO₂ to fertilizers

Urea is the main component of the nitrogen fertilizer family, widely utilized in the agriculture sector, that can be produced from CO₂. 70 % of global fertilizer production is urea [107] and about 80 % of urea is used directly as a fertilizer [108]. Urea synthesis is currently the activity that uses the most CO₂ of all CO₂ utilization pathways, utilizing more than 150 MtCO₂/y [70] to produce 180 Mt of urea [107]. The utilization rate is roughly 0.7 tCO₂ per ton [109]. The market is expected to grow by 3 % per year which represents the setup of 6 new 1 Mt-urea-production plants each year, corresponding to population growth [110]. In 2019, Hepburn et al. argued that increasing urea production may have a negative impact on climate [22] and that fertilizers should move to harmless alternatives. Indeed, CCU for urea production is often criticized for its short-term sequestration of CO₂ estimated at a few days [111]: as soon as urea is spread onto fields, it reacts with water to form ammonia and CO₂ again. Subsequently, CO₂ is delivered to the atmosphere. Worse, the decomposition reaction is also accompanied by the oxidation of nitrogen, producing nitrous oxide N₂O, a greenhouse gas 300 times more active on the global warming effect than CO₂.

CO₂ to carbonates

Finally, the only pathway in which CO₂ is more likely to be removed from the atmosphere is CO₂-to-carbonates. Carbonates are solid compounds that are naturally present in the geosphere, or made by reacting CO₂ with a metal oxide MO where M is a divalent metal cation, typically calcium or magnesium ions [18]. Industrial waste from iron and steel, cement, aluminum, and pulp and paper industries can be recovered through the carbonation process, which is an interesting pathway considering that such waste has negative to low market prices [70]. If not mineralized with industrial wastes, CO₂ is reacted with rocks (serpentine or olivine) by roughly 1.6–3.7 tons of rock for 1 ton of CO₂ [98].

The applications of carbonate minerals are wide-ranging: fertilization [66], ceramics, paints, cosmetics, adhesives [70], and construction [112]. However, some of these utilizations result in the decomposition of the carbonate, and thus in CO₂ emissions (Fig. 5). Therefore, the

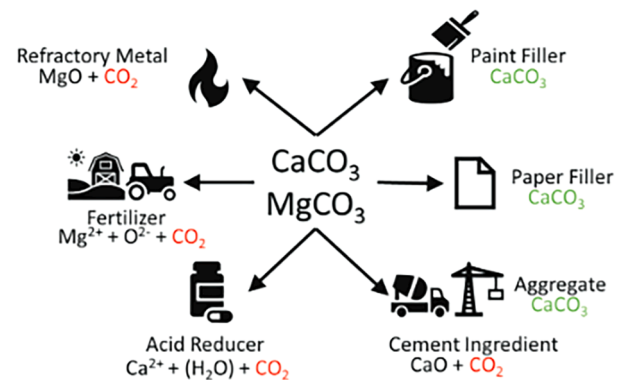


Fig. 5. Industrial application of carbonates and relative impact on the environment [18].

preferred pathways are carbonates used as paint fillers or paper fillers and for concrete manufacture. Since carbonates are more stable than CO₂, converting CO₂ to carbonates could permanently sequester GHG [98].

The direct mineral carbonation of wollastonite (CaSiO₃) to produce CaCO₃ could sequester about 50 Mt of CO₂ per year if the extraction of limestone were entirely replaced by mineral carbonation [86]. However, mineralization is an expensive CO₂ conversion process (\$60–100/tCO₂ removed) due to the large amount of heat and pressure required for the reaction to process [113]. Although the carbon mineralization of CO₂ into magnesite is not mature enough, some forecasts suggest that if applications are found, the demand for CO₂ to be mineralized could exceed 300 Mt/y in the coming years [20]. Mineral carbonation also has an advantage over pure CO₂ conversion because the CO₂ to be converted can come directly from the flue gas [114], thus not requiring expensive capture units.

Cement is mixed with water to form concrete but also to cure it, i.e. to enhance its strength and durability [115]. The curing of concrete through CO₂ injection consists in injecting both water and CO₂ into the cement so that a carbonation reaction occurs. Depending on the duration of the curing and the type of concrete, this operation can capture 24–43 m³ of CO₂ per m³ of concrete [116]. Assuming a density of CO₂ (resp. cement) equaling 1.98 kg/m³ (resp. 2400 kg/m³), and considering that the global market produces around 4.2 GtCO₂ annually [117], this could result in the sequestration of 83 to 149 MtCO₂ per year. Currently, the CarbonCure company claims to save roughly 15 kg of CO₂ per m³ of concrete.

Perspectives for CCU

Based on our overview of CO₂ utilization processes, only two types of CO₂-based product can durably sequester CO₂ over their lifetime and are suited to bringing negative emissions, namely plastics (polyols, polycarbonates, linear carbonates and cyclic carbonates) and carbonates (CaCO₃ and MgCO₃) for paper filling, paintings, cement manufacturing and concrete manufacturing. Concerning its direct utilization, CO₂ can be used within a closed loop in the form of solvents, refrigerants and working fluid for ECBM and geothermal recovery, but it is more difficult and hazardous to assess the extent to which such processes can be deployed. We call these pathways CCUNET because they capture, utilize and store atmospheric or biogenic CO₂, either inside processes or goods. Stemming from this analysis, Table 1 estimates the potential negative emissions that could be achieved utilizing CO₂. As it is much more difficult to make estimates for DUC processes, we subtotal the CCUNET potential between 139 and 458 Mtpa.

The majority of publications reviewing CCU options do not focus on CO₂ removal and negative emissions with the exception of Ref. [22]. In this publication, the authors estimated the removal potential in 2050 as

Table 1
Summary of CCUNET options and estimation of their negative emission potential.

CCUNET option	MtCO ₂ trapped/y	Ref	Uses
Calcium carbonate	50	[94]	Cement aggregate, paintings, papers
Polyurethane	4.5	[94]	Insulation panels
Polycarbonates	0.87 – 2.15	[94] - [118]	Plastics
Ethylene carbonate	0.1	[94]	Plastics
Propylene carbonate	0.086	[94]	Plastics
CO ₂ curing	83–400	[119]	Building materials
Subtotal	139–458		
Solvents	<1	[20]	Perfumes, chemicals
Refrigerant	–	[20]	Cooling
ECBM recovery	30–2701 ¹	[20,37]	Fuel
EGS	–	–	Power and heat

¹ The latter value was estimated according to the findings of Ref. [37] and the global production of natural gas (3,868 billion cubic meters) by BP assuming that all methane demand comes from ECBM recovery. The potentials for solvents, refrigerants, ECBM, and EGS are not included in the subtotal due to the high uncertainty involved.

between 5.8 and 23.1 GtCO₂ removed per year. This estimation takes into account non-conventional utilization pathways through bio-engineering techniques such as afforestation, biochar, or enhanced weathering. In the case of conventional utilization only (chemicals, building materials, and EOR), the potential is between 220 and 3,230 MtCO₂ removed per year. Our estimation of 139–458 MtCO₂ removed per year detailed in Table 1 is close to the latter but differs in many aspects. First, we consider only conventional use of CO₂ to which we add CDU pathways. We choose not to include the potentials for CDU in the subtotal due to the high ranges associated with ECBM and refrigerants. Second, our estimation is based on current global demands for goods. It does not consider how demand could evolve in 2050. Third, our estimation provides more details on the CO₂-to-chemicals pathways.

The exploration of various CCU pathways reveals that the targeted markets are extraordinarily complex to comprehend. They are multi-dimensional chains subject to global production and prices, CO₂-intense processes, energy-intense processes, process costs, social benefits, technology readiness levels (TRL), and storage lifetimes. Considering this wide variety of attributes and specificities for each route, a sustainable and beneficial future of CCU is hard to design and forecast. The latter estimation is made up of the current market sizes and assumes that all demands are satisfied thanks to CO₂ utilization processes, which is not quite realistic. Therefore, we looked at the results of prospective

energy models. Prospective energy models aim at representing these complex chains by integrating them into an energy system that makes explicit the links of every block of the chain and projects the future development of these systems, considering climate and environmental policies, in order to give insights on the best technologies to deploy [120–122]. The aim is to understand the debate on what role CCU can play in the energy transition. Notably, interpreting the results of prospective studies allows us to assess the value of CCU as a NET. Based on a former publication in which we provided a state of the art of CCU modeling [123], we browsed the scientific literature by selecting studies with keywords such as “negative emissions”, “CO₂ utilization”, “CCU”, and “energy models” in different combinations. Moreover, we investigated the IAMC database which lists global energy models [121]. We found that only six studies or models are able to draw a future of CCU in the context of climate mitigation policies, utilizing energy models. Those models are reported in Table 2.

We note that a few energy models 1) represent the use of CO₂ in their framework [123], 2) allow the solver to choose CCUNET solutions, and 3) observe in their outputs the deployment of CCUNET, even under climate constraints. On the first point, CCU is not a common option represented by energy modelers mainly due to the lack of data [124]. Modelers prefer technologies such as nuclear, biomass, renewable electricity generation through wind and solar, hydrogen and CCS, as considerable information can be found in the literature. We count 22 models that include CCU as an alternative. On the second point, as explained in the previous section, the selection criteria are that the model represents the capture of CO₂ from biomass or directly from the atmosphere (DAC) – which is not systematic in energy modeling – and that the production of CO₂-based products involves long-term carbon sequestration. Even when it is considered, the potential for CCUNET deployment is either difficult to retrieve in the published results or not reported at all because of null values.

One study gives a promising potential of CO₂ conversion into calcium carbonate of up to 5.4 MtCO₂ per year, for the UK alone [127]. This results from a cost-optimal design of CCUS value chains in the UK, whose objective is to mitigate 6.4 MtCO₂pa, and CO₂-to-carbonates is the preferred option. CCU thus contributes 84 % of this target. CO₂ is certain to be trapped into calcium carbonate when it is used as a paint filler, paper filler, or aggregates (Fig. 5), but the modelers provide no insight on the end-use of CaCO₃ except that part of it is exported and sold. In addition, there is no information on the origin of CO₂. There are different CO₂ point sources considered in the model taken from Ref. [130], including biomass power plants. Potentially, part of the captured CO₂ is bio-based, which is eligible for negative emissions. In such a case, the results report a substantial amount of negative emissions through CCU and the model prefers the CCU route to the CCS route,

Table 2
Energy models allowing CCUNET as a solution for the future of energy systems Bold characters refer to possible options for CCUNET pathways.

Ref.	Model	Region	Time horizon	Climate target	CO ₂ capture options	CO ₂ utilization options	CCUNET results
[125]	Technology Choice Model	World	2030	Decarbonization of the chemical industry	Industry; DAC	Power-to-Gas; Methanol; Olefins; Polymers	Estimated between 1.1 and 2.2 GtCO ₂ pa utilized
[126]	No name	Europe	2050	Decarbonization of the chemical industry	Power plants; Industry; Biomass; DAC	Urea; Methanol; Power-to-Gas; Power-to-Liquids; Plastics	Unknown
[28]	IEA ETP	World	2060	75 % cut in CO ₂ emissions compared to 2017 levels	Industry; DAC ; Power plants; Biomass ; Hydrogen	Urea; Methanol; Concrete ; Other chemicals; Plastics ; Power-to-Gas; Power-to-Liquids	0
[127]	No name	UK	2030	6.4 MtCO ₂ /yr emissions reduction	Not stated	Methanol; Power-to-Gas; Polyurethane ; Horticulture; Concrete ; Calcium carbonate	Unknown
[128]	COFFEA-TEA	World	2100	N/A	Power plants; Hydrogen; Industry	EOR	Unknown
[129]	No name	North-East China	NA	70 MtCO ₂ /yr emissions reduction	Power plants; Industry; Biomass	EOR	Unknown

thanks to CaCO₃ sales. This raises the question of importation dependence, and one can wonder whether the results would be the same if the importing countries produced their own calcium carbonate.

The IEA studied the following three scenarios under the Energy Technology Perspectives (ETP) model that are:

- The Reference Technology Scenario (RTS) acting as a *business-as-usual* scenario.
- The Clean Technology Scenario (CTS) aiming at a 75 % cut in CO₂ emissions compared to current levels.
- The Limited CO₂ Storage (LCS) scenario in which the total cumulative CO₂ storage is limited to 10 GtCO₂pa.

However, no CO₂-based products are in the output of these scenarios. Naturally, the CCU route is never an alternative in the RTS, as there is low motivation for the model to choose expensive CO₂ conversion technologies. Thus, the use of CO₂ follows the current demands of the market, mainly for urea production. In the CTS scenario, the quantity of CO₂ stored highly dominates the total amount of CO₂ captured, but the LCS scenario shows that the availability of CO₂ storage is a crucial driver for the deployment of CO₂ utilization.

In the European chemical energy system, Bazzanella and Ausfelder (2017) explored the potential benefit in CO₂ emissions reduction from CO₂ conversion processes, including CO₂-to-plastics as an option. The results show that, for a decarbonization constraint applied in 2050, 100 % of the CO₂ feed is converted into methanol, which is either sent directly to the market or used to produce ethylene, propylene and aromatics. None of the latter are intrinsically suitable for negative emissions but part of the propylene and ethylene will be converted into plastics, without any insight into the dedicated shares or the CO₂ origin – although biogenic or fossil-based are modeled [126].

In the COFFEE-TEA model [128], the documentation features CO₂ usage as a working fluid for recovering oil. This documentation does not mention the capture units represented and we found no papers describing CCUS value chains for this model. However, one can imagine that the CO₂ injected comes from biomass or DAC to recover oil. The same assumption can be made in the model by Zhang et al. [129].

Five of the six models found perform a cost minimization to obtain their results, meaning that the results are mostly based on cost competitiveness. However, one study performs a minimization of GHG emissions [125] resulting in much more optimistic results for CCUNETs. According to the two scenarios considered, the amount of CO₂ utilized varies from 2.77 to 3.72 GtCO₂ of which roughly 40 % is effectively used to manufacture polymers, hence the estimation of 1.1 to 2.2 GtCO₂pa used and stored in the final product.

Thus, of the six models representing the CCUNET options, only one gives potentials for negative emissions in its results.

Discussion

The review of CCUNET pathways demonstrates that achieving negative emissions through the utilization of CO₂ is not an easy task. The concept itself – which requires capturing climate-neutral CO₂ and the long-term sequestration of CO₂ in the final product or process – is challenging. First, the capture of atmospheric CO₂ is not commercially available and is already known to be very expensive [24,131]. As for the capture of biogenic CO₂, its climate-neutrality is questionable, especially because of the delay in CO₂ uptake by biomass, the change in albedo due to harvesting, and the changes in soil carbon [132]. These factors make up the carbon debt of biomass. The balance between the uptake of CO₂ from biomass and the GHG emissions incurred from growing the biomass needs to be negative to ensure the sequestration of biogenic CO₂ truly removes CO₂ from the atmosphere. In terms of utilization, the duration of sequestration is also critical. In the latter part of our review, we argued that the CO₂ used to manufacture plastics is sequestered for a sufficiently long time period to allow negative emissions. Indeed, CO₂

can be sequestered in plastics for decades [22]. However, a recently published paper has raised concerns about the GWP factors involved in temporary storage of CO₂ in CCU products using a 100-year time horizon [133]. The authors calculated that the CO₂ stored between 10 and 50 years has a GWP of 0.85 and 0.42 respectively. Together, these factors compromise the effectiveness of negative emissions with CCU. Besides, other challenges need to be addressed in order to achieve negative emissions:

1. Large amounts of energy are required to capture CO₂ and use it. This energy must be CO₂-free to ultimately achieve negative emissions. Today, the production of electricity and heat is becoming cleaner in some regions of the world but remains carbon-intensive globally [134]. However, it may be more efficient to prioritize these new clean production assets in sectors such as road transportation and residential heat pumps. In Table 2, Ref. [125,126] explore the impact on the energy system due to CCU deployment, and both conclude that CO₂ conversion processes put intense strain on the energy system. While CCU is deployed broadly in their scenarios, they report that the global generation of hydrogen should be multiplied by 5 to 8 compared to current levels [125], and that European demand for low-carbon power is set to exceed the total low-carbon power available in 2050, as predicted by the IEA [126]. The stress on the energy system would be much higher if all of the CO₂ transformed in these studies were atmospheric or biogenic.
2. Deploying CCUNET could be extremely costly, especially due to the high costs incurred in the capture of climate-neutral CO₂ [5,24]. On the utilization side, some pathways are already profitable such as building materials and EOR [22], and others such as plastics may be in the future [135,136].
3. CCUNET routes can have a significant impact on land if the captured CO₂ is biosourced. BECCS is often criticized for the large areas required to grow biomass, and the possible impact on food prices [137,138].
4. No leakages should occur – or at reasonable rates. This is even more true in the case of DUC processes, and especially during the decommissioning phase of the process. One can imagine that the remaining CO₂ could be sold or transported by truck for geological storage when a facility closes.

Thus, a handful of CO₂-based products exist that can bring negative emissions, but they are not ready yet because of their low maturity – notably for plastics, the lack of demand, and their reliance on other technologies and breakthroughs. Besides the resolution to increase the TRL of CO₂ conversion technologies, it is crucial to assess the environmental advantage of deploying and replacing CO₂ utilization plants compared to the continued use of traditional plants. Researchers have made an urgent call for LCAs on CCU processes to establish the potential of CO₂ utilization routes to reduce emissions [103,139].

We argue that all of these drawbacks linked to CCUNET could explain why researchers do not implement CCUNET options in their models. Our estimation of CCUNET potentials from global markets and the estimations from prospective models reveal that the prospects for CCUNET deployment are uncertain and quite limited. Apart from the low feasibility of generating negative emissions with CCU at present, models exploring the future of energy systems see poor potential for CCUNET deployment. As a matter of fact, we found no models that intentionally studied the role and potentials of CCU as a NET. The aforementioned obstacles may hinder the motivation of modelers who do not trust CCUNET to bring negative emissions. Another simple explanation of the poor representation of CCUNET in energy models is that there is very little information and data about these processes, which make it difficult to implement them in energy models. When modeled, CCUNET options rarely penetrate the energy mix, mainly because the models employed optimize the cost of energy systems. If the value added from CO₂ conversion cannot cover the cost of producing

CO₂-based products or services, there is little chance that the CCUNET options will be deployed. On the contrary, CCUNET options can represent a promising set of technologies that would reduce the overall cost of generating negative emissions. Thus, there may be a need to better represent the CCUNET value chains in energy models in order to validate or invalidate the need to use these technologies to reach the NZE target. The modeling paradigm is also of great importance: Table 2 shows that the results can vary widely depending on whether the model performs a cost minimization or a GHG emissions minimization.

CCUNET is interesting only if it can bring significant amounts of negative emissions. Considering the market size of the eligible products and sequestration durability, attention should be paid to building materials. Nonetheless, if the aim is to generate negative emissions, CCUNET should be compared with BECCS and DACS. In a cost perspective, as long as transporting and storing CO₂ underground is cheaper than utilizing it, then DACS and BECCS are more interesting than CCUNET options. The same conclusion could be drawn regarding the energy requirements. In terms of efficiency, the geological storage of CO₂ ensures a permanent sequestration of CO₂, which is not the case for CCUNET. Besides, much larger negative emissions can be achieved with BECCS and DACS because they are not constrained by the markets, but rather by storage capacities. In many studies, the estimations of CO₂ storage capacities have proved to be large enough whatever the global decarbonization scenario [4,13,140]. However, if the geological storage of carbon is not available, then higher amounts of CO₂ need to be utilized. This is also related to social acceptance of carbon sequestration, which has been proven to be much lower than for CO₂ utilization [141,142]. In addition, CCUNET has the advantage of generating negative emissions and consumptions goods simultaneously, just as

BECCS does with electricity, while DACS only removes CO₂ from the atmosphere. This means that stakeholders of CCUNET projects could generate profits both from the industrial product manufactured and the negative emissions it contains. Overall, we believe that there is no silver bullet to generate negative emissions if they are to be deployed globally. Although CCUNET faces many hurdles, negative emissions would be generated from a mix of NETs, depending on geographic disparities among regions due to social acceptance, CO₂ storage capacities, biomass availability, land availability, economics, and low-carbon electricity affordability. Furthermore, the production of negative emissions should also be discussed with other non-conventional alternatives provided by nature-based solutions such as afforestation or enhanced weathering.

In reviewing the different options concerning the use of CO₂, we became aware of a confusion stemming from the general term CCUS. Regrettably, the term ‘CCUS’ generally embodies two antinomic fates: the capture then sequestration of CO₂ (CCS), and the capture then use of CO₂ (CCU), with no information on the origin of the CO₂. The former aims at abating CO₂ emissions from processes where other mitigation options are not feasible. CCS is especially a relevant technique to abate inevitable CO₂ emissions generated by the industrial sector [143,144]. The latter – CCU – is intended more to produce goods, but it is still part of the mitigation portfolio, notably due to its capability to decarbonize the aviation sector, its lower water-intensiveness compared to fossil fuels [145], and to lower the costs of capture, which could bring about a large deployment of CCS facilities. In some cases, the CO₂ remains trapped in the final product, therefore we can truly call it Carbon Capture Utilization and Storage, or CCUS, although this route clearly does not dominate the debate. The durable sequestration of CO₂ in products seems to be a bargain but not an end for CCU. As a result, we argue that

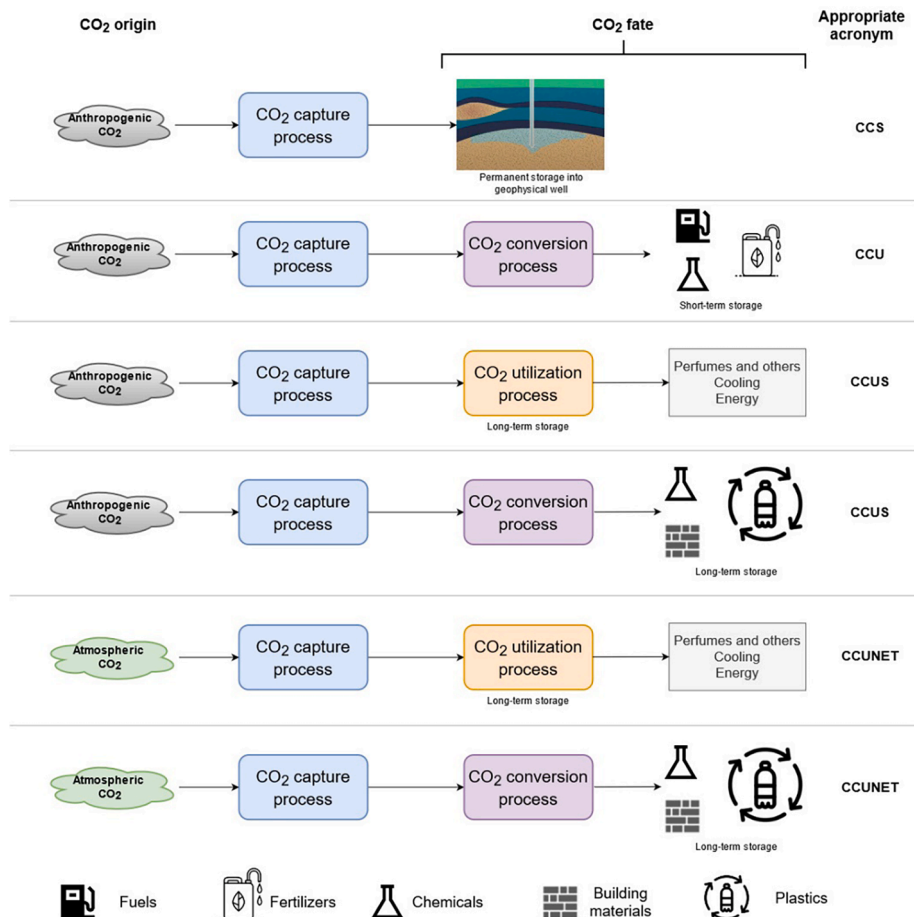


Fig. 6. . Correct acronyms for CCUS, N.B.: The CCUNET acronym refers to goods with long sequestration durations produced from atmospheric or biogenic CO₂.

CCS, CCU, CCUS and CCUNET should be treated separately in the debate because their outcomes and benefits are different. Fig. 6 below proposes a clarification of the acronyms and relates them to their appropriate value chain.

Conclusion

In the face of the growing need to remove CO₂ from the atmosphere in order to achieve the NZE target, attention is turning to NETs and especially to DACS and BECCS. Conceptually, a third option is possible, which consists in using and storing CO₂ in products or processes, which we call CCUNET. Carbon capture and utilization comprises a set of technologies that provide alternative processes to manufacture industrial goods in which CO₂ can be stored. Due to this opportunity of storing CO₂ inside a product, CCU can deliver negative emissions if the consumption of the good does not release the stored CO₂. Unfortunately, most of the end-products that CCU offers do not have this specific feature. Thus, urea, fuels, some chemicals, and certain direct utilizations of CO₂ such as EOR, are disqualified. However, calcium carbonate aggregates, CO₂ cured concrete, solvents (supercritical CO₂), ECBM, refrigerants, plastics, and some chemicals are good candidates. Other candidates for negative emissions include utilizing supercritical CO₂ as a working fluid to recover methane from coal beds, or heat from geothermal systems. Thus, we identify eligible CO₂-based products with which negative emissions are possible. If deployed, these value chains could be a game-changer in the energy transition for their capability to generate value and mitigate climate change. However, the current markets do not provide large opportunities for CCUNETs. Given the low representativeness of these value chains in energy models, coupled with the complexity of CCUNET and the numerous dependencies and impacts to which it is subject, the technique does not appear to be a future solution for generating negative emissions significantly. Nonetheless, when modeling negative emissions through CCU, the competition between CCUNET, DACS and BECCS might be worth discussing.

CRedit authorship contribution statement

Lucas Desport: Conceptualization, Methodology, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Sandrine Selosse:** Conceptualization, Supervision, 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

No data was used for the research described in the article.

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