Norkobilov Adham (Orcid ID: 0000-0002-8664-5306)
Kamolov Azizbek (Orcid ID: 0000-0002-7402-0691)
Variny Miroslav (Orcid ID: 0000-0001-6163-7273)
Fallanza Marcos (Orcid ID: 0000-0003-3834-5787)

Zafar Turakulov (ORCiD: https://orcid.org/0000-0002-8664-5306, e-mail: webdastur@gmail.com
Azizbek Kamolov (ORCiD: https://orcid.org/0000-0002-7402-0691, e-mail: azbkamolov@gmail.com)
Adham Norkobilov (ORCiD: https://orcid.org/0000-0003-2112-1365, e-mail: adham.norkobilov@gmail.com)
Miroslav Variny (ORCiD: https://orcid.org/0000-0001-6163-7273, e-mail: miroslav.variny@stuba.sk)
Guillermo Díaz-Sainz (ORCiD: https://orcid.org/0000-0002-8687-300X , e-mail: guillermo.diazsainz@unican.es)
Lucia Gómez-Coma (ORCiD: https://orcid.org/0000-0001-7586-6552 , e-mail: lucia.gomezcoma@unican.es)
Marcos Fallanza (ORCiD: https://orcid.org/0000-0003-3834-5787, e-mail: marcos.fallanza@unican.es)

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Assessing Various CO_2 Utilization Technologies: A Brief Comparative Review

Zafar Turakulov [1,4,‡], Azizbek Kamolov [1,4,‡] , Adham Norkobilov [2,a] , Miroslav Variny [3] , Guillermo Díaz-Sainz [4], Lucia Gómez-Coma [4] & Marcos Fallanza [4]

[1]Tashkent Institute of Chemical Technology, Department of IT, Automation, and Control, Tashkent, 100011, Uzbekistan
[2]Shahrisabz branch of Tashkent Institute of Chemical Technology, Department of Engineering Technologies, Shahrisabz, 181306, Uzbekistan
[3]Slovak University of Technology in Bratislava, Department of Chemical and Biochemical Engineering, Radlinského 9, 812 43 Bratislava, Slovakia
[4]Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Avenida de los Castros s/n, 39005, Santander, Spain

‡ These authors contributed equally to this work and shared first authorship.
a Corresponding author, e-mail address: adham.norkobilov@gmail.com

Abstract: Carbon dioxide (CO_2) utilization technologies have emerged as a promising approach to address the direct and indirect consequences of climate change and the need for sustainable resource management. Those innovative technologies aim to capture and utilize CO_2 by converting it into valuable products or directly using it as a chemical feedstock in various industries, thus, avoiding their release into the atmosphere. In this study, different CO_2 utilization pathways including CO_2 to chemicals and fuels, CO_2 to building materials, CO_2 to enhanced oil recovery (EOR), and CO_2 to bio-products are discussed in terms of their status - economical, environmental, and technology readiness level performances. Moreover, various CO_2 utilization pathways are comparatively analyzed considering their advantages and drawbacks, CO_2 uptake potentials, and overall climate benefits. According to the comparison results, photocatalytic and electrochemical reduction of CO_2 along with the bio-fixation of CO_2 are gaining more attention in the recent research and investigations from the energy intensity and environmental point of view, while EOR still dominant in terms of the scalability, maturity, and economical benefits. However, limitations of EOR related to the capacity, life cycle, and different geolocations, as well as the complexities of other mature approaches make room for emerging technologies to be more energy-effective and environmentally friendly. Overall, most of the promising CO_2 utilization techniques are either technologically immature or limited in scale to deploy globally. One of the main barriers to reusing CO_2 is associated with the high cost of CO_2-based production and the low value of the CO_2 market.

Keywords: Climate change, carbon reduction, CO_2 conversion, CO_2 utilization, market size, maturity, CO_2 uptake

Nomenclature

CCSU	Carbon capture, storage, and utilization
COP	Conference of the Parties
EOR	Enhanced oil recovery
EGS	Enhanced geothermal systems
EGR	Enhanced natural gas recovery
ECBM	Enhanced coal bed methane
IE	Industrial ecology
F-T	Fischer-Tropsch
ER	Electrochemical reduction
PR	Photochemical reduction
SNG	Synthetic natural gas
DMC	Dimethyl carbonate
DME	Dimethyl ether
DRM	Dry reforming of methane
TRL	Technology readiness level
RWGS	Reverse water gas shift reactions

1. Introduction

Carbon dioxide (CO_2) is non-flammable, colourless, and odourless gas in the ambient conditions. Its greenhouse effect in the atmosphere plays an important role in maintaining the heat balance of the planet within the habitable range. CO_2 is also a key component for the existence of flora and fauna through the natural photosynthesis and respiration processes. However, excessive amounts of CO_2 in the atmosphere can lead to the retention of more heat on Earth, causing a rise in the average global temperature, thereby contributing to global warming, the main part of climate change[1]. Compared to the pre-industrial level, the concentration of CO_2 in the atmosphere increased by 50% reaching 421 parts per million (ppm), equivalent to nearly 1 °C increase in the global average temperature [2]. Those numbers can increase as high as above 1300 ppm and 4 °C by 2100 leading to catastrophic, devastating consequences of climate change, if no actions are taken to reduce the greenhouse gas emissions [3].

In order to withstand climate change impacts, a global consensus, the so-called Paris Agreement was adopted by 196 countries in December 2015 limiting the average global temperature rise below 2 °C above pre-industrial level [4]. Concerning the 2 °C scenario adopted in the Paris Agreement, the goal of 1.5 °C was set in the 26th "Conference of the Parties" (COP) in Glasgow 2021 [5, 6] to reduce the risks associated with higher temperature rise. Furthermore, the COP27 event, which took place in Egypt in 2022, came with the agreement of "Loss and damage" fund [7] to aid the most climate-vulnerable places worldwide by large emitting countries, while the COP28 meeting in Dubai highlighted the path to decarbonization through a transition to renewable energy and the integration of CO_2 capture, storage, and utilization (CCSU) technology [8].

Since the fossil fuel-based energy, industry, and transportation sectors are principally the largest CO_2 emitting sources [9], the decarbonization of those sectors is considered the main target to meet the net zero emission requirements.

In this context, as mentioned in COP28, renewable energy transition strategies in combination with CCSU technology implementation can be promising options for global climate change abatement [10, 11]. Thus, nowadays, the majority of the research and investigations are focused on CCSU applications, making it a prominent subject of interest.

CCSU is a technology designed to combat climate change by reducing CO_2 emissions from large point sources such as power generation and industrial processes [12-14]. The typical CCSU process is based on three stages which include separating the CO_2 from gas mixtures in the power plants and industrial facilities, storing the captured CO_2 deep underground in geological formations, and using the CO_2 in other applications through physical and chemical CO_2 utilization pathways [15].

The CO_2 capture process is divided into three methods including pre-combustion, post-combustion, and oxy-fuel combustion. In pre-combustion approach, CO_2 is separated from syngas mixtures, which mainly comes from the gasification process before the fuel is burned. In the case of post combustion method, the CO_2 is separated after the combustion process from the flue gases which might typically consist of CO_2, carbon monoxide (CO), nitrogen (N_2), water vapor (H_2O), oxygen (O_2), and other trace amount of nitrogen and sulfur oxides (NO_X, SO_X). As for the oxy-fuel combustion technique, the fuel is burned with oxygen resulting in the only two components in the flue gas, water vapor and CO_2. The CO_2 is then easily separated through condensation of water vapor. However, unlike post-combustion, oxy-fuel and pre-combustion methods are required to retrofit the existing combustion block of the plants [16-19].

In terms of CO_2 utilization, the major purpose is to build a human-caused carbon cycle in which the captured CO_2 can be converted into useful products or raw materials for another industry. In this case, it is possible to capture and reuse the CO_2 multiple times in the cycle preventing the emission of a new CO_2 source into the atmosphere at the same time [20]. CO_2 utilization techniques are principally divided into two – conversion and non-conversion – categories [21, 22]. Chemical (conversion) and physical (non-conversion) routes of CO_2 utilization are provided in Figure 1.

In the non-conversion approach, the molecule of CO_2 physically remains in its state without any change and is used as pure or in mixtures. The application of the physical route of CO_2 utilization includes several direct and indirect uses including dry ice, refrigerant, fire extinguisher, carbonated beverages, solvent, welding medium, and power via supercritical CO_2 cycle, extra oil in enhanced oil recovery (EOR), enhanced natural gas recovery (EGR), heat via enhanced geothermal systems (EGS), enhanced coal bed methane (ECBM), etc. [23, 24]. No matter how the majority of non-conversion use of CO_2 is limited in scale and small impact on CO_2 abatement, EOR using CO_2 has already been put into practice on a large scale, particularly in the USA and Canada [23-25].

In the conversion pathway, the CO_2 molecule is used in a chemical reaction as a feedstock, which converts to valuable chemical products and fuels. Various products come from CO_2 by catalytic or non-catalytic chemical reactions including calcium carbonate, polypropylene carbonate, formic acid, syngas, urea, cyclic carbonate, salicylic acid, acetylsalicylic acid for direct application, and indirect application involves polyurethane, algae biofuel, Fischer-Tropsch (F-T) products, dimethyl ether (DME), dimethyl carbonate (DMC)[21-23]. One of the main drawbacks of the conversion technique is that it is not mature enough and is significantly energy-consuming. Nevertheless, since this method is appearing as the key to a zero-emissions future, it is gaining progressive interest and support from manufacturers, investors, and governments [20, 21, 24].

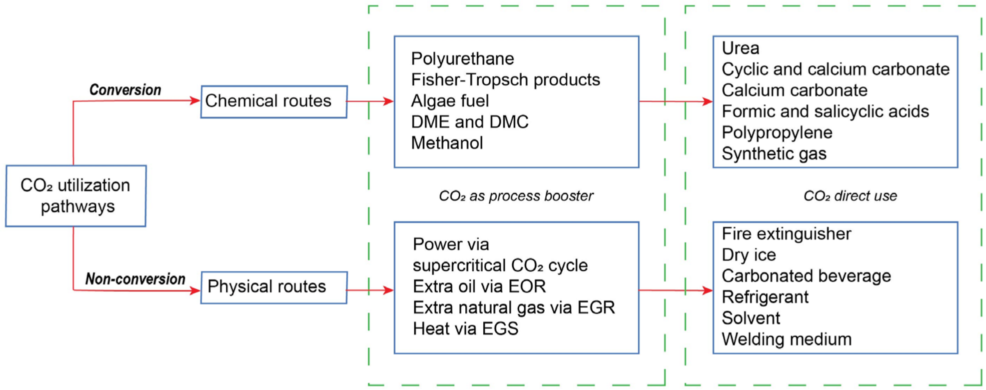

Figure 1. CO_2 utilization pathways by categories (Based on [23]).

Another option to contribute to CO_2 emissions reduction is industrial ecology (IE) which means organizing process integration among plants based on technical, environmental, and economic aspects to minimize waste and transportation costs [26]. Switching the industry from an open loop to a closed-loop where the waste of one process is utilized as inputs for another process is the simplified concept of IE [27]. There are numerous benefits-improved environmental protection, profits from waste and by-product sales, and cost-savings (from the material, licensing, and disposal fees) — connected with IE systems [28]. Apart from those benefits, the usual way of thinking in society about conventional linear systems and industry needs to be replaced by closed-loop systems ideology [29]. In addition, the concept is relatively infant, and deployment of the existing industrial facilities is almost impossible due to the challenge linked to geolocations and technical issues.

In the current critical condition of increasing anthropogenic CO_2 emissions, CCSU plays a vital role in the reduction of greenhouse gas effects on global warming. Therefore, the scientific community worldwide also focused on the research and investigations of CCSU technology. Since the main problem for the global application of this technology is associated with the low market value of captured CO_2, there is a significant demand for further investigations of CO_2 valorization and utilization pathways. This paper also focuses on the discussion of possible CO_2 utilization pathways, their applicability, opportunities, and challenges, as well as their social, economic, and environmental concerns.

This review paper offers a timely contribution to the field of sustainable carbon management and circular economy. While numerous studies exist on individual CO_2 utilization approaches, this paper stands out for its broad understanding and comparison of a diverse array of various CO_2 utilization pathways. By examining several routes for CO_2 recycling, the paper provides an update on the recent development and technology readiness level (TRL) of the different pathways and their overall carbon reduction potentials. From this perspective, this paper enables researchers, policymakers, and industrial stakeholders to make informed decisions in shaping effective strategies for the acceleration of the transition toward a sustainable zero-carbon future.

In terms of the outline for this study, a brief overview of recent publications and trends on CO_2 utilization technologies is provided through a bibliometric survey in Section 2, followed by Section 3 in which each of the major CO_2 utilization techniques is introduced. In Section 4, an assessment of different CO_2 utilization technologies about their main challenges and opportunities, market size, TRL, CO_2 uptake potentials, and other environmental benefits are discussed.

2. Recent research trends and challenges in CO_2 utilization

Recent research trends and challenges are reflected by short bibliometric surveys by analyzing the number of published papers and their research directions in the scientific databases. A bibliometric survey helps to identify the scientific tendency systematically in which areas of research are being focused more and which of those investigations have more potential in the future prospects. Therefore, published research articles in the literature are used to summarize the recent and prospective research tendency in the field of CO_2 utilization.

Scopus web search engine (https://scopus.com/search) was used to search the related research papers on CO_2 utilization. Scopus is Elsevier's abstract and citation database which covers around 35k peer-reviewed journals from more than 10k publishers [30]. This search for articles was carried out in June 2023 using the related keywords. Search result data was obtained in RIS format and entered into VOSviewer software which has been considered as a valuable tool to make a bibliometric analysis. The following keywords were used to search appropriate data with OR function: 'CO_2 utilization', 'CO_2 to fuel', 'CO_2 to chemicals', 'CO_2 enhanced recovery', 'CO_2 market', 'CO_2 bio fixation', and 'CO_2 mineralization carbonation'. The search result was limited to only the recently published or publishing original papers in 2022 (9496), 2023 (5461), and 2024 (9) written in the English language from four different subject areas including 'Chemical engineering', 'Engineering', 'Environmental engineering', and 'Material science' (see Figure 2).

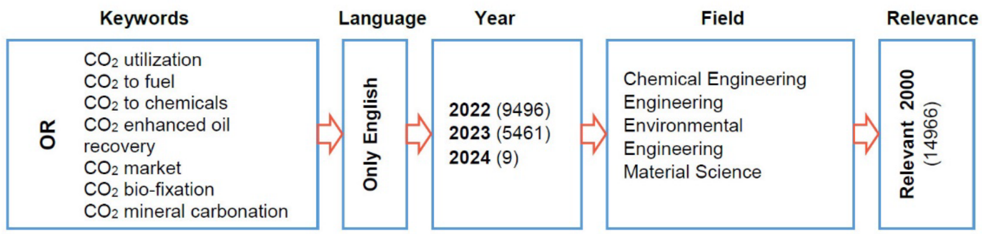

Figure 2. Data search criteria and limitations for the creation of network visualization map.

The most relevant 2000 articles were selected out of 14966 papers after the limitations. Based on the 307 keywords that were co-occurred at least 20 times, a network visualization map was created shown in Figure 3.

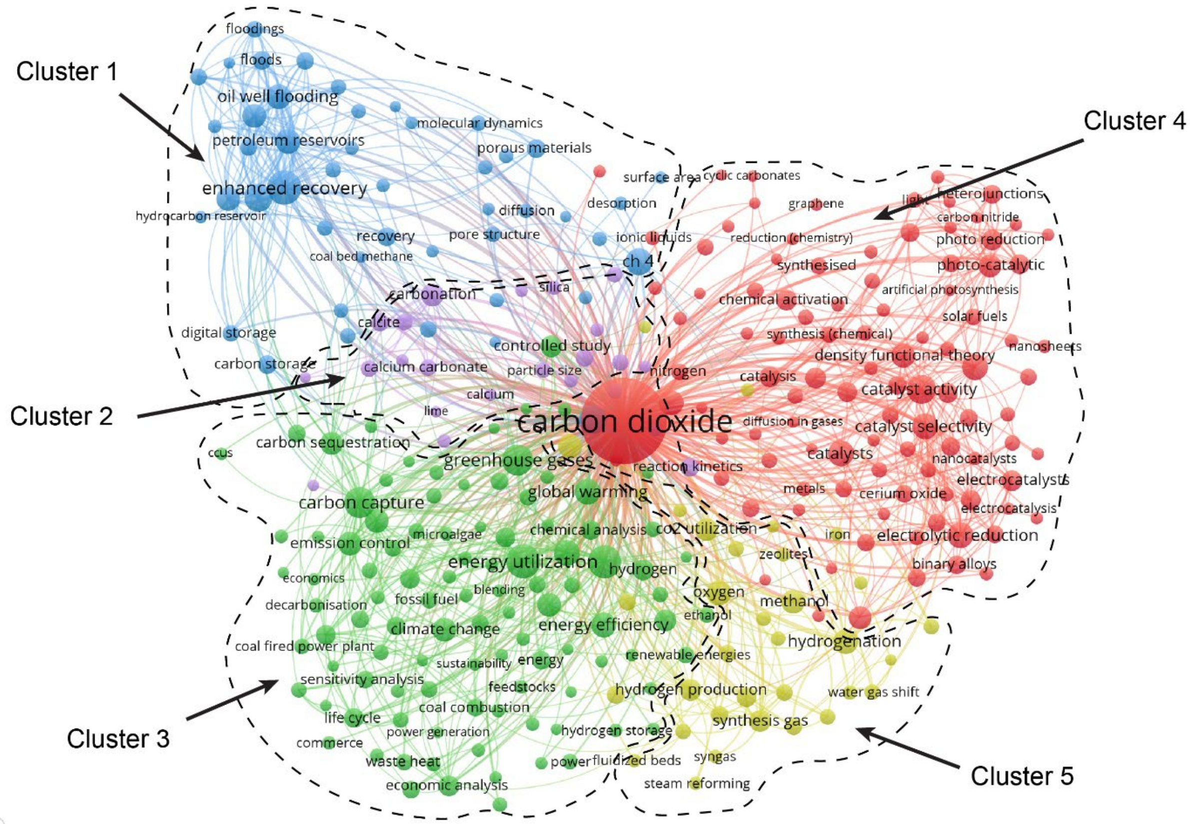

Figure 3. Keyword co-occurrence network visualization of search results and their clusters.

In Figure 3, the network visualization map in 5 clusters via 5 different colors are represented. The specific keywords are shown with nodes and arcs indicating co-occurrences of those keywords. Cluster 1 stands for CO_2 direct use as a boosting agent through injection into the reservoirs with EOR, EGR, and ECBM. The co-occurrences of process life cycle and efficiency, economics, and impact assessments are represented by green color in Cluster 3 which has been most investigated in recent years together with Cluster 1, and Cluster 4 reflecting the catalyst-based research. In contrast, syngas production, CO_2 hydrogenation, and hydrogen production-based works in Cluster 5 were studied less in Cluster 2 which covers the carbon mineralization area. Overall, recent scientific tendencies and futuristic prospects of CO_2 utilization can be focused on finding good catalysts and improvements of the existing ones to intensify CO_2 to chemicals and fuels processes, while enhanced commodity production, its process economics, and efficiency with the life cycle assessment will probably stay in the priority.

3. CO_2 utilization pathways for decarbonization of power and industrial sectors

3.1. CO_2 to chemicals and fuels

As mentioned in the introduction, CO_2 can be utilized in two – direct and indirect – categories. The conversion process goes under high temperature to break the bond between C and O_2 at 394 kJ per mole of CO_2 based on Gibbs free energy formation as CO_2 is an inert molecule but the use of renewables can contribute to reducing additional CO_2 release. Novel catalysts are also needed to increase the rate of the reaction. There are more than 150 products, particularly fine chemicals, that can be produced by CO_2 conversion although most of them attract a very limited amount of market [31]. Methanol, however, is considered the most efficient reactant among others such as formic acid/formate, methane, ethanol, F-T products, etc., in the production of ethylene, propylene, DMC, and aromatic hydrocarbons [32, 33]. In addition, urea production utilizes CO_2 with ammonia, which has already been commercialized and implemented on the largest scale so far.

CO_2 to chemicals and fuels conversion process can be a single or multiple-step process until the final product is obtained. There are several CO_2 syntheses pathways such as CO_2 hydrogenation, reverse water gas shift reaction (RWGS), CO_2 methanation or Sabatier reaction, electrochemical reduction (ER) of CO_2, photochemical reduction (PR) of CO_2, and dry reforming [34-36]. There are many routes to convert CO_2 into a valuable product, some types of overall reactions and descriptions of CO_2 to chemicals and CO_2 to fuel pathways are provided in Table 1.

Table 1. Overall reactions of some CO_2 to chemicals and CO_2 to fuels pathways (Based on [34, 35, 37-39])

Product	Main chemical reactions	Comments	Applications
		CO_2 – based fuel (gaseous and liquid)	
Methane	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ ***R1***	When the H_2/CO_2 ratio equals to 4, methane formation occurs through the Sabatier reaction ***R1***. Between 200–250 °C, CH_4 and H_2O are the main products. Above 450 °C, the formation of CO by-product increased due to the RWGS reaction.	Synthesized methane can be used as fuel and a precursor for the creation of additional chemical compounds.
Methanol	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ ***R2*** $CO_2 + H_2 \leftrightarrow CO + H_2O$ ***R3*** $CO + 2H_2 \leftrightarrow CH_3OH$ ***R4***	CO_2 can directly be transformed into methanol via ***R2***. The indirect path is that CO_2 is converted into CO and water with renewable hydrogen by RWGS ***R3*** reaction followed by additional H_2 and subsequent methanol production by F-T reactions ***R4***.	Methanol serves as an alternative fuel, functions as a widely used solvent, and serves as an intermediate in the chemical industry.
Ethylene	$2CO_2 + 2H_2O \leftrightarrow C_2H_4 + 3O_2$ ***R5***	In an electrochemical process conducted in an aqueous solution, CO_2 undergoes selective conversion to ethylene at the cathode, while simultaneously, oxygen gas evolves at the anode ***R5***.	Ethylene can be used in several applications such as fuel or fuel additive, fruit/plant ripening, polymer industry, etc.
Ethanol	$2CO + 4H_2 \leftrightarrow C_2H_5OH + H_2O$ ***R6***	The reaction occurs in two steps, involving the processes of RWGS ***R3***, followed by CO hydrogenation to ethanol ***R6***.	Ethanol is commonly used as a food and fuel additive, solvent, chemical intermediate, and formulation in the cosmetics / pharmaceutical industry.
DME	$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$ ***R7***	DME can be obtained from methanol through catalytic methanol dehydration ***R7***. In the reaction, both DME and water are noted to function as inhibitors.	DME serves as a clean fuel and chemical building block for producing valuable materials, including light olefins such as ethylene and propylene.
F-T product	$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$ ***R8***	CO_2 is first converted to CO through RWGS reaction ***R3***, and then transformed into hydrocarbons via CO hydrogenation F-T pathway ***R8*** [40].	Synthetic fuel can be obtained by hydrocracking. This route can also be used in the production of plastics, heating, lubricants, and additives.
	CO_2 – based intermediates, chemicals, and chemical products		
Syngas	$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2$ ***R9***	CO_2-based synthetic gas can usually be obtained through hydrogenation (RWGS) reaction ***R3*** or CO_2 reforming reaction ***R9***.	Syngas is a versatile mixture of CO and H_2, and it finds applications across the majority of industries as an intermediate.

Urea	$CO_2 + 2NH_3 \leftrightarrow NH_2COONH_4 \leftrightarrow CO(NH_2)_2 + H_2O$ ***R10***	Urea production from CO_2 involves two steps: the formation of ammonium carbamate through the reaction of CO_2 and ammonia, followed by the decomposition of ammonium carbamate into H_2O and urea (***R10***). The synthesis typically occurs under high pressure (130 to 300 bar) [41] and moderate temperature (170 to 200 °C). generally, no catalyst is needed as it is exothermic [42].	The common application of urea is as mainly fertilizer, cosmetic ingredient, plastic, and resin.
Formic acid / Formate	$CO_2 + H_2 \leftrightarrow HCOOH$ ***R11***	Formic acid and formate can be produced through the ER of CO_2 ***R11***. The production of either formic acid or formate depends on the pH level of the reaction. When the reaction occurs under an acidic environment (pH<3), formic acid tends to be produced. Otherwise, at higher pH levels and weak alkaline conditions, the reaction favors the production of formate.	Formic acid has a wide variety of applications as a sanitizing and cleaning solution, precursor for perfumes, and other chemicals such as amides and ketones.
Oxalic acid	$2CO_2 + H_2 \leftrightarrow HOOCCOOH$ ***R12***	Two molecules of carbon dioxide and one molecule of hydrogen forming oxalic acid through ER of CO_2 ***R12***.	Oxalic acid is mainly used as a cleaning (rust removal) and bleaching agent in metal and textile industries. It is also used as a cleaning agent (stain removal) in households
Acetic acid	$CO_2 + CH_4 \leftrightarrow CH_3COOH$ ***R13***	While the BP/Monsanto process is the dominant industrial method for acetic acid production using methanol, in theory, acetic acid can be generated through the direct reaction of CH_4 and CO_2 ***R13*** [43].	Acetic acid is used in antiseptics, dyeing, and food processing.
Carbonates	$CO_2 + 2NaOH \leftrightarrow Na_2CO_3 + H_2O$, ***R14*** $CO_2 + (CH_2)_2O \leftrightarrow (CH_2)_2CO_3$ ***R15***	CO_2 in the gas phase passes through the aqueous solution of sodium hydroxide to obtain sodium carbonate and bicarbonate ***R14***, which typically occurs at room temperature and atmospheric pressure. In terms of producing ethylene carbonate, ethylene oxide is carbonated with CO_2 ***R15*** under mildly elevated temperature and pressure with an appropriate catalyst such as K_2CO_3.	Their potential application involves a wide range of industrial and non-industrial processes including water treatment, food processing, and glass manufacturing.

*The list presented here is not conclusive and limited to only some of the general CO_2 conversion reactions and products.

Since there are hundreds of CO_2-based chemical reactions and products, the primary reaction routes including Sabatier, F-T reactions, CO_2 hydrogenation, CO_2 reforming, ER and PR of CO_2 processes are briefly discussed in the following paragraphs emphasizing the standard reaction conditions and the main catalysts used in each process.

CO_2 methanation or Sabatier reaction (***R1***) is one of the widely investigated and existing techniques, of which the reaction is exothermic and occurs through catalytic conversion between 200-450 °C with the pressure of 1-100 bar depending on the desired CO_2 conversion rate. The selection of an appropriate catalyst for this reaction is important. Although noble metals, including Rh, Ru, and Pd have a favorable performance from activity and selectivity, the drawbacks associated with their high-cost make room for transition metals, for instance, Ni, Fe, Co with other supportive catalysts (alumina, silica, and metal oxides). Ni-based catalysts are commonly applied in CO_2 methanation, due to their high activity, selectivity, and cost-effectiveness [44, 45].

The CO_2 hydrogenation (hydrogenative CO_2 reduction) process is one of the key techniques to convert CO_2 with H_2 into many types of value-added products and intermediates including CO, methanol (***R2, R4***), ethanol (***R6***), DME (***R7***), methane, formic acid [46-49]. The reaction condition vary depending on the desired product. For example, CO_2 hydrogenation through RWGS (***R3***), which involves the reaction between CO_2 and H_2 in the ratio of 1, is the most widely-used first-stage reaction to form further chemicals and hydrocarbon fuels. RWGS reaction is mildly endothermic and usually occurs between the pressure 1-25 bar and temperature 550-950 °C [50]. As for the selection of catalysts used in hydrogenative CO_2 reduction, especially for RWGS, Fe and Cu-based catalysts are popular among the academia due to their better absorption performance [35]. In addition, there is a common requirement for metal active sites to be well-dispersed and a large surface area of metallic oxide support. Thus, Co, Pt, Pd, and Rh have been widely investigated in terms of metal sites, while CeO_2 has extensive application in the case of better support [51].

In the case of ER and PR of CO_2, the processes mainly occur using electricity and light respectively room temperature and ambient pressure, which is why in recent years, those methods have attracted great attention in the scientific community. For instance, the ER of the CO_2 process can synthesize carbon monoxide, methanol [52], methane [53], ethane [54], ethylene (***R5***), formic acid (***R11***) and formate [39, 55, 56], oxalic acid (***R12***), and other value-added products supplying the required electricity by renewable sources. However, it is not a viable option so far to implement at a large scale [57]. In the context of catalysts employed in the ER of CO_2, noble metals such as Pd, Au, and Ag are attractive choices here as well with their higher selectivity and better performance [35]. However, there is a significant demand for the discovery of new catalysts derived from abundant, readily available, and cost-effective materials found on Earth. For instance, the cost per kilogram of Re or Ru stands at approximately 14,000 and 2000 euros, respectively, with annual productions of 50 and 12 tons, respectively. In contrast, the cost is 16 euros for Ni and 0.16 euros for Fe, with productions of 1.3 million tons and 2400 million tons, respectively [58]. Therefore, transition metals including Fe, Ni [59], Co [60], and Cu-based catalysts [61] are a significant attention among scientists worldwide. As for the PR of CO_2 catalysts, in fact, ER and PR of CO_2 processes use almost similar catalysts or catalyst precursors [62].

F-T process or Modified F-T process (***R8***) is a set of catalytic chemical syntheses used to convert syngas into liquid hydrocarbons. This reaction typically follows the CO_2 hydrogenation or dry reforming process to obtain CO and H_2, which proceeds under specific conditions and ratios with an appropriate catalyst. The F-T process is a conventionally crucial reaction in the production of coal-based liquid fuels and Gas to Liquid technology. The reaction undergoes within a broad range of pressure from 1 to 40 bar and the temperature between 150 and 300 °C [63]. Those conditions can vary based on obtaining desired products including wax, diesel, aviation fuels and light hydrocarbons. Transition metals such as Fe [64, 65], Co [66, 67], and Ni [68], are extensively studied in F-T reactions.

Dry reforming or CO_2 reforming (***R9, R13***) is another common method of making CO_2-based chemicals and intermediates using CH_4. The reforming process is endothermic and occur at high temperatures, typically between around 650 and 1000 °C. It can take place at ambient pressure or higher up to 30 bar [69]. The reaction is also catalyzed by certain metal-based catalysts, such as Ni, Co, or Ru, Pt, etc. supported on suitable substrates like alumina or magnesium oxide. The catalysts utilizing noble metals are reported to exhibit reduced sensitivity to coking in comparison to Ni-based catalysts when applied to the $CH_4 + CO_2$ reaction. Nevertheless, Ni-supported catalysts remain dominant in this field due to the factors related to the limited availability and high price of noble metals [70].

Generally, although CO_2 utilization via reforming, Sabatier reactions, or hydrogenative route is a common and most investigated method, ER and PR of CO_2 have increasingly become favorable due to their reaction performance under mild conditions. PR of CO_2, however, still requires further research and investigation due to the issues related to the photoreactor designing and product selectivity, whilst achieving high selectivity for the desired product over competing side reactions is a significant challenge in the ER of CO_2.

3.2. CO_2 mineral carbonation

Several CO_2 capture and utilization techniques including biological CO_2 fixation and mineral carbonation are applied to the direct conversion and utilization of CO_2 due to the physicochemical property of CO_2 that is reformed after the capture process. Therefore, no extra site for CO_2 storage is needed with the capture facility [71-74].

Mineral carbonation is an accelerated form of weathering of naturally occurring rocks and has been proposed as an alternative approach to CO_2 sequestration. Typically, accelerated carbonation or mineralization can be achieved by either in situ or ex-situ carbonation [75, 76]. Through in situ carbonation, the concentrated CO_2 is transported into subsurface magmatic rocks (basalt) or peridotite minerals and fixed as solid carbonates inside the hosting rocks. In the ex-situ carbon mineralization method, the carbonation takes place in a chemical plant by mineralization of captured CO_2 into carbonates [77]. Materials suitable for ex-situ carbonation are commonly rich in metal oxides, such as calcium, magnesium, iron, aluminium, and manganese oxides [78, 79]. The flow diagram of basic mineral carbonation technology (see Figure 4) shows that industrial solid wastes (mostly alkaline solid wastes), liquid, and flue gas are directly sent to the accelerated carbonation reactor. The reacted slurry is separated into a liquid solution and carbonated solid products after accelerated carbonation. The liquid solution that has been separated can be heated using flue gas in a heat exchanger and then circulated back into the reactor for the subsequent carbonation. Although mineral carbonation has a higher potential to store CO_2 than other storage types (geological, ocean, or biological), there are some drawbacks related to slow reaction kinetics, energy demand, and a large waste disposal area requirement [80-82].

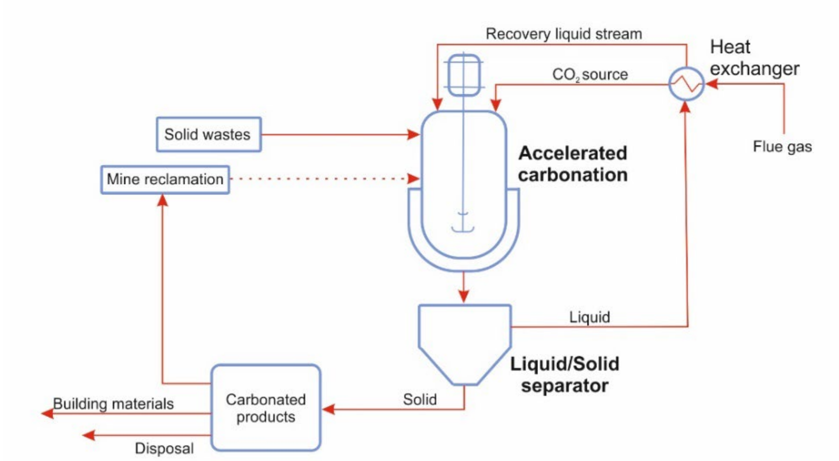

Figure 4. Flow diagram of basic mineral carbonation technology for CO_2 capture (Modified from [83, 84]).

3.3. CO_2 to biological algae cultivation and enzymatic conversion

Biological algae cultivation and enzymatic conversion stand out as attractive pathways for CO_2 utilization, facilitating the conversion of CO_2 into valuable products in biological routes. The biological method provides natural CO_2 incorporation into biomass at a relatively low cost in terms of energy. Photoautotrophy and chemolithotrophy are natural mechanisms that have resulted in the consumption of CO_2 biologically [85]. Algae-based CO_2 utilization, among others, can be a promising route that uses photosynthesis to capture CO_2 from flue gas for carbon fixation, particularly in the availability of wastewater resources [86]. Photosynthesis is a process in chloroplasts that converts solar energy into chemical energy in the form of lipids and carbohydrates, which may then be used to make biofuels, food, and other compounds. The overall photosynthesis reaction can be written as follows [87]:

$$6H_2O + 6CO_2 + \text{Photons (light)} \longrightarrow C_6H_{12}O_6 + 6O_2 \quad \text{(R16)}$$

In terms of algae applications, Trivedi et al.[88] have studied the various applications of algae in manufacturing dividing them into two main categories:

- "Bioenergy": Biodiesel, biogas, bioethanol, biojetfuel, etc.
- "Non-energy bioproducts": protein, pigments, carbohydrates, biomaterials, animal feed, etc.

According to Jacob et al., [89], microalgae can be cultivated in a closed system (photobioreactor) and an open system (raceway ponds) shown in Figure 5. They also mentioned that optimal temperature ranges and CO_2 concentration in flue gas had been observed at 20-35 °C and 10 mol% respectively. However, Algae sensitivity to impurities, growth control, and large area requirements are some of the main drawbacks of this technology (see Table 2).

Figure 5. Tubular (**a**) (adapted from [90]) and raceway (**b**) (adapted from [91]) ponds photobioreactors.

Regarding enzymatic conversion, process involves the use of specific biological catalysts, known as enzymes, to facilitate the conversion of CO_2 into other chemical compounds [92]. The enzymatic conversion of CO_2 yields higher outputs compared to alternative conversion approaches. This method encompasses diverse types of enzymes, such as carbonic anhydrase and carboxylases, each playing distinct roles in the conversion process. Enzymes catalyze the bioconversion of CO_2 under mild reaction conditions, involving lower temperatures and pressures and demanding less energy. Enzymes exhibit high specificity, meaning they can be designed or selected to target specific reactions. This specificity can lead to more efficient and selective conversion of CO_2 into desired products [93]. Despite these advantages, enzymatic conversion of CO_2 faces challenges such as high production costs and difficulties in scaling up processes for industrial applications.

3.4. Enhanced oil and gas recovery

EOR by CO_2 injection is becoming more widespread in the petroleum industry because it utilizes the captured CO_2 and increases oil production at the same time otherwise, the CO_2 would be released into the atmosphere [94]. Apart from that, EGR is another option to inject CO_2 into the reserves boosting the production of natural gas. In both approaches, CO_2

is injected into the deep reservoirs, which leads to the pressure increase in the reservoirs resulting in the growth in the extraction of oil and natural gas (see Figure 6) [95].

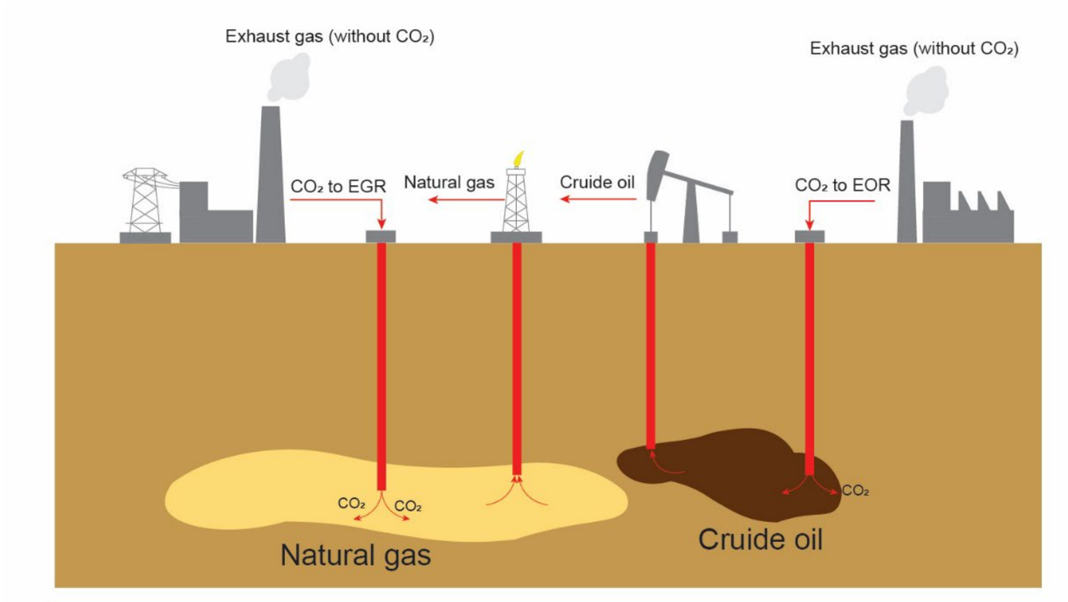

Figure 6. Direct pathways of CO_2 utilization: Enhanced oil and gas recovery (source: own elaboration).

EOR with CO_2 is, by far, the most mature and commercialized technology since this is economically viable compared to other utilization pathways, and there is no need to change the state of CO_2 as a solvent. This technique involves the injection of CO_2 deep into underground reservoirs, creating favourable conditions for the mobilization and displacement of trapped hydrocarbons, ultimately resulting in increased yields of valuable oil and gas resources. Moreover, in order to reduce transportation expenses, captured CO_2 needs to be close to the oil/gas extraction source (see Table 2). However, the main drawback of this approach is that it also brings about additional environmental concerns due to boosting hydrocarbon extraction rates.

3.5. CO_2 utilization in food, drink, and other industries

The direct use of captured CO_2 is possible in beverage carbonation avoiding the production of industrial CO_2. Another direct utilization pathway is to use the CO_2 as a freezing and chilling agent, in fire extinguishers, as well as in packaging applications (see Figure 7). In this way, it can be used as dry ice, refrigerant gas, and an atmosphere-modifying agent for packaging [96].

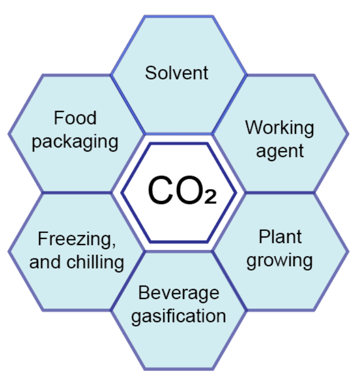

Figure 7. Direct pathways of CO_2 utilization: CO_2 utilization in food and drink industry [96].

Since CO_2 in supercritical form is an inert, and non-toxic gas, it served as an excellent solvent for many processes including coffee decaffeination [97], aroma, flavour and oil extraction [98, 99], dry cleaning, power generation, and the pharmaceutical industry [100]. According to Rafiee et al., [101], one of the main disadvantages of those sectors is that they are very limited in scale and relatively low effect on abatement compared to the amount of global CO_2 emission.

4. Assessment of CO_2 utilization techniques

In this section, we analyze the main advantages and drawbacks and the techno-economic and environmental performances including maturity, market size, energy efficiency, utilization potentials, and environmental benefits of each CO_2 utilization technology. In this way, it is possible to fully evaluate the engineering, economic, and environmental performances of each technique.

4.1. The main advantages and disadvantages of CO_2 utilization technologies

The main advantages and drawbacks of CO_2 utilization pathways are summarized in Table 2.

Table 2. Main advantages and disadvantages of CO_2 utilization technologies [6, 23, 31, 34, 37, 96]

Advantages	Disadvantages
CO_2 to chemicals and fuels	
Most mature in the production of urea and CO_2-based inorganic carbonates, methanol, etc More than 150 products can be made by CO_2 conversion A source of energy capable of replacing fossil fuels The "Power-to-fuel" concept combines electric power and transportation	Most of the produced chemicals with limited amounts of demands CO_2 hydrogenation leads to an increase in CO_2 emissions unless renewables are used Suitable catalyst development required Cost of hydrogen and purifying CO_2 CO_2 leakage Thermodynamic efficiency needs to be improved for electrochemical CO_2 reduction
CO_2 mineralization	
Possibility to capture CO_2 directly from exhaust gas (when CO_2 content should be greater than 10%) Ample resources (industrial wastes, organic matters, minerals) Permanent CO_2 sequestration	The kinetics of the natural weathering process is very slow Huge amount of reagents needed Using chemicals leads to environmental pollution A large waste disposal area requirement
Enhanced commodity production	
Large scale application CO_2 stays physically unchanged Economically viable compared to other pathways Already commercialized	CO_2 injection for EOR/EGR causes additional hydrocarbon extraction Captured CO_2 needs to be close to oil/gas extraction source
CO_2 to bio-products	
There is no necessary inlet stream quality An alternative source of energy that can replace fossil fuels Excellent performance at low CO_2 concentrations Regeneration of CO_2 is not necessary Mild reaction conditions for enzymatic conversion Enzymes are targeted for specific final products	Algae sensitive to flue gas impurities and pH Controlling the cultivation and drying processes is expensive. A large area is needed to grow CO_2-based bio-products Slow kinetics Scale-up challenges
Food and drink and other applications	
Considerable performance of supercritical CO_2 as a solvent for extraction Can replace industrial CO_2	Limited in scale Narrow effect on global CO_2 abatement High-purity CO_2 is required

According to Table 2, each CO_2 utilization technology has numerous positive and negative aspects from different perspectives. In a brief comparative summary of Table 2, EOR, EGR, and food and beverage pathways stand out for their direct utilization of CO_2 and relative economic benefits. However, the limited availability of oil and gas reserves, along with the requirement for the close location of CO_2 sources, serves as the main barrier to the global large-scale implementation of EOR and EGR, while the demand for CO_2 in the food and beverage industries is relatively low. Concerning CO_2-to-chemicals and fuels pathways, each synthesis process has its own nature in response to various conditions, given that more than 150 different types of chemical products and fuels can be made from CO_2. At first glance, although CO_2-based synthetic fuels seem to have significant potential to create a large market demand worldwide, this route is likely to lack cost competitiveness with conventional fuels and may face controversy regarding environmental benefits unless challenges related to finding novel catalysts and a low-cost renewable hydrogen supply are overcome. However, the majority of these technologies have much lower potential for reducing CO_2 emissions. Biological CO_2 utilization and carbon mineralization route both share a similar drawback associated with the large space demand required to integrate with emitting point sources, which can present a considerable challenge in urban places. The slow kinetics of natural weathering or photosynthesis reactions also pose a problem. In contrast, those pathways offer exclusive CO_2 capture and utilization technology simultaneously, such as the formation of microalgae and sodium carbonate or bicarbonate. Apart from that, CO_2-to-bio-products and carbon mineralization coincide with the overall environmental benefit discussed in the 4.3 subsection as well.

4.2. Maturity of CO_2 utilization technologies

When it comes to the TRL performances of CO_2 utilization pathways, several technologies are fully developed and reached the level of TRL 9 including urea, methanol, polyols, salicylic acid, and EOR (see Table 3). Formic acid, ethanol, sodium carbonate, calcium carbonate, CO_2 curing concrete, and CO_2-derived syngas production technologies are in the development stage and are expected to reach the commercial stage by 2030. As for methane production, the hydrogenation-based methanation process is currently in the demonstration stage [102], while methanation based on electrochemical CO_2 reduction is still in the research and development stage [103]. Methanol production has also been carried out in hydrogenation and electrochemical CO_2 reduction methods, and its maturity has been assessed in the same way as methane production. Many remaining CO_2 utilization technologies are still in their infancy and need further research and development. It may take at least 10 years from now for these technologies to reach the commercial stage.

Table 3. TRL performances of some of the CO_2 utilization technologies

Technology	**Process/reaction/method**	**TRL**	**Reference**
	CO_2 to chemicals and building materials		
Urea	Organic synthesis	9	[31, 83, 104, 105]
Salicylic acid	Organic synthesis from phenol and CO_2	9	[104, 106]
Formic acid	Electrochemical CO_2 reduction	5-6	[35, 104, 107]
Ethylene glycol	Photoelectrochemical reduction of CO_2	3-4	[104, 107]
Polyols	Organic synthesis from epoxide and CO_2	8-9	[31, 104]
Polyethylene	Three steps; hydrogenation to methanol; methanol-to-olefins process; polymerization of ethylene	7	[35, 107]
Sodium bicarbonates	Mineral carbonation	5-9	[35, 104, 107]

CO_2 to concrete	CO_2 mineral carbonation curing of Portland cement, combined with coarse aggregates	6-7	[35, 107]
	CO_2 to fuels		
DME	Dry reforming of methane to syngas; direct synthesis of DME	3	[31, 107]
F-T fuels	RWGS to syngas; F-T process	6-7	[83, 107]
Methanol	Hydrogenation of CO_2	7-9	[31, 83, 104, 107-109]
Methanol	Electrochemical CO_2 reduction	1-3	[35, 104, 107, 108]
Ethanol	Hydrogenation of CO_2	6	[110]
Methane	Hydrogenation of CO_2 methanation	7-9	[21, 31, 104, 107]
Methane	Electrochemical CO_2 reduction	2-4	[104, 111]
	CO_2 to enhanced hydrocarbon recovery		
CO_2 to EOR	CO_2 injection into a depleted oil field to recover oil	9	[83, 107]
CO_2-ECBM	CO_2 injection into a coal seam to recover methane; Part of the CO_2 stays behind	2-3	[107, 112]
	CO_2-based biological conversion		
CO_2 – based products	CO2–based enzymatic and microbial products	3	[31]
Dry algae powder	CO_2 conversion by microalgae	7-8	[104]
Microalgae	Microalgae cultivation and biomass co-firing for power generation	4-6	[96, 111]

4.3. Environmental performances of CO_2 utilization technologies

In evaluating the environmental benefits of CO_2 utilization technologies, features such as carbon retention time, safety and health considerations, and eco-toxicity to the environment are considered (see Figure 8). Carbon retention time describes the duration CO_2 remains sequestered in different CO_2 utilization routes, ranging from short-term to potentially millions of years [21]. Eco-toxicity of CO_2-derived products shows the harmful effects on the ecosystems, while safety and health considerations highlight the potential harm associated with the final products and specify the necessary measures to control and mitigate these risks. When it comes to carbon retention time, on the one side, carbon mineralization can be the most viable technology as it is another way of CO_2 capture and sequestration at the same time for hundreds of thousands of years without requiring regular monitoring of possible CO_2 leakage. Nevertheless, the limited potential of CO_2 abatement and the slow kinetics of the natural mineral carbonation process make this technology less attractive. The retention time for CO_2 can be assessed positively in the application of food, beverage, and other industries as the manufactured CO_2 might be replaced by captured one. Biological algae cultivation is also a promising technology for its reliability for lifetime CO_2 abatement by converting it to biofuels while EOR stays in the middle neither the best CO_2 retention nor the worst. On the other side, in most cases, CO_2 to chemicals and fuels technology provides the least period to CO_2 reduction from several days to months but it has the highest potential for future research directions since there is still huge demand for further investigations on this field. As for the eco-toxicity, safety, and health considerations, the best indicators are found to be in CO_2 mineralization, bio-fixation, food, beverage, and polyol production. Although methanol production is rated well in terms of life cycle indicators (carbon retention time, acidification, and global warming impact) the average environmental performance is not the best due to its toxic effect on human vision.

Figure 8. CO_2 utilization methods comparison based on carbon retention time, eco-toxicity, and health and safety considerations. This comparative assessment aims to identify key highlights of CO_2 utilization routes without making a final decision. Green tick, yellow exclamation, and red cross marks represent good, neutral, and bad aspects, respectively (Source: own elaboration).

Regarding urea production, however, boosting the production of urea may not be suitable because of some factors like the intensive process of ammonia production and N_2O release to the atmosphere which has a 300 times higher negative effect than CO_2. Further detailed information can be found in Hepburn et al. [113]. In addition, due to the release of CO_2, ammonia [114], and cyanic acid from urea under the influence of heat, it is essential to implement preventative and protective measures before dispersing it into the environment.

4.4. CO_2 uptake and market size of CO_2 utilization technologies

In terms of CO_2 uptake potential and market size, a limited number of utilization pathways can be profitable involving the production of polycarbonate polyols, salicylic acid, urea, and other mature technologies that have already been commercialized with the largest scale accounting for 180 Mt [1] of CO_2 utilization per year. The targeted long-term CO_2 utilization potential is estimated as 1-2 Gt/year, which could cover about 12-25% of global CO_2 emissions. The increasing global CO_2 uptake potential highly depends on global market size, government policies and regulations, competition with alternatives, and advances in non-commercialized CO_2 utilization technologies. As for the market size of CO_2-based chemicals and building materials, according to calculations based on data in ChemAnalyst [115], the most significant market is shared by methanol, urea, calcium carbonate, and sodium carbonate production, and currently, the overall size of them takes 80% of the total market. One example of CO_2-derived fuels is Carbon Recycling International's George Olah plant in Reykanes, Iceland which produces 4000 tons of methanol using CO_2 annually [116].

Figure 9 illustrates a summary assessment of the maturity, environmental, and CO_2 sequestration potentials of some chemicals, fuels and construction materials. The CO_2-derived products are sorted according to their specific mass for CO_2 utilization and their current global market size. Methane and F-T products are not included here due to their large market sizes compared to other substances. The specific mass or CO_2 utilization capacity of CO_2-derived fuels, chemicals, and building materials refers to the amount of CO_2 that is captured and used as a feedstock to produce these products. It is typically measured in terms of tons of CO_2 utilized per unit of the final product, such as per ton of fuel or chemical produced. The utilization capacity can vary depending on the specific production process, the type of fuel or chemical, and the source of the captured CO_2. For DME and methanol, this value is higher than 1, and for formic acid, urea, acetic acid, and ethylene carbonate, it is between 0.5 and 1. The environmental performance of the CO_2-based products was assessed based on the data of ReCiPe 2016 v1.1 [117] and Chauvy et al. [104] in terms of global warming, fossil depletion, eco-toxicity, safety, and health considerations (see subsection 4.2).

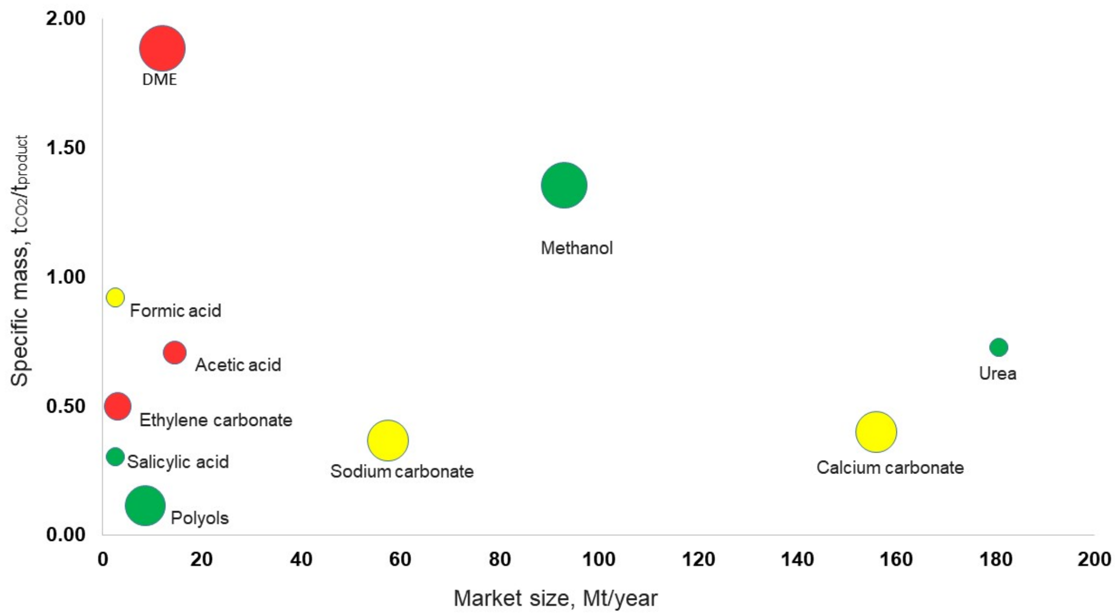

Figure 9. Maturity, environmental and CO_2 uptake potentials of some chemicals, fuels, and building materials (excluding methane and F-T products). In order to illustrate the maturity and environmental performances of CO_2-based products, colorful circles are used in different sizes. Green, yellow, and red circles represent TRL 8-9, TRL 5-7, and TRL 1-4, respectively. The size of the circles shows the environmental performances of CO_2 utilization technology – a larger size means it is considered more environmentally friendly.

CO_2-derived fuels such as methane, gasoline, aviation fuels, and DME may have significant potential in CO_2 utilization since they can decarbonize the transport sector by replacing the use of fossil fuels. According to [21], CO_2 to fuels technology has the greatest potential to utilize CO_2 by volume with average climate benefits. In addition to the CO_2 methanation that is capable of 775 Mt of CO_2 utilization in Europe [31], CO_2 hydrogenation to methanol is, among others, seen as a promising approach as long as the hydrogen is supplied in an environmentally friendly manner [118]. Regarding CO_2 bio-fixation, CO_2 can play a crucial role in boosting algae and crop cultivation [119]. For instance, the Netherlands stands out as a country where CO_2 is used in greenhouses up to 6.3 Mt per year. Although carbon bio-fixation is generally at low TRL levels [111], its estimation for the end of this decade is relatively large as the demand for biofuels and bio-based feed products rises. Overall, most of the CO2-derived fuels are obtained by Sabatier or F-T reactions. Hydrogenation and electrochemical CO_2 reduction techniques require a certain amount of hydrogen. In this manner, hydrogen should be produced as green as possible to increase the capacity of net CO_2 utilization. Another concern is related to the lifetime of the CO_2 that leads to reemitting once the fuel is combusted again.

In terms of direct use of CO_2, among the utilization pathways, EOR is dominant with its maturity, large-scale application, and economic benefits. Currently, according to the appendix of the "Global Status of CCS 2021" report [120], global commercially operating CCSU projects have an average potential to capture 40 Mt of CO_2 per year with nearly 70% of EOR due to its economic profitability. However, since EOR boosts the residual oil production, full life cycle assessments are needed to evaluate its total CO_2 removal. For example, Mavar et al. [121], analyzed CO_2-EOR life cycle emissions and concluded that 40% of injected CO_2 comes back in the form of fossil fuel and the rest remains in the reservoir. As far as other direct CO_2 to utilization pathways including the food, beverage, and other uses of CO_2, are concerned, their contribution to the global CO_2 abatement is quite limited in scale owing to relatively low demand compared to the total greenhouse emissions.

One of the largest barriers to growing the market size of CO_2-derived chemicals, fuels, and building materials is the availability of alternative products in the global market. For example, currently, CO2-derived fuels cannot compete with traditional fuels in terms of operating expense, capital expenditure, and feedstock costs [122]. To compete with traditional fuels, the cost of CO_2 capture and utilization must be relatively lower and a combination of inexpensive energy costs and high CO_2 pricing is required. The cost of chemicals and building materials, which are obtained by CO_2 utilization, depends on the factors mentioned above, but some conventional chemicals and building materials may not be able to compete in price with their CO_2-derived counterparts, such as polyols and CO_2-cured concrete.

In the following, we made a generalized comparison of CO_2 utilization technologies (see Figure 10). In terms of technological performances, it is quite challenging to discuss and compare by group due to the individual assessment for each specific technology, particularly in CO_2 conversion techniques. For example, CO_2 to methanol conversion, which attracts a huge amount of market owing to its various applications, has been evaluated as an almost mature technology in terms of F-T reactions followed by RWGS reactions. At the same time, methanol by ER of CO_2 technology is assessed TRL 1-3 since the process is energy intensive and requires green hydrogen with its small scale. This case is nearly the same as CO_2 to methane conversion by two of those technologies. As for CO_2 mineralization, CO_2 for concrete curing is at TRL 6-7, while CO_2 carbonate mineralization in both aggregates and natural weathering is evaluated as a mature technique. Regarding CO_2 to enhanced hydrocarbon recovery, the ECBM recovery method is estimated as TRL 2-3 due to the availability of any active ECBM project worldwide [112] compared to the most mature and commercialized EOR technology. CO_2 to bio-products have also similar differences depending on the pathway used.

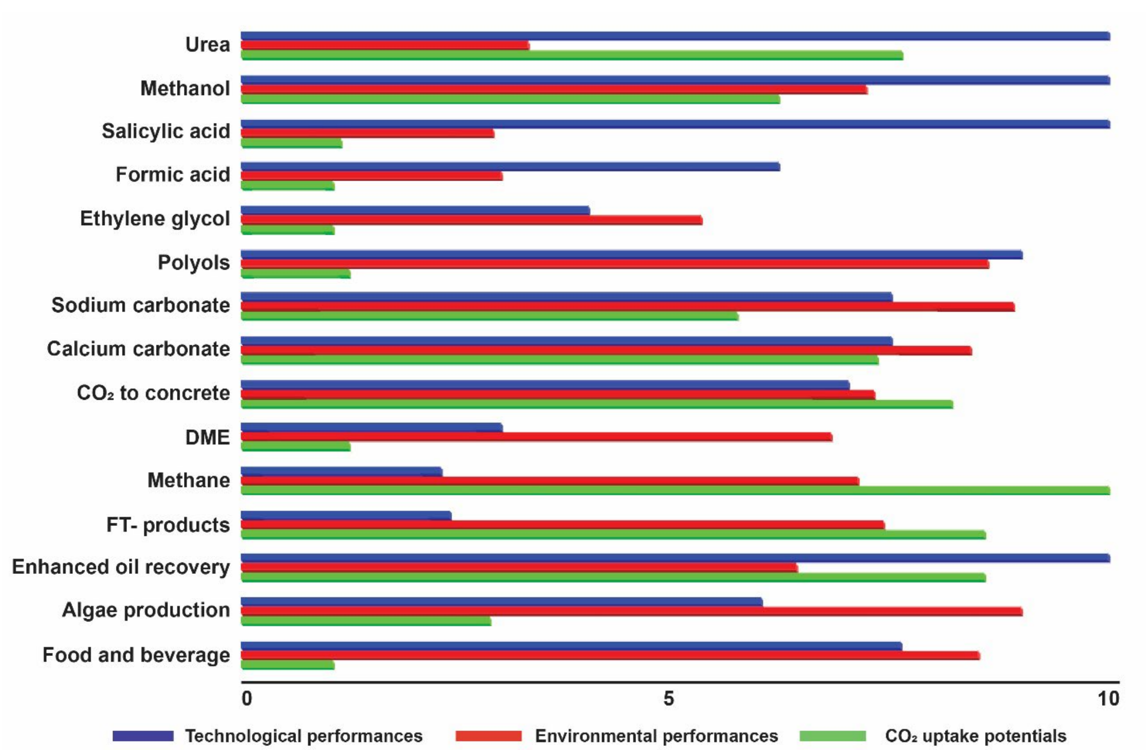

Figure 10. CO_2 utilization pathways comparison based on technological, environmental, and CO_2-uptake performances.

As for the CO_2 uptake potentials, EOR, CO_2-based methane and F-T products are more potent than any other utilization techniques. Otherwise, CO_2 conversion technologies such as urea and methanol production, and CO_2 to fuel conversion in the availability of hydrogen can be applied at a large scale. However, both of those methods do not fully guarantee CO_2 reduction as it depends on very specific conditions. Microalgae photosynthesis, from this context, is possibly assessed as medium or even higher scale technology taking into account its limitations including large space requirement, algae sensitivity to the impurities, and high cost of control. However, it is considered the best fitting technique for flue gas streams with relatively low CO_2 content such as the flue gas from natural gas combined cycle (NGCC) power plants. In the case of CO_2 to construction aggregates similar to concrete curing, it can be a very suitable option for coal-fired power plants, cement and steel industries as the concentration of CO_2 is high enough in these processes. However, they can be evaluated as small-scale technologies because the CO_2 utilization capacity per ton of aggregate production is 80 kg of CO_2 [96].

4.5. Applicability of low CO_2 concentration streams for different CO_2 utilization pathways

When it comes to CO_2 sources, it can be from a wide variety of emission sectors. Nevertheless, the majority of CO_2 emissions come from fossil fuel combustion sources such as coal, oil, and natural gas. Those fuels are mainly used in the power and industrial processes (65% CO_2 emission in 2022) in which the necessary CO_2 content is obtained in relatively low concentration in the flue gas mixture, particularly in the coal and natural gas combustion [123]. In this context, there appears a significant demand for finding the most suitable CO_2 conversion technique which can directly use the flue gas mixture without prior separation of CO_2. Regarding the suitability of CO_2 utilization pathways for these low CO_2 concentration streams, the properties of the flue gas and the amount of CO_2 content play a crucial role in the utilization process. The CO_2 content in flue gas varies across power and industrial sectors in response to the type of fuel, combustion process, and other reaction-specific conditions. For instance, CO_2 molar concentration in coal-fired power plants is 12–16%, natural gas-fired power plants 7–10%, natural gas combined cycle power plants 3–6.5%, oil-fired power plants 12–14%, cement plants 14–33%, and iron and steel industry 15–27%. The flue gas composition also differs in the emitting source but mainly consists of N_2, H_2O, O_2, CO_2, and trace amounts of SO_x, NO_x, and particulate matter [6].

There are currently several conversion reactions that can directly use flue gas as a reactant instead of pure CO_2 stream such as algae cultivation using light photosynthesis [124], mineral carbonation using silicate minerals [125] or alkaline solution [126], and CO_2 hydrogenation including CO_2 to methane and methanol production [127-129]. As for the CO_2 hydrogenation reactions, Iaquaniello et al. [130], explored methanation reaction based on the direct application of natural gas-fired power plant flue gas assuming the absence of SO_x and NO_x, which can serve as both CCSU technology and renewable hydrogen storage. The authors reported that some of the flue gas impurities such as N_2 and H_2O play an important role in better temperature control and additional steam replacement respectively, while the O_2 content needs to be removed as it leads to H_2 overconsumption through forming H_2O exothermically. According to the economic estimation of Iaquaniello et al., synthetic natural gas (SNG) can be achieved at 0.34 € and even 0.20 € per Nm^3 SNG when the carbon tax is at 30 €/tCO_2 and 100 €/tCO_2 respectively. However, the main electricity consumption for renewable hydrogen production and flue gas multistage compression is assumed as zero, since they proposed to use excess free electricity sources. Miguel et al. [131], also studied the CO_2 to methane and methanol process directly using flue gas as a CO_2 source and reported a methanation process with better performance than methanol synthesis in terms of a thermodynamic point of view.

Microalgae cultivation can also be a promising option as a direct utilization pathway for low CO_2 concentration flue gas as mentioned earlier. This route is favored not only by its ambient reaction conditions but also by tolerance of flue gas impurities including SO_x and NO_x [132]. Oliveira et al. [133], explored the economic viability of utilizing microalgae for CO_2 bio-fixation through photobioreactors from the NGCC power plant flue gas. According to their results, although the CCSU facility is very large and requires a significant amount of investment, they concluded it as techno-economically viable with an estimated payback period of 10 years. In contrast, there is a considerable demand for water or wastewater and large space [132]. Regarding the conversion of CO_2 into mineral carbonates, there are mainly two options including silicate and alkaline minerals transformation such as $CaCO_3$, $MgCO_3$, and Na_2CO_3 using the flue gas with CO_2 content [134]. In this pathway, however, only certain industrial flue gases containing more than 10% concentration of CO_2, especially iron, steel, and cement plant exhausts can benefit from direct CO_2 utilization from the waste stream without the necessity to purify CO_2. As for the coal and natural gas combustion flue gases, this pathway may not be suitable due to the energy intensity and economic considerations [31].

From the general overview, for the current conditions, EOR stands out as the potential CO_2 utilization technology coupled with fewer drawbacks compared to other technologies. However, more research and investigations can lead to overcoming the barriers of alternatives such as CO_2 to chemicals, minerals, and bio-products.

5. Conclusions

CO_2 utilization through both conversion and non-conversion methods is the only option that can make a value from captured CO_2. This paper discusses and compares various CO_2 utilization pathways including CO_2 to chemicals and fuels, CO_2 to building materials, CO_2 to enhanced oil and gas recovery, and CO_2 to bio-products. From the comprehensive analysis of those different CO_2 utilization directions, the following key conclusions are drawn:

- According to the short bibliometric search results in Section 2, CO_2 utilization technologies present one of the current research trends in the global scientific community.
- Recent and future prospects of CO_2 utilization technologies are likely to find better catalysts and improve their performances.
- Photocatalytic and ER of CO_2 are gaining the most attention worldwide since those technologies are highly efficient and selective as well as under mild reaction conditions.
- Most of the mature CO_2 utilization pathways are either energy-intensive or limited in scale and geolocations, while sustainable and promising routes such as microalgae cultivation and ER of CO_2 are not fully mature yet.
- CO_2 to sodium and calcium carbonates, concrete, polyols, and algae cultivation can be more sustainable pathways concerning their low carbon footprint.
- Methane, urea, and methanol production using CO_2 are quite high in market size but their energy intensity is also high, and environmental benefits are uncertain.
- Directly converting CO_2 in flue gas, without prior separation, promises near-term cost reduction for CCSU. However, addressing challenges in large-scale implementation, such as barriers in renewable hydrogen/electricity production, flue gas impurities, along requirements for large space, water, and catalyst development, is crucial.

Overall, techno-economic, energy, environmental, and life cycle assessment of the CO_2 utilization process is essential in planning circular economy strategies. One of the main challenges in the utilization of CO_2 is the cost of CO_2-used production. CO_2 capture technologies also need to be further developed in terms of cost and process efficiency to compete with conventional CO_2 production technologies.

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