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Transformation Technologies for CO_2 Utilisation: Current Status, Challenges and Future Prospects

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Abstract

To prevent global warming and climate change caused by CO_2 emissions, the Intergovernmental Panel on Climate Change (IPCC) recommends lowering CO_2 emissions to limit the global temperature to 1.5°C. In addition to carbon capture and storage (CCS) technologies, there is a growing interest to explore CO_2 utilisation. Several review papers exist in the literature either focusing on one or two CO_2 transformation technologies or covering only experimental studies. This review paper addresses the gap by classifying CO_2 transformation technologies and looking at products from CO_2 conversion. It reviews experiment and modelling/simulation-based studies for CO_2 biological and chemical conversion processes to assess their technical barriers. A detailed analysis of their technology readiness level, cost, market and environmental benefits are also elaborated. Finally, the research trend and projects for CO_2 transformation technologies worldwide as well as the key challenges hindering their commercial deployments are carefully outlined. The analysis of the research trend shows a significant increase in research for CO_2 utilisation with hydrogenation and electrochemical reduction being the most studied technologies since 2016. 53% of the projects are laboratory projects whereas, only 14% account for commercial projects. There is currently no commercial project for plasma catalysis, photochemical, electrochemical and non-photosynthetic technologies. The USA holds the highest number of 45 projects including 8, 6, 10 and 21 commercial, demonstration, pilot and laboratory projects, respectively. The development of improved catalysts and process intensification techniques are highly needed for successful scale-up of CO_2 transformation technologies.

Keywords

CO_2 utilisation; Chemical conversion; Biological conversion; Catalyst; Modelling and simulation; Process intensification

1. Introduction

1.1. Background

Various anthropogenic activities (e.g. burning fossil fuels and transportation) result in CO_2 emissions into the atmosphere. Global CO_2 emissions have increased from roughly 16 GT in 1970 to 37.5 GT in 2018 [1]. This has led to major concerns about global warming and climate change. The importance of reducing CO_2 emissions to prevent global warming consequences such as rising sea levels and melting glaciers has been widely recognised. It is recommended that CO_2 emissions should be lowered to net-zero around 2050 to limit the global temperature increase below 1.5°C by 2100 [2]. Several approaches have been considered for mitigating CO_2 emissions among which carbon capture and storage (CCS) are viewed as a viable approach for meeting CO_2 emission reduction [3].

As of 2019, 19 large-scale CCS facilities are operating worldwide with 4 more under construction. These facilities have an annual capture and storage capacity of around 40 million tonnes of CO_2 which corresponds to only 0.1% of global CO_2 emissions [4]. Furthermore, the reported facilities are lower than the 60 CCS commercial projects predicted by the International Energy Agency (IEA) in 2011 [5]. This is due to the high costs of CCS technologies which have made their commercial deployment quite difficult [6]. As a result, the term CCS has become CCUS (Carbon capture, utilisation and storage) wherein the economic value of the captured CO_2 is promoted through utilisation [7].

It is worth emphasizing that CO_2 utilisation technologies alone cannot mitigate enough CO_2 emissions. To illustrate, the cumulative total of CO_2 used for the global chemical industry in the period 2010–2050 is estimated to 15.42 $GTCO_2$ which represents about 2% of CO_2 reduction targets by 2050 [8]. The economic advantage of CO_2 utilisation, together with CCS for permanent CO_2 storage has made CCUS a more acceptable and lucrative concept for achieving CO_2 reduction targets. However, CCS technologies are beyond the scope of this review paper and several good discussions can be found somewhere else [6,9]. Only CO_2 utilisation technologies are addressed in this paper. CO_2 utilisation is classified into direct and indirect uses. Direct use involves using CO_2 at its pure state or suspended in a solution. For instance, in enhanced oil recovery (EOR), carbonated drinks, food preservation and fire extinguishers [10]. Whereas, indirect CO_2 utilisation converts CO_2 into chemicals, materials and fuels through different chemical and biological processes [11].

1.2. CO_2 molecule and its challenges for transformation

CO_2 is a linear molecule constituted by an atom of carbon which gives up all its four electrons to covalently double bond to two atoms of oxygen (O=C=O). Thermodynamically, the oxygen bonds with carbon are very strong making CO_2 molecule highly stable. Moreover, CO_2 Gibbs free energy ($\Delta G°$ = -394 kJ/mol) is much lower than that of the products from CO_2 conversion (Figure 1) [12]. Therefore, CO_2 stability must be overcome for the synthesis of value-added products. This leads to three main scientific challenges namely (1) the *need for substantial energy input* which must come from carbon-neutral sources to avoid further CO_2 emissions [11], (2) the *need for active catalysts* to lower the activation energy of CO_2 conversion processes and (3) *high temperatures and/or pressures* to weaken the CO_2 stability [13].

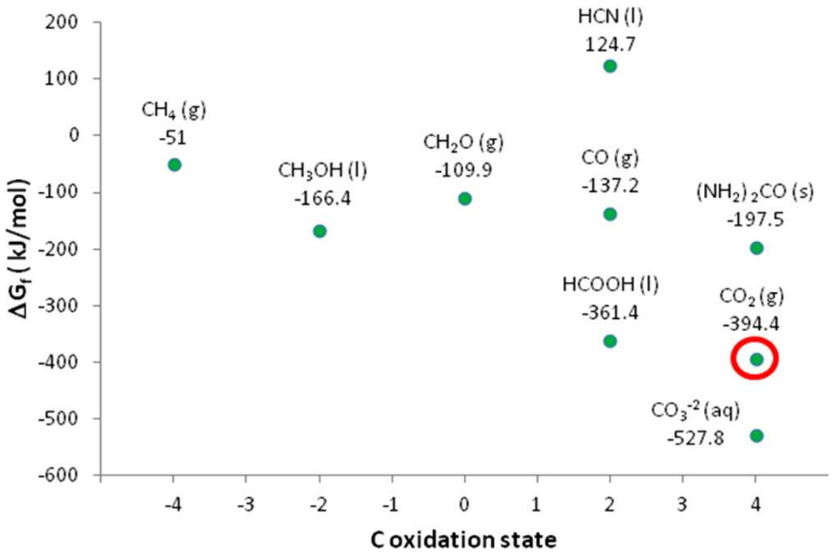


Figure 1: Gibbs free energy of formation for some products from CO_2 conversion [12].

1.3. Motivation for CO_2 utilisation via transformation

The motivations behind CO_2 utilisation seem obvious in the context of global warming and climate change. Table 1 presents the current estimates of CO_2 utilisation through direct and indirect routes. These estimations are based on data for CO_2 used in 2016 [14] and estimated data for the next ten years [15]. The total current amount of CO_2 for direct uses worldwide is 42.4 MT/yr which represents nearly 18% of CO_2 consumed for indirect uses. Furthermore, CO_2 demand for direct uses is predicted to remain constant since its application in the industry is quite stable [15,16]. On the other hand, the efficient use of CO_2 as feedstock is forecasted to be above 332 MT/yr by 2030 [14]. Though CO_2 utilisation via transformation presents some challenges, its potential of contributing to climate change mitigations while at the same time turning waste CO_2 emission into a wide range of value-added products is a powerful driving force. Therefore, it is paramount to summarize the recent advances in CO_2 transformation technologies and discuss their challenges and future research needs.

Table 1: Current estimates of CO_2 utilisation [14,15].

Utilisation mode	Application/Product	CO_2 used (MT/yr)	Production ($MT_{product}$/yr)
	Enhanced oil & gas recovery	25.0	25.0

Direct uses	Food preservation	8.2	8.2
	Industrial gases	6.3	6.3
	Carbonated drinks	2.9	2.9
	Total	42.4	-
Indirect uses	Urea	132.0	180.0
	Inorganic carbonates	70.0	250.0
	Methanol	10.0	60.0
	Formaldehyde	5.0	25.0
	Dimethyl ether (DME)	5.0	20.0
	Tertiary butyl methyl ether	3.0	40.0
	Algae	2.0	1.0
	Polymers	1.5	15.0
	Acrylates	1.5	3.0
	Carbamates	1.0	6.0
	Formic acid	0.9	1.0
	Organic carbonates	0.5	5.0
	Total	232.4	-

1.4. The aim and novelty of this review paper

This paper aims to critically review the current status of CO_2 utilisation via transformation. Several good review papers on CO_2 utilisation can be found in the literature. An analysis of some recent reviews is presented as follows:

- Alper and Yuksel Orhan [13] reviewed CO_2 conversion to C1-building chemicals via hydrogenation, dry reforming, carboxylation, electrochemical and photochemical reduction.
- Zheng et al. [17] reviewed the mechanisms and energy involved in thermochemical, electrochemical and photochemical CO_2 conversion processes.

- Jarvis and Samsatli [10] compared the cost, CO_2 consumption and TRL of CO_2 conversion technologies such as electrochemical reduction to formic acid, Fischer-Tropsch synthesis, urea production, hydrogenation to methane, formic acid and methanol.
- Ye et al. [18] discussed the mechanisms and heterogeneous catalysts of CO_2 hydrogenation to hydrocarbons and oxygenated compounds.
- Centi et al. [19] reviewed CO_2 conversion to syngas, methane, methanol, formic acid and C_2-C_3 olefins using renewable energy.
- Hepburn et al. [20] analysed the scale and economics for the conventional (chemicals, fuels, microalgae, building materials and EOR) and non-conventional (BECCS, enhanced weathering, forestry, land management and biochar) uses of CO_2.
- de Vasconcelos and Lavoie [21] assessed the recent advances in chemicals and fuels from CO_2 via hydrogenation and electrochemical reduction.
- Grim et al. [22] focused on the technical barriers of CO_2 conversion to C_1-C_3 compounds via hydrogenation, electrochemical, bioelectrochemical and plasma techniques.
- Zhang et al. [23] discussed the key challenges of CO_2 utilisation via direct and indirect routes. They also analysed the trend of CO_2 utilisation projects in USA, China, UK, Australia, Norway and Germany.
- Salehizadeh et al. [24] reviewed the microbial CO_2 fixation and conversion into chemicals and fuels.
- Mustafa et al. [25] looked into the catalysts and operating conditions of CO_2 electrochemical, plasma, biochemical, photochemical and solar thermochemical conversion into high-value products.

Some of the review papers aforementioned only focus on one or two specific CO_2 conversion methods [18,19,21,24]. Others looked into CO_2 conversion to specific products [10,13,19,20,22,25]. Furthermore, none of these papers reviewed the recent modelling and simulation-based studies for CO_2 transformation technologies. Modelling and simulation approaches can help for process design and optimisation at a lower cost. Therefore, it is important to analyse the current advancement in the proposed modelling and simulation studies to assess the role they can play in improving the performance of CO_2 transformation technologies.

For beginners, this manuscript offers a clear definition of CO_2 transformation technologies according to first principles and recapitulates the different products from CO_2 conversion. For experienced researchers, this paper reviews the recent progress in both experimental and modelling/simulation studies of CO_2 transformation technologies and proposes future research directions. The present article is different from most of the previous review papers in the following ways: (1) it classifies and defines CO_2 transformation technologies according to first principles then links the products from CO_2 conversion and CO_2 transformation technologies; (2) it critically reviews the current advancement in modelling/simulation studies and draws the readers' attention on process optimisation and process intensification for CO_2 transformation technologies; (3) it presents a detailed analysis of the different laboratory, pilot, demonstration and commercial projects for CO_2 utilisation via transformation worldwide and (4) finally, it tries to identify the key challenges hindering their commercial implementation and predict possible prospects.

2. CO_2 transformation technologies

CO_2 transformation technologies are classified into biological and chemical transformations which are then respectively subdivided into two and seven CO_2 conversion processes (Figure 2).

2.1. Biological transformation

2.1.1. Photosynthetic CO_2 fixation

Photosynthetic CO_2 fixation is divided into two methods: (1) *natural photosynthesis* wherein green plants absorb sunlight energy to convert CO_2 and water into energy-rich components such as glucose [26]; (2) *algae production* (e.g. cyanobacteria and eukaryotic microalgae) using CO_2 as carbon source, light energy, inorganic nutrients and water [27]. The natural photosynthesis is not taken into consideration in this review since it is a natural process that helps to maintain life on

Earth. Therefore, the photosynthetic method will refer to as algae production. There are two most significant systems for algae production including open or raceway pond (RP) systems which are open to the air (Figure 3a) and photobioreactors (PBRs) wherein algae cultivation is enclosed in a transparent array of tubes (Figure 3b) [27,28].

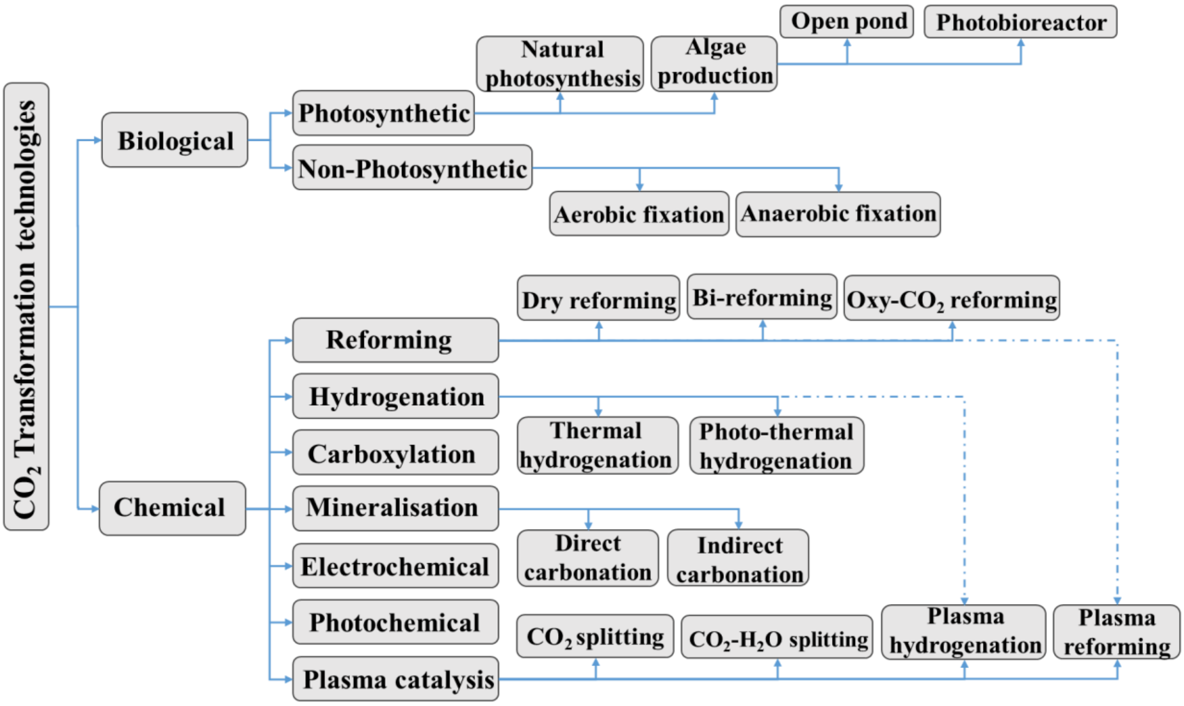


Figure 2: Chemical and biological CO_2 transformation technologies.


(a)
(b)

Figure 3: Algae production in (a) open ponds and (b) photobioreactors [28].

2.1.2. Non-photosynthetic CO_2 fixation

The non-photosynthetic method uses microorganisms (such as methanogens and acetogens) and a source of high-energy electrons for CO_2 reduction into useful bio-products. The process is performed either under aerobic or anaerobic conditions. In *aerobic fixation*, microorganisms access oxygen directly from the surrounding environment while during *anaerobic fixation*, oxygen is prevented from entering the system [29,30].

2.2. Chemical transformation

2.2.1. Reforming

Reforming is a strongly endothermic process wherein a hydrocarbon-containing gas (e.g. natural gas) is heated in the presence of a metal-based catalyst to produce a gas, commonly called syngas ($CO+H_2$). Because methane (CH_4) is the main component of natural gas, the process is often referred to as methane reforming. In the CO_2 utilisation context, there are three types of methane reforming processes including *dry reforming* (DRM), *bi-reforming* (BRM) and *Oxy-CO_2 reforming* (ORM) [31]. Table 2 details the chemical reaction and enthalpy of formation at 298K (ΔH_{298K}) of each reforming process. The main issue with the reforming is the coke or carbon deposition (Table 2) on the catalyst surface leading to catalyst deactivation due to blockage of active sites [31,32].

Table 2: Different types of reforming processes and coke formation reactions [31,32].

Reforming type	**Chemical reaction**	**ΔH_{298K} (kJ/mol)**
Dry reforming of CH_4	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247.3
Bi-reforming of CH_4	$3CH_4 + 2H_2O + CO_2 \rightarrow 4CO + 8H_2$	220
Oxy-CO_2 reforming of CH_4	$3CH_4 + CO_2 + O_2 \rightarrow 4CO + 6H_2$	175.1
Formation of coke (side reactions)		
CH_4 decomposition	$CH_4 \rightarrow C + 2H_2$	75
CO_2 hydrogenation	$CO_2 + 2H_2 \rightarrow C + 2H_2O$	-90
CO reduction	$H_2 + CO \rightleftharpoons C + H_2O$	-131
Boudouard reaction	$2CO \rightleftharpoons C + CO_2$	-172.4

2.2.2. Hydrogenation

CO_2 hydrogenation is simply defined as the addition of H_2 to CO_2. Because H_2 has a higher Gibbs free energy ($\Delta G° = 0$) than CO_2, CO_2 activation via hydrogenation is, therefore, more favourable.

However, the H_2 source is among the key challenges for CO_2 hydrogenation as it must come from renewable sources [33] to prevent further CO_2 emissions. Addition of H_2 to CO_2 is performed using heat (*thermal hydrogenation*), a combination of light and heat (*photothermal hydrogenation*) and plasma (*plasma hydrogenation*). Combining light and heat or using plasma has the advantage of reducing the intensive heat required for thermal CO_2 hydrogenation [34,35].

Looking at the products, CO_2 hydrogenation is usually divided into *direct* and *indirect hydrogenation*. Direct CO_2 hydrogenation mostly synthesizes C_1 products including CO, methane, methanol and formic acid [18,35]. Since direct CO_2 hydrogenation to C_{2+} hydrocarbons (HCs) and oxygenates (e.g. dimethyl ether, olefins, liquid fuels and higher alcohols) is more kinetically challenging due to the high C–C coupling barrier, CO_2 hydrogenation to C_{2+} compounds is mainly performed through *modified Fischer-Tropsch synthesis* (FTS) or *methanol-mediated* process [18,33]. The modified CO_2-FTS combines CO_2 reduction to CO/syngas through the reverse water gas shift (RWGS) reaction and CO hydrogenation to C_{2+} products via FTS. The methanol-mediated route consists of CO_2 hydrogenation to methanol followed by methanol dehydration or coupling to C_{2+} compounds [18].

2.2.3. Carboxylation

The carboxylation process consists of attaching functional CO_2 molecule to another reactant for the production of organic carbonates (ROC(O)OR), ureas (RRNCONRR), carbamates ($R_1R_2NCOOR_3$) and polymers (the latter also called polymerization). Another form of carboxylation is the insertion of CO_2 into C–H bond of olefins, aromatics or alkanes for the synthesis of carboxylic acids such as acetic acid and toluic acid [13,36].

2.2.4. Mineralisation

CO_2 mineralisation or carbonation refers to as CO_2 reaction with chemical components containing alkaline earth oxides (e.g. CaO and MgO) to produce corresponding inorganic carbonates (calcium and magnesium carbonates). The process is called *indirect carbonation* when there is first extraction of Mg or Ca from minerals then carbonate precipitation in different reactors [37].

Thermodynamically, inorganic carbonates have a lower Gibbs free energy than CO_2. Therefore, in theory, the mineralisation process can release energy as shown in Reaction 1 wherein Me stands for alkali and alkaline-earth metals for example, Na, Mg and Ca [13,38].

$$CO_2 + \mathrm{MeO} \rightarrow \mathrm{Me}CO_3 + \mathrm{Heat} \qquad (1)$$

2.2.5. Electrochemical reduction

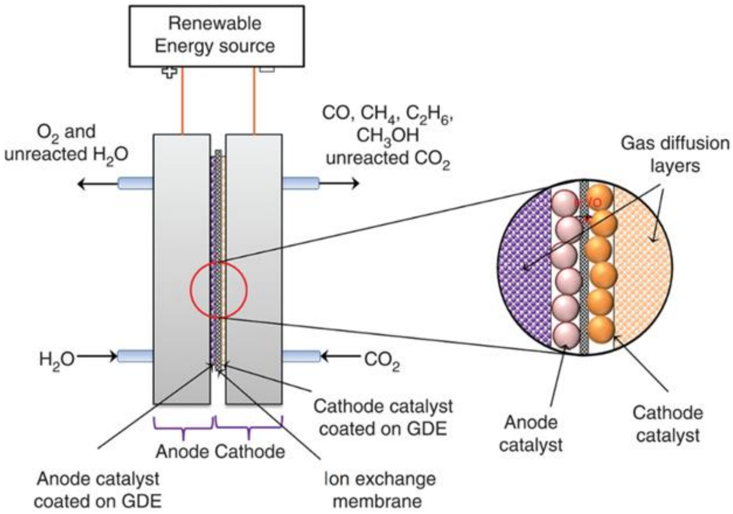


Figure 4: Schematic of a typical electrochemical reduction of CO_2 [39].

CO_2 electrochemical reduction is defined as CO_2 conversion to chemicals and fuels in an electrolytic cell using electrical energy. The electrolytic cell consists of three fundamental elements: the cathode or negative electrode, electrolyte and anode or positive electrode. During CO_2 electrochemical reduction (Figure 4), there is H_2O oxidation at the anode to produce O_2 and electrons/protons (e^-/H^+) whereas, at the cathode, there is CO_2 reduction into value-added products [39]. However, in high-temperature electrolyser such as solid oxide electrolysis cells (SOEC), there is CO_2 electrolysis or CO_2/H_2O co-electrolysis at the cathode for CO or syngas synthesis and oxygen ions (O^{2-}). O^{2-} ions are transported to the anode through the electrolyte, where they combine and generate O_2 [40].

2.2.6. Photochemical reduction

Photochemical reduction aims to mimic natural photosynthesis. Hence, CO_2 photochemical reduction is an artificial photosynthesis process wherein photocatalysts absorbs light for CO_2

reduction into high-energy products [41]. It is important not to confuse with the photosynthetic method which uses microorganisms for CO_2 fixation [26]. Figure 5 depicts the five steps of a typical CO_2 photochemical reduction process: (1) Light/Photons absorption to produce electrons (e-) and holes (h+), (2) separation of the generated holes and electrons, (3) adsorption of CO_2 on the photocatalyst surface, (4) CO_2 and e- photoreduction and H_2O oxidation, and (5) desorption of the formed products from the photocatalyst [42].

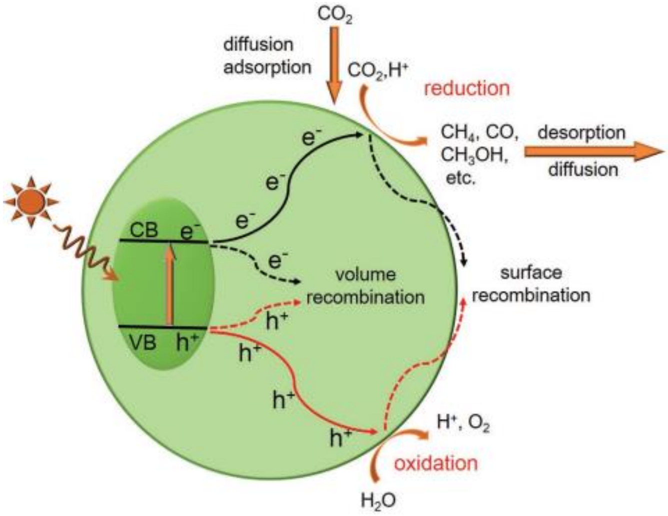


Figure 5: Steps of CO_2 photochemical reduction [42].

2.2.7. Plasma catalysis

Various forms of energy - Electrical discharges (such as plasma jet and microwave discharge), heat (e.g. electrically heated furnaces) and light (from laser or UV light) - can be used to sufficiently heat a gaseous substance until its electrons are stripped from their respective atoms to create a set of free electrons and ions called ionized gas. The ionized gas is in the 4th state of matter known as plasma. Since there is an equal amount of opposite charges, substances in plasma state are neutral overall. In non-thermal plasma (NTP) technology, the ionized gas is activated to create highly energetic electrons (energy between 1-10 eV) which can activate highly stable molecules such as CO_2 [43].

However, the use of NTP alone showed low selectivity towards desired products. Lately, an increasing interest has been devoted to combining heterogeneous catalysis with NTP, known as plasma catalysis, which has demonstrated better process efficiency, higher adsorption on the catalyst surface, lower activation barriers and reduction in catalyst's operating temperatures [43,44]. CO_2 plasma catalysis is usually performed either with pure CO_2 (*CO_2 splitting*) or in reaction with hydrogen-containing gas such as CH_4 (*plasma reforming*), H_2 (*plasma hydrogenation*) and H_2O (*CO_2-H_2O splitting*) [43].

2.3. Energy required and typical operating conditions

2.3.1. Biological transformation

The photosynthetic method requires light as energy whilst the non-photosynthetic CO_2 fixation uses electrons as an energy source. Electrons are provided either directly from an electrode by applying electricity or indirectly using chemicals such as formate ($HCOO^-$) and H_2 [27,29,30]. Both methods are commonly carried out at atmospheric pressure and temperatures ranging from 20 to 35°C (Figure 6) [45,46].

2.3.2. Chemical transformation

Photochemical and electrochemical processes are commonly performed at ambient conditions [42]. Although the electrochemical process is performed at ambient temperature, SOECs used for CO_2/H_2O co-electrolysis operate at high temperatures (above 700°C) which lower the process needs in electricity [47]. Plasma catalysis is usually performed at atmospheric pressure with temperatures ranging from 25 to 150°C [43,48]. The reforming and hydrogenation processes are typically carried out at 600–900°C and 200–500°C, respectively. While the reforming operates at ambient pressure, the hydrogenation has a broad operating pressure range of 1–100 bar [31,33,49]. The carboxylation process also has a wide pressure range of 1–150 bar with operating temperatures between 25–350°C [41,50].

An explanation of these large pressure ranges could be the wide range of products from CO_2 hydrogenation and carboxylation as elaborated in Section 3. Regarding the mineralisation, operating temperatures and pressures are around 20–100°C and 1–30 bar [37]. However, CO_2

mineralisation using silicate rocks such as serpentine and olivine operates at temperatures and pressures up to 500°C and 150 bar [37,38]. The type of energy required for each CO_2 chemical transformation is shown in Figure 6. It is estimated that 5,630 TWh of electricity will be required to produce 2,680 TWh (roughly 491 GT) of gaseous and liquid fuels from CO_2 in 2060 [51]. The development of carbon-neutral energies is therefore critical to provide climate benefits for CO_2 conversion technologies.

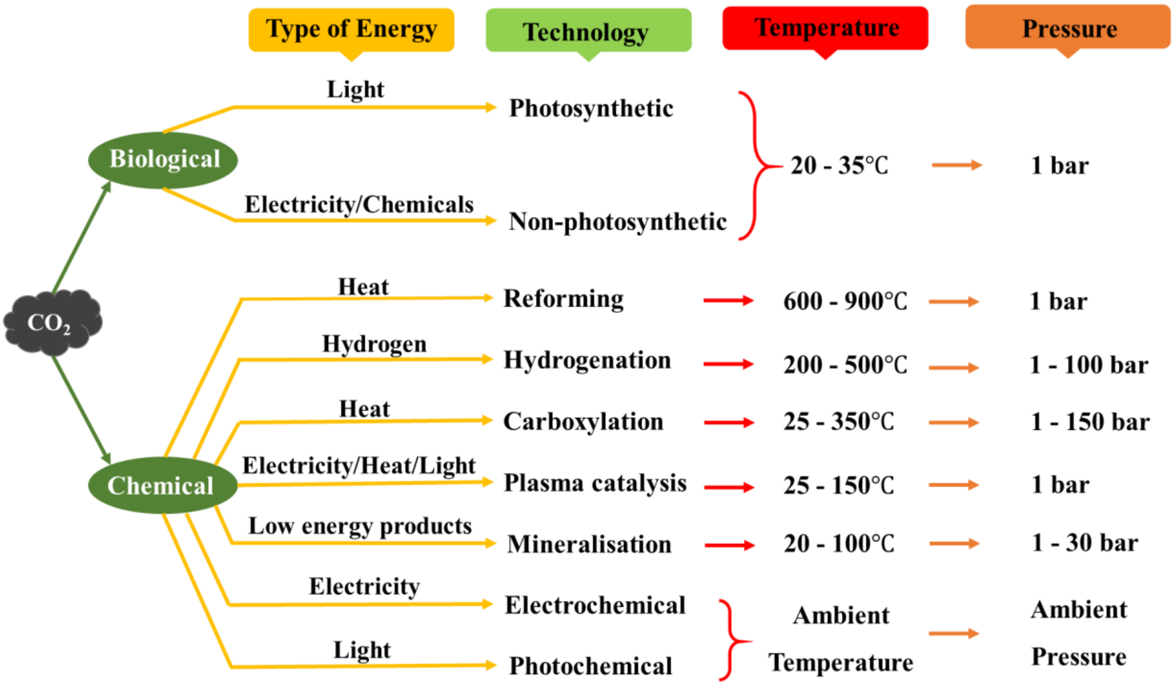


Figure 6: Type of energy required and typical operating conditions for CO_2 transformation technologies.

3. Products from CO_2 conversion

Because CO_2 utilisation is a vast domain, not every possible product can be mentioned. Only the most common products are highlighted in this section. Products from CO_2 conversion are divided into five groups (Figure 7): *bio-products*, *solid materials*, *fuels*, *chemicals & materials* and *fuels-chemicals* (i.e. components used either as fuels or chemicals). The wide range of fuels, chemicals and materials from CO_2 conversion are already available in today's market and have an application in the current industry (Table 3) including transportation (e.g. diesel, jet fuel and methanol), agriculture (e.g. urea), cosmetics (e.g. algae and formic acid), construction (e.g. cement) and aviation (e.g. polycarbonates and polyurethanes). Given the predicted growth of CO_2 utilisation via transformation, it is therefore sensitive to believe that CO_2-derived products could have a large impact not only on climate change mitigation but also on many aspects of daily life and industry.

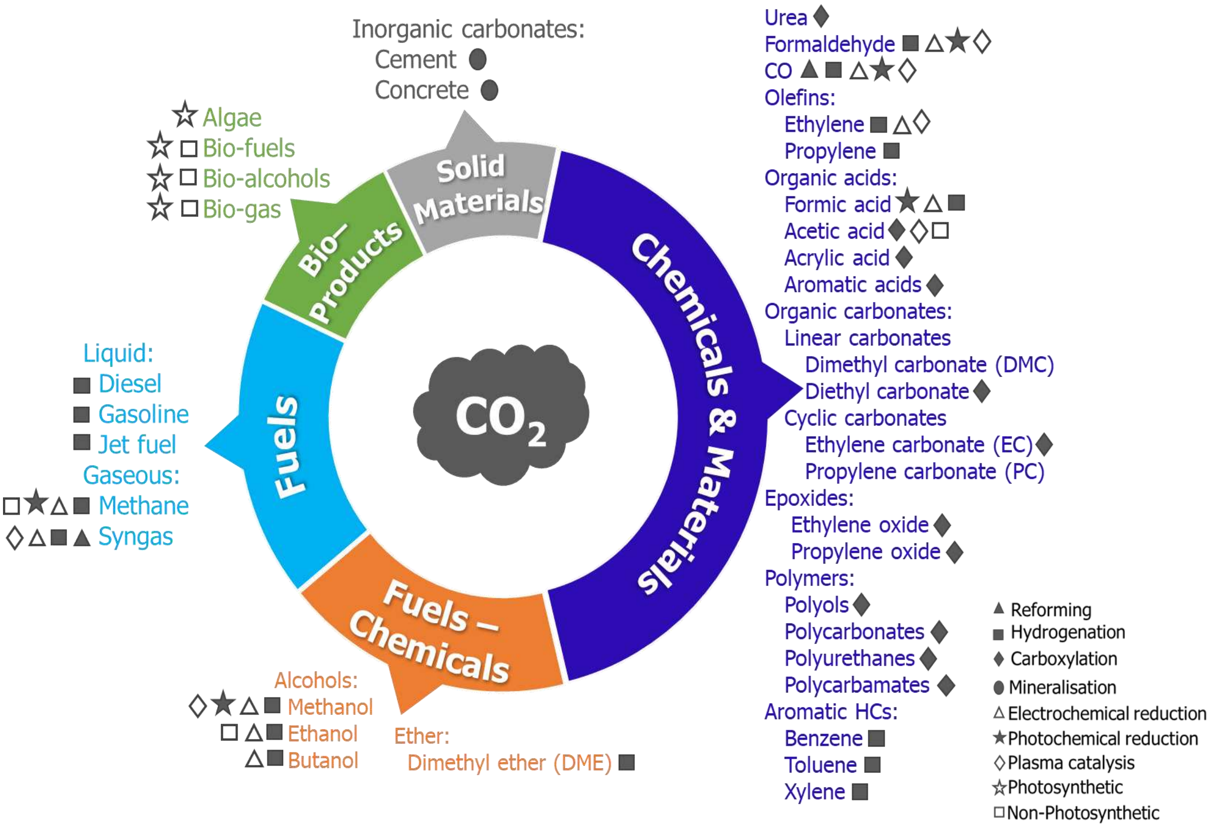
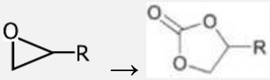
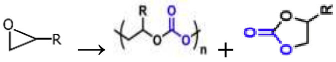
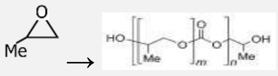


Figure 7: Products from CO_2 conversion.

Table 3: Application and chemical reaction of products from CO_2 conversion.

Product	**Technology**	**Chemical reaction**	**Application**	**Source**
Syngas	Reforming	See Table 2	Intermediate for the synthesis of several chemicals and fuels via FTS.	[31,43,47]
	Hydrogenation (RWGS)	$CO_2 + H_2 \rightleftharpoons CO + H_2O$		
	Plasma catalysis	$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$		
	Electrochemical (SOEC)	$CO_2 \longrightarrow CO + 0.5O_2$ $H_2O \longrightarrow H_2 + 0.5O_2$		
Urea	Carboxylation	$CO_2 + 2NH_3 \rightarrow NH_2CONH_2 + H_2O$	N_2 source for fertilizers, H_2 source, feedstock for adhesives, plastics and resins.	[52]

Methanol	Hydrogenation	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	Alternative transportation fuel, additive, H_2 storage, feedstock for DME, formaldehyde, acetic acid and DMC.	[13,43,53]
	Plasma catalysis			
	Electrochemical	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$		
	Photochemical			
Algae	Photosynthetic	–	Synthesis of bio-diesel, bio-gas, bio-fuel, bio-alcohols, bio-H_2, cosmetics.	[27,45]
DME	Hydrogenation	$CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O$	Fuel alternative for power plants and diesel engines, intermediate for the synthesis of olefins, gasoline and aromatics.	[54]
Methane	Hydrogenation	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	Production of compressed natural gas and syngas, feed gas purification in ammonia production.	[13,33,46]
	Non-photosynthetic			
	Electrochemical	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$		
	Photochemical			
Higher HCs	Hydrogenation (FTS process)	$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$ $nCO + (2n-1)\ H_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$	Fuels for transport and combustible engines, heating, additives, manufacturing of plastics etc.	[55]
Formic acid	Hydrogenation	$CO_2 + H_2 \rightarrow HCOOH$	Disinfection and cleaning solution, raw material for perfumes and chemicals such as amides, ketones and aldehydes.	[13,18]
	Electrochemical	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$		
	Photochemical			
Acetic acid	Carboxylation	$CH_4 + CO_2 \rightarrow CH_3COOH$	Antiseptics, dyeing, food processing (e.g. vinegar)	[56,57]
	Plasma catalysis			

			synthesis of ester and acetic anhydride.	
Cyclic carbonates	Carboxylation	CO_2 + 	Monomers for polycarbonates, diluents for resins, electrolytes in secondary batteries.	[13,14]
Linear carbonates		$CO_2 + 2ROH \rightarrow (RO)_2CO + H_2O$	Medicines, additive to gasoline, cosmetics, solvent, pesticides, polymers.	
Inorganic carbonates	Mineralisation	$CaO + CO_2 \rightarrow CaCO_3$ $CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$ $MgO + CO_2 \rightarrow MgCO_3$ $Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$	Dusting powder, drying agent, dyeing, manufacturing of bricks and construction materials, fire extinguishers, detergents.	[37,38]
Polycarbonates	Carboxylation	CO_2 + 	Plastics, medicines, automotive and aircrafts components, electronic devices such as phones, batteries and DVDs.	[58]
Polyurethane		nCO_2 + mn 	Coatings, sealants, adhesives, foams and elastomers.	

4. Experiment-based studies

4.1. Biological transformation

4.1.1. Algae production

Algae cultivation has the advantages of operating at mild conditions and using free sunlight as an energy source. However, using free light might limit its application in zones with high solar radiation or its production rate might be affected by seasonal changes, weather conditions and/or day/night cycles. Indeed, a microalgae productivity of 39 g/m^2.day was reported during June–July using PBR of 7.5L at 22 °C under natural light in a greenhouse whereas, only 10 g/m^2.day productivity was achieved in December [59]. Artificial lighting (such as light-emitting diodes and fluorescent tubes) showed continuous algae production but at higher costs due to additional energy requirement [60,61]. In addition to the light source, algae production requires rigorous control of several parameters including light intensity, pH and nutrients [62].

Overall, microalgae growth increases with the light intensity till a certain intensity threshold above which the productivity decreases due to photoinhibition [63–65]. The technical challenge is to evaluate the effect of light intensity on microalgae growth and lipid content (source of biofuel synthesis from algae) on a specie-by-specie basis. For instance, *Chlorella* sp. reached its maximum growth at 8,000 lux while *Nannochloropsis* sp. keeps growing at a light intensity of 10,000 lux [63]. The lipid contents of some species such as *Chlorella* sp. and *Nannochloropsis* sp. decrease with a rise in light intensity [63] whereas, higher or no effect on lipid contents was observed for other species including *Ettlia* sp., *Scenedesmus* sp. and *Desmodesmus* sp. [64,66,67].

In many studies, pH was kept between 6.5–10.5 by regulating CO_2 concentration or using acidic solutions [64,66–70]. The effect of pH on microalgae growth also depends on the microalgae strain. *N. salina* optimum growth rates were observed at pH around 8 [68] while high *Ettlia* sp. productivities were achieved at pH of 6.5 [64]. Deficiency in nutrients (N_2 or P) can lower algae productivity by up to 32% [71]. Although effective nutrients supply can increase algae growth by up to 150% [71], the cost for nutrients raises additional concerns. Simultaneous nutrient-rich wastewater treatment and microalgae cultivation was recently investigated to provide a more sustainable option [72,73]. Nevertheless, CO_2 loss and/or microalgae adaptation to higher N_2 loading is still an open challenge.

4.1.2. Non-photosynthetic CO_2 fixation

Non-photosynthetic CO_2 fixation has the advantages of operating at mild conditions and securing a large range of bio-products. So far, seven biological pathways have been proposed for CO_2 fixation including the reductive pentose phosphate (Calvin-Benson-Bassham), citric or tricarboxylic acid (Arnon-Buchanan), Acetyl-CoA (Wood–Ljungdahl), 3-hydroxypropionate

(Fuchs-Holo), 3-hydroxypropionate/4-hydroxybutyrate, dicarboxylate/4-hydroxybutyrate and glycine pathways [24,74]. Highest product yields and energy efficiency are commonly observed for CO_2 fixation pathways which need low ATP for occurring bio-reactions [24]. This may explain why most studies focused on CO_2 fixation via the Wood–Ljungdahl (WL) pathway (consumes less than 1 ATP molecule per pyruvate) using acetogenic and methanogenic microorganisms under anaerobic conditions [46,75–80]. The main products for methanogens and acetogens are respectively methane and acetate. Other chemicals such as ethanol, formate, butyrate, butanol and 2,3-butanediol were also reported [46,75–77,81].

Using H_2 as an electron donor for anaerobic CO_2 fixation, the key controlling parameters are temperature, pH, H_2 partial pressure and hydraulic retention time [75,82]. Increasing the retention time increased both CO_2 conversion and product yield [46,76,77] while high H_2 pressure lowered methane production [46]. Leu et al. [75] observed that CH_4 production increased till up to 21 µmol/ml when pH and temperature increased until a certain value (respectively 8 and 40°C) above which CH_4 production starts decreasing due to inhibition of methanogen activity. Some studies investigated inorganic compounds (Na_2S, $Na_2S_2O_3$ and $NaNO_2$) as electron donors under aerobic [83] and anaerobic [84] conditions. Under both conditions, Na_2S and $Na_2S_2O_3$ showed higher CO_2 fixation efficiency than $NaNO_2$ as they released a higher amount of energy during oxidation.

The use of electricity has been commonly studied via abiotic anode configuration under anaerobic conditions (Figure 8) [78–80]. The mechanism through which electrons are provided from the electrode by applying electricity is yet to be clarified. Some studies suggested that microorganisms can directly accept electrons from electrode [85,86] whilst others argued that there is first H_2 formation which acts as intermediary electron carrier since operating potentials are more negative than H_2 evolution potential [78,87]. Different cathode materials have been investigated to enhance the current density thus CO_2 reduction rate including Ni-nanoparticle coated graphite (-1.7 A/m^2) [88], carbon-felt (-5 A/m^2) [87,89], Ni-nanowire coated graphite (-8.9 A/m^2) [88], gas diffusion electrode (-11 A/m^2) [90] and multiwalled carbon nanotube (-200 A/m^2) [91]. These studies reported a Faraday efficiency (FE) between 70-99% for acetate and methane whereas, other products such as formate, ethanol and isopropanol only achieved FE between 4-22% [87,89–91].

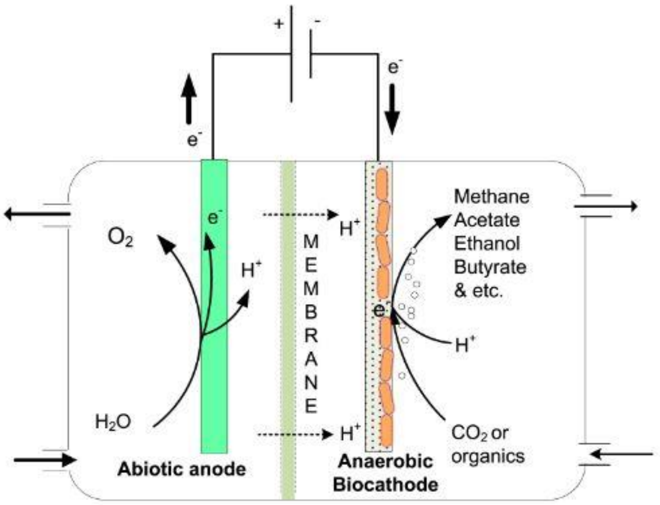


Figure 8: Abiotic anode configuration for microbial CO_2 reduction [78].

4.2. Chemical transformation

4.2.1. Reforming

The reforming process has the advantage of turning two greenhouse gases (CO_2 and CH_4) into valuable compounds. However, coke formation leading to rapid catalyst deactivation is still of great concerns for its commercial application. A comparison of noble metals (Rh, Ru, Pd, Pt and Ir), Ni and Co-based catalysts over Al_2O_3 support for DRM at 800°C showed that Ni and Co achieved maximum CO_2 conversions of 77.1% and 66.0%, respectively with a coke deposition between 24.0-49.4 mg/$g_{catalyst}$. On the other hand, noble metals showed almost no coke formation due to their efficient dispersion on Al_2O_3 support with up to 64.4% CO_2 conversion [92]. Nevertheless, noble metals are limited in use due to their low availability and high costs [93]. The morphology and nature of supports also have an impact on Ni catalyst stability. An analysis of different supports at 400 °C revealed the following classification of activity performance: $Ni/SiO_2 < Ni/Al_2O_3 < Ni/MgO < Ni/TiO_2 < Ni/Siral10 < Ni/PuralMG30 < Ni/ZrO_2 < Ni/La_2O_3\text{-}ZrO_2$ [94]. $Ni/La_2O_3\text{-}ZrO_2$ achieved 180 hours of stability due to stronger Ni interaction with mesoporous

La_2O_3-ZrO_2 [94]. Ni-Mo/MgO nanocatalyst recently achieved the highest stability of 850 hours with no coke formation at 800°C due to its very low particle size of 2.9 nm [95].

A comparison between BRM and DRM using Co-Pt/Al_2O_3 catalyst at temperatures between 300-800 °C indicated that due to H_2O presence, BRM has lower operating temperatures and coke deposition than DRM. Furthermore, BRM achieved H_2/CO of 1.3 while H_2/CO of 0.84 was observed for DRM [96]. Li et al. [97] compared Ni/ZrO_2 and LA-NiO/ZrO_2 catalysts for BRM at 850°C. LA-NiO/ZrO_2 exhibited higher stability and activity (92% CO_2 conversion and 84-95% selectivity towards CO and H_2) than Ni/ZrO_2 due to enlarged oxygen vacancies and intensified Ni-support interaction.

4.2.2. Hydrogenation

CO_2 hydrogenation has the advantage of converting CO_2 to a wide range of fuels and chemicals. Another challenge for the hydrogenation process is to identify the catalysts which promote product selectivity and how their performance can be enhanced to achieve the desired product selectivity and CO_2 conversion. An analysis of the recent progress for the most common products is presented below.

- **CO via RWGS reaction**

The thermodynamic analysis shows that RWGS is favoured in excess H_2 and at high temperatures (around 500-700°C) due to its endothermic nature [98,99]. Hence, improving catalyst activity and CO selectivity at low temperatures is a key challenge for RWGS. At temperatures below 400°C, RWGS competes with exothermic reactions (methane synthesis and WGS reactions) since they are more prominent under these conditions [98–101]. Therefore, appropriate catalysts should also promote RWGS activity with little to no CH_4 selectivity. Fe and Cu-based have been widely studied for RWGS due to their good absorption of intermediates and sintering tolerance. However, Cu catalysts were found more adequate for low operating temperature [99]. Formate dissociation mechanism was reported as the key route for CO formation mechanism over Cu/Al_2O_3 [102]. A recent study achieved 100% CO selectivity with 20% CO_2 conversion using Cu nanoparticles over

CeO_2 support at 300°C and 1 bar [103]. Noble metals (e.g. Pt/La-ZrO_2 [98] and Au/TiO_2 [104]), metal alloys (e.g. Fe-Cu/Al_2O_3 [99] and Pd-In/SiO_2 [105]) and metal-oxides (e.g. Ni-FeO_x/ZrO_2 [106] and Fe-oxide nanoparticles [107]) were also investigated. The noble metals were reported at temperatures between 150 – 250°C while the other catalysts operated at 400-750°C. All catalysts achieved 90-100% CO selectivity with 15-60% CO_2 conversion. Nevertheless, the catalyst stability is reported for less than 25 hours which might mask the unstable nature of catalysts.

- **Methane**

Methane synthesis is favoured at temperatures below 350°C (exothermic reaction) and can achieve 99% CH_4 selectivity using adequate catalysts [33]. Some studies have explored methane synthesis at temperatures as low as 100-200°C to reduce heat requirement of the process. However, active catalysts that can achieve acceptable CH_4 selectivity is still an open challenge [108]. Au, Mo, Pt and Pd-based catalysts were reported as less reactive since methanation reaction competes with CO and CH_3OH synthesis while Ru, Rh and Ni-based catalysts produce nearly only CH_4 [33,109]. Although Ni catalysts have lower activity than Ru and Rh catalysts and are easily deactivated due to sintering, Ni-subcarbonyl formation, interaction with CO intermediates and coke deposition, they are preferred due to their easy availability and low cost [109,110]. Various supports have been investigated to overcome these limitations including Ni/Al_2O_3 [110,111], Ni/ZrO_2-Al_2O_3 [112], Ni/Al_2O_3-HT [113] and Ni/γ-Al_2O_3-ZrO_2-TiO_2-CeO_2 [114] with 80-82.5% CO_2 conversion and 84–99.5% CH_4 selectivity at 220-350°C.

- **Methanol**

Considerable progress has been made for methanol synthesis using Cu catalysts. Current industrial processes reach 70% methanol selectivity using $H_2/CO_2=3$ and Cu/ZnO/Al_2O_3, CuO/ZnO/Ga_2O_3 and CuO/ZnO/ZrO_2 at 200-300°C and 70-100 bar [33,115]. In addition to low CO_2 conversion, high operating pressures are still a barrier for its application in industry. Some recent studies were reported at 30–50 bar with 5-20% CO_2 conversion. Cu/ZnO_x nanoparticles in MOFs showed strong structural interaction resulting in 100% methanol selectivity with high catalyst stability for more than 100 hours at 250 °C and 40 bar [116]. Cu-ZnO-Al_2O_3 was mixed with hydrotalcite (60wt.%CZA-40wt.%HT) and achieved 73.4% methanol selectivity with 6% CO_2 conversion at 250°C and 30 bar [117]. Other promising catalysts include In_2O_3/ZrO_2 and Pd/In_2O_3 [118,119]. In_2O_3/ZrO_2 reached 100% methanol selectivity and 5.2% CO_2 conversion with catalyst stability of 1000 hours [118] whereas, Pd/In_2O_3 exhibited enhanced CO_2 adsorption due to easy creation of oxygen vacancies leading to 20% CO_2 conversion and 70% methanol selectivity at 300°C and 50 bar [119].

- **Dimethyl ether (DME)**

For DME synthesis, adequate catalysts must simultaneously promote CH_3OH synthesis and dehydration of CH_3OH to DME. The process mostly suffers from excessive water production via RWGS which lowers methanol synthesis rate hence DME yield [18,120]. DME selectivity varies between 19-52% with up to 20% CO_2 conversion using H_2/CO_2=3-5 and Cu-hybrid catalysts at 250-300°C and 30-50 bar [54,120]. Due to their acid sites and acid strength, using zeolites (HZSM-5) as promoter improved DME selectivity (up to 77%) [120]. A drastic increase in pressure to 360 bar and H_2/CO_2=10 achieved 89% DME selectivity with 97% CO_2 conversion using CZA/HZSM-5 hybrid catalyst at 300°C [121].

- **Olefins and liquid HCs**

The methanol-medicated route has been mostly studied using Cu-Zn catalysts. Although significant advances have been made in catalysts development, the process usually synthesizes light alkanes which are subsequently converted into olefins [122]. By creating surface oxygen vacancies and acid sites, bifunctional catalysts composed of metal oxide and zeolites (e.g. $ZnGa_2O_4$/SAPO-34 [123], ZnZrO/SAPO-34 [124] and In_2O_3/HZSM-5 [125]) achieved 80-90% and 78% selectivity towards C_2-C_4 olefins and gasoline, respectively at 330-380°C and 20-30 bar.

Co and Fe-based catalysts are the most used catalysts for FTS. The FTS process is changed into methane synthesis when using Co-based catalysts and feed gas with high CO_2 content whilst Fe catalysts promote WGS activity thus the synthesis of light olefins and C_{5+} HCs with no excessive

CH_4 [126–129]. Some studies explored metal alloys such as Fe-Mn [130] and Mn-Zr-Co [131] at 360°C and 240°C, respectively. Fe-Mn achieved 59.2% and 20.5% selectivity towards C_2-C_4 olefins and C_{5+} HCs respectively whereas, Mn-Zr-Co reached 80% selectivity to liquid fuels. The importance of surface oxygen vacancies and acid sites through bifunctional catalysts was also demonstrated by Wei et al. [132]. The authors reported 78% gasoline selectivity using Na-Fe_3O_4/HZSM-5 nanocatalyst and H_2/CO_2 ratio of 1/1 at 320°C and 30 bar.

4.2.3. Carboxylation

Carboxylation technology also offers a wide range of accessible products. The most common products include urea, carboxylic acids, polymers and inorganic carbonates. Their recent progress and challenges are discussed below.

- **Urea**

Urea represents the largest use of CO_2 (Table 1) and is commercially produced at roughly 150–210 °C and 150–250 bar with up to 90% CO_2 conversion [10,133,134]. Electron-attaching techniques have been recently investigated for urea synthesis at mild conditions. Xiang et al. [133] found that under negative corona discharge, NH_3 radicals and anions reduce CO_2 to urea at 1 bar and 20 °C with 82% CO_2 conversion and 51% urea selectivity. Chen et al. [134] studied electrochemical urea synthesis by coupling CO_2 and N_2 in H_2O using PdCu/TiO electrocatalyst in an H-cell at ambient conditions. The authors reported 8.92% FE at -0.4V. Although these studies might overcome the harsh operating conditions of the conventional urea synthesis process, the energy efficiency associated with electron-coupling methods is yet to be clarified.

- **Carboxylic acids**

Various transition-metal complexes (such as (Triphos)MoH_4PPh_3 and $Ru(CO)_4PPh_3$) and metal alloys (e.g. Pd-Rh/TiO_2, V_2O_5–$PdCl_2$/Al_2O_3 and Co–Cu) have been studied for the synthesis of acetic acid and acrylic acid [57,135]. However, no satisfactory results have been made for industrial practices. Aromatic carboxylic acids have been successfully produced using Lewis acids as catalysts [136,137]. 88% benzoic acid yield was reported for the first time by Olah et al. [136] at

70°C and 50 bar using $AlCl_3/Al$. Two reaction mechanisms were suggested via formation of CO_2-$(AlCl_3)n$ complexes using $AlCl_3/Al$ [136] and synthesis of CO_2-$AlCl_3$-R_4Si using Si/Al-based catalysts [137]. The incubation technique (mixing CO_2 and Lewis acid for 1 hour before adding toluene) showed that various Lewis acids including $AlCl_3$, $MoCl_5$ and $TiCl_4$ promote toluic acid with up to 95% yield at 69 bar and 80°C [138].

➢ Polymers

Inoue et al. [139] reported the first study for polypropylene carbonate (PPC) synthesis with very low selectivity using $ZnEt_2/H_2O$ catalyst at 25°C. Since then, considerable progress has been made using metals complexes for instance, Zn-Co-dmc [140], ZnGA [141], SalenCo(III) complexes [142,143] and dinuclear Zn [144]. Up to 90% PPC and Polycyclohexene carbonate selectivity were achieved at roughly 60-120°C with some amounts of cyclic carbonates as by-products. Due to its high co-polymerisation activity, Zn-Co-dmc is preferred for the synthesis of CO_2-polyols which further react with isocyanate for polyurethane production [58,145,146]. In addition to Zn-Co-dmc, using starters as initiation-transfer agents promote a higher catalytic activity with better carbonate unit (CU) content [147]. At 80°C and 40 bar, 1,3,5-benzenetricarboxylic acid [147], oligomeric alcohol [145] and dicarboxylic acid [146] starters achieved 54%, 62.5% and 75% CU content, respectively.

➢ Linear and cyclic carbonates

Due to its equilibrium nature, DMC synthesis mostly suffers from low yield [148]. Greish et al. [149] explored SnO_2/Al_2O_3 catalyst and observed 17.8% DMC yield at 130°C and 16 bar. An increase in pressure to 120 bar achieved 44% DMC yield at 110°C using Fe-Zr catalyst [150]. Depending on whether CO_2 or methanol is first adsorbed on the catalyst, the reaction mechanism is either via the synthesis of carboxyl/carbonyl groups or methoxy compounds [149]. Synthesis of cyclic carbonates have been investigated using lanthanide oxychlorides (LnOCl) [151], metal complexes [152,153] and organic bases [154,155] as catalysts reaching 70% propylene carbonate selectivity at 50-140°C and 10-100 bar. Though organic base catalysts are easily accessible, higher activity was observed for metal complex catalysts as they provided higher surface area [150]. Ionic liquid (IL) were also studied for linear and cyclic carbonate production. Results indicated that combining ILs with a super base or Lewis basic anion enhanced the catalyst activity hence improved CO_2 conversion with up to 76% propylene carbonate yield [156,157].

4.2.4. Mineralisation

The main challenge for CO_2 mineralisation is to enhance reaction kinetics as the process is naturally very slow [37,38]. Kinetic tests during lignite fly ash production and steel slag carbonation suggested that carbonation rate increased with temperature [158,159]. Furthermore, the highest Ca conversion is reached at the highest temperature of 75°C (Figure 9) using 10-30vol.% CO_2 [158].

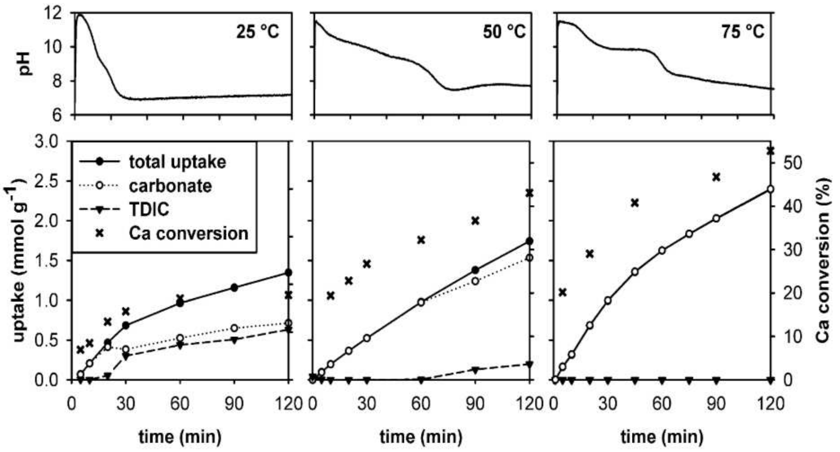


Figure 9: Dependence of CO_2 carbonation on temperature [158].

Therefore, energy input is required to speed up the process. Since the reaction is exothermic (Reaction 2), heat integration can be performed to improve the process efficiency [13,38]. Ebrahimi et al. [160] investigated carbonated fly ash production from CO_2 mineralisation at 30-70°C and reported 83.5% carbonation efficiency with CO_2 utilisation of 73 $kg_{CO2\text{-}eq}/t_{cement}$ and 42 $kg_{CO2\text{-}eq}$/GWh. Another study performed CO_2 mineralisation using EAFRS (mostly CaO and SiO_2) and achieved 86% carbonation efficiency with CO_2 utilisation of 0.38 $t_{CO2\text{-}eq}/t_{EAFRS}$ [161].

4.2.5. Electrochemical reduction

Two possible reactions mechanisms were proposed for CO_2 electrochemical reduction on metal electrodes (Figure 10). $CO_2^{\cdot-}$ formation is followed by either HCOO* or *COOH via protonation of carbon atom or oxygen atom. $HCOO^*$ is then reduced to $HCOO^-$ whereas, $^*COOH$ is converted to CO which is why CO_2 electrochemical reduction mostly leads to $HCOO^-$/formic acid and CO [42,162]. CO has been successfully synthesized with FE up to 90% using noble metals such as Pd, Au and Ag at the moderate potential of -0.6V. However, their high costs impede large-scale applications [163].

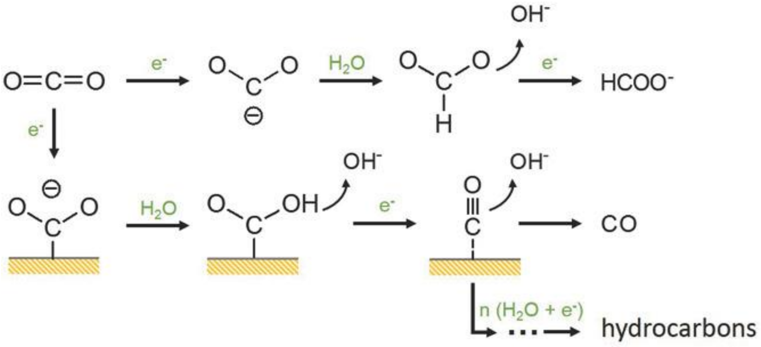


Figure 10: Reaction mechanisms of CO_2 electrochemical reduction on metal electrodes [42,162].

- **Formic acid**

Due to its non-toxicity and low cost, Sn is the most interesting metal cathode for formic acid synthesis [164,165]. However, excess potential is needed to achieve high FE (>70%). Using Sn electrode, different electrolytes ($KHSO_4$, KCl, $KHCO_3$, and KOH) were tested at 20°C. It was observed that high Cl^- nucleophility in the electrolyte lowered the overpotential hence KCl achieved the highest FE of 69.5% at 1.4V [165]. Gas diffusion electrode (GDE) combined with Sn electrocatalyst was studied by Wang et al. [166] using $KHCO_3$ electrolyte. The authors reported that the total area of gas–liquid–solid phase interface increased with Nafion and Sn fractions. Although FE of 73% was achieved at -1.8V and 13.45 mA/cm^2, the process depicted serious liquid flooding issues. To solve this problem, an anion exchange membrane and imidazole nanoparticle Sn catalyst was added at the cathode and for the first time pure formic acid (94% FE) was obtained at 3.5V and 140 mA/cm^2 [167]. Other metals, such as $Pd_xPt_{(100-x)}/C$ nanoparticles [168] and PbO_2 electrode with ionic liquid catholyte [169] were also studied and achieved FE above 88% at 40.8 and 5 mA/cm^2, respectively.

- **Above $2e^-/2H^+$ products**

Limited catalytic materials and/or electrodes have been able to further reduce CO (Figure 10) to above $2e^-/2H^+$ transfer, such as methanol ($6e^-/6H^+$), methane ($8e^-/8H^+$) and ethylene ($12e^-/12H^+$). Due to their high binding energy towards the CO intermediate, only Cu and Co were successfully reported for the synthesis of above $2e^-/2H^+$ products [170–172]. However, these products usually have low FE or require high cell voltage to achieve adequate current densities or CO_2 conversion [22,162]. For instance, at -1.44V and 5 mA/cm^2, polycrystalline Cu electrocatalyst achieved FE of 33.3%, 25.5% and 5.7% for methane, ethylene and ethanol, respectively [162]. At -1.2V, 30-40 mA/cm^2 and using Co protoporphyrin-coated PG electrode, a methane FE of 2.5% was obtained with evidence of methanol but below the detection limit of gas chromatography measurements [172]. Although current accumulative FE to above $2e^-/2H^+$ products has achieved up to 80% at 275 mA/cm^2 using advanced electrode materials and state-of-the-art technology cell configuration [22], high FE for single compounds is yet to be achieved. A recent study demonstrated the perspective for CO_2 electrochemical reduction to methanol by reporting for the first time 77.6% methanol FE at 41.5 mA/cm^2 and -2.1V using $Cu_{2-x}Se(y)$ nanoparticles [173].

- **Syngas via SOEC**

The main challenges for SOEC are low CO_2 conversion/activation and stack degradation. Since the process operates at high temperatures, RWGS also occurs making CO_2/H_2O co-electrolysis reaction pathways difficult to elucidate [47]. Ni-YSZ/YSZ/LSM-YSZ materials have been commonly studied as cell configuration (cathode/electrolyte/anode) at 800-850°C and 1 bar [174–177]. As the results indicated similar specific resistances between CO_2/H_2O co-electrolysis and H_2O electrolysis (Figure 11), it is widely believed that the performance for CO_2/H_2O co-electrolysis and H_2O co-electrolysis are comparable [47]. Furthermore, Stoots et al. [174] concluded that CO_2 is mainly reduced via RWGS but not through electrolysis. Nevertheless, some studies reported that CO was synthesized through both CO_2 electrolysis and RWGS [175,178]. It was also observed that for 0.25 A/cm^2 current density, cell degradation mostly occurred at Ni-YSZ electrode whilst above 1.0 A/cm^2, both LSM-YSZ and Ni-YSZ electrodes contributed to the total cell degradation due to

[174–177]. To improve Ni-YSZ/YSZ/LSM-YSZ limitations (such as Ni oxidation to NiO and LSM-YSZ delamination), other SOEC material configurations were explored including Ni-YSZ/ScSZ/LSM-ScSZ [178], Ni-SDC-YSZ/YSZ/LSM-SDC-YSZ [179], Ni-YSZ/YSZ/LSCF [180] and Ni-YSZ/ScSZ/LSCF-GDC [181]. The highest CO_2 conversion of 76% was achieved using Ni-YSZ/YSZ/LSCF and $40\%CO_2/40\%H_2O/20\%H_2$ feed gas at 1.0 A/cm^2 and 800℃ [180].

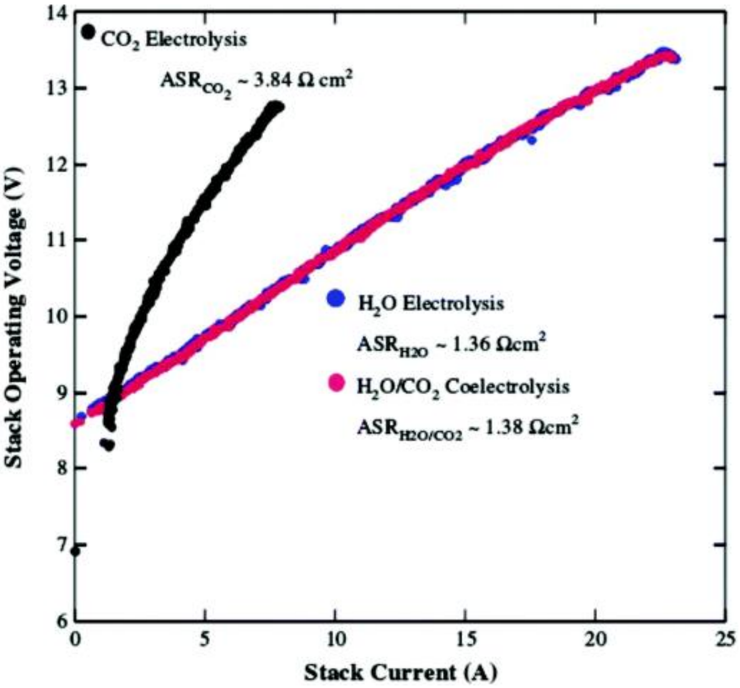


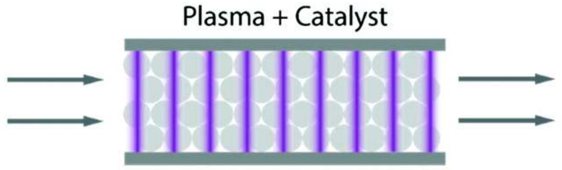
Figure 11: Polarization characterization of CO_2 electrolysis, H_2O electrolysis and CO_2/ H_2O co-electrolysis [174].

4.2.6. Photochemical reduction

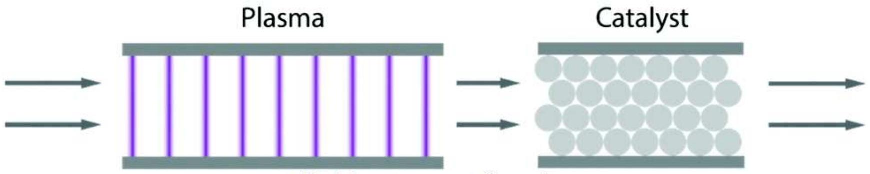
Several photocatalysts can be used for CO_2 photochemical reduction including In_2O_3, ZnS, Ga_2O_3 and TiO_2. TiO_2 is the most commonly used due to its ease to prepare, good stability, low cost and low toxicity [41,42,182]. Studies have shown that TiO_2 can be enhanced by modifying its surface or doping with novel metals [183,184]. For instance, Zhang et al. [183] studied a series of Pt loaded TiO_2 at 50℃ with CO_2/H_2O ratio of 5 and observed no activity for TiO_2 alone while $0.15Pt/TiO_2$ led to CH_4 yield of 0.34 μmol/h.g$_{cat}$. The process still suffers from low selectivity/yield due to low photon absorption and slow reactions. Some studies focused on nanocomposites to enhance CO_2 activation and facilitate product synthesis. Different Ag concentrations on TiO_2 nanocomposite were studied by Zhao et al. [185] at 20℃ using 97.2%CO_2/2.2%H_2O/0.6%CH_3OH. Results showed that 2% Ag concentration synthesizes CO and CH_4 with production rates of 87 and 10 µmol/h.g_{cat}, respectively. The CH_4 formation rate of 100.22 ppm/h.cm^2 was achieved by Li et al. [186] using Pt loaded on MgO/TiO_2 nanotubes as photocatalyst at 25℃. Cheng et al. [184] achieved a methanol yield of 454.6 µmol/h.g_{cat}, using porous TiO_2 film in an alkaline environment at 25℃. By combining reduced graphene oxide with TiO_2 nanoparticles, Olowoyo et al. [187] observed an upward shift of TiO_2 bands by 0.2eV and achieved the highest methanol rate of 2.33 mmol/h.g.

4.2.7. Plasma catalysis

Plasma catalysis is typically carried out in two configurations as shown in Figure 12. One-stage (mostly for dielectric barrier discharge (DBD)) and two-stage (using gliding arc (GA) and microwave (MW) discharges) [43]. Combination of plasma and catalyst has shown both physical and chemical advantages on the system formed (Section 2.2.7). The catalyst packing method also affects the chemical and physical interactions between plasma and catalyst. Tu and Whitehead [188] observed that fully packing Ni/γ-Al_2O_3 in DBD significantly reduced the discharge volume which inhibited the formation of filamentary discharge. Whereas, partial catalyst packing showed large void fraction in the discharge gap with strong filamentary microdischarge which considerably improved the chemical and physical interactions between plasma and Ni/γ-Al_2O_3.



(a): One-stage configuration



(b): Two-stage configuration

Figure 12: Schematic of plasma catalysis configurations [43].

Most studies used DBD combined with metal-based catalysts (Ni, Cu, Au and Pt) since DBD is the most mature plasma technology and operates at low temperatures and atmospheric pressure

[22,35,56,188–192]. The process suffers from low CO_2 conversion, energy efficiency and product selectivity/yield. However, CO and syngas synthesis achieved 40-70% CO_2 conversion and 80-90% product selectivity with a low energy efficiency of 0.14-3.7 mmol/kJ using 12%wt Ni/γ-Al_2O_3 [193] and $NiFe_2O_4/SiO_2$ [190] catalysts. 40.2% acetic acid, 11% methanol and 7.5% ethanol selectivities were reported during plasma reforming using Cu/γ-Al_2O_3 [56]. Zhang et al [192] obtained 32.1% ethane selectivity with 7.5% CO_2 conversion via plasma reforming with zeolite HY. Another study achieved 53.7% methanol selectivity, 21.2% CO_2 conversion and 0.1 mmol/kJ energy efficiency using Cu/γ-Al_2O_3 for plasma hydrogenation at ambient conditions [35]. On the other hand, GA and MW discharges (sometimes referred to as warm plasma) have shown 40-50% energy efficiency. However, high efficiencies were observed for low CO_2 conversion (below 20%) and in some cases where CO_2 conversion reached 80-83%, the energy efficiency dropped to 5% or less [43]. This is mostly due to high power discharges which negatively affect energy efficiency but enhance CO_2 conversion by improving the electric field and electron density [194].

5. Modelling and simulation-based studies

The aforementioned experimental studies provide a good understanding of reaction mechanisms, catalyst activity and general process performance. However, to achieve commercial implementation, further insights into the effects of operating conditions, component properties and how different components (reactors, heat exchangers, pumps etc.) interact and influence the process performance are required. In this respect, modelling and simulation are irreplaceable methods for process design and optimisation enabling scale-up from laboratory to commercialisation.

5.1. Categories of process modelling

Modelling of any process depends on the aim of the specific study. Therefore, there are several ways to carry out a modelling and simulation study (Figure 13). The basic distinction is between mechanistic and empirical models. Mechanistic models are based on physics laws and first principles. Hence, they require prior knowledge of the process. Mechanistic models are used to explain the physical meaning of reactions and the reason why a process behaves the way it does. Empirical or data-driven modelling does not require full knowledge of physics behind the process. However, considerable experimental data are needed for model calibration and it can only describe the correlation between data. Combination of both types is known as semi-empirical modelling [195,196].

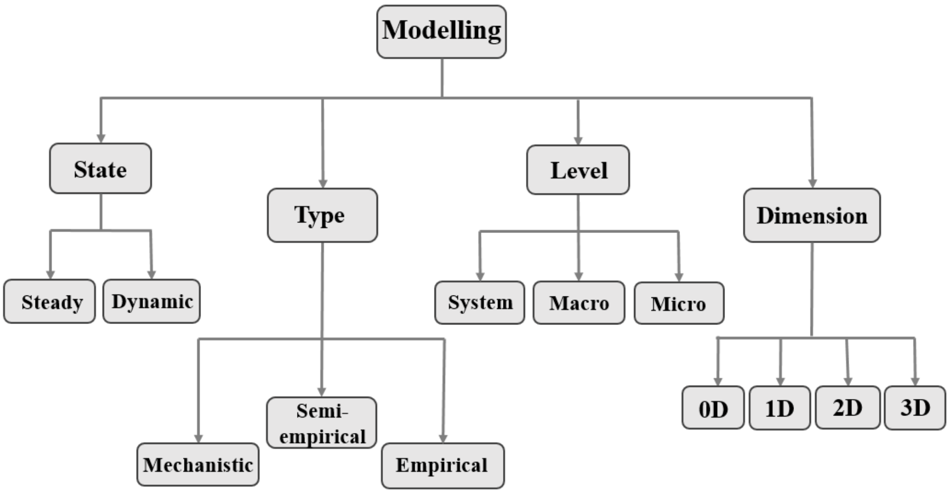


Figure 13: Categories of process models [195].

Other ways to differentiate models is by state, level and dimension. Steady-state models are usually developed in early stages of modelling for initial process analysis and performance prediction whereas, dynamic modelling is used to understand the actual operations such as control strategies and safety considerations in transient operations. At the system level, the model is a simple thermodynamic system whereas, macro and microscale modelling is used for process optimisation at component and microstructure levels, respectively. Dimensional modelling varies from 0D to 3D wherein each number represents the number of space variables considered. In general, the model complexity increases with the number of dimensions [195]. Based on this classification criteria, some recent modelling and simulation studies carried out for CO_2 transformation technologies are elaborated in Table 4. Unless specified in the description, the models are system-level and 0D.

5.2. Current status of modelling CO_2 transformation technologies

Except for algae production, most studies have reported mechanistic and steady-state models. Though several modelling/simulation studies on microbial fuel and electrolysis cells are available in the literature [197], the first "model-for-learning" on non-photosynthetic CO_2 fixation in abiotic anode cell was recently proposed by Samarakoon et al. [198] in 2019. Regarding transformation technologies that lead to several products such as carboxylation, hydrogenation and electrochemical reduction, it was found that studies mostly focused on urea and DMC, methanol and CO/syngas, respectively. For liquid fuel synthesis from CO_2, steady-state models of integrated SOEC-FTS and RWGS-FTS systems have been reported based on Anderson-Schulz-Flory (ASF) equation and Langmuir–Hinshelwood–Hougen–Watson (LHHW) adsorption theory for FTS product distribution and reaction kinetics, respectively [55,199–205].

The popularity of steady-state models could translate the early development stage of most CO_2 transformation technologies which are still not commercial. This would suggest algae production [206–211], CO_2 hydrogenation to methanol [212] and SOEC [213] are promising CO_2 transformation technologies since they are being optimized in dynamic mode and take into consideration operational disturbances. Nevertheless, very few of these models were validated in dynamic mode [207,211,212]. On the other hand, very limited studies were found for technologies such as mineralisation and carboxylation to urea which are quite mature processes showing that dynamic modelling does not necessarily illustrate the technology maturity.

5.3. Process analysis and process optimisation

During process analysis, one parameter is varied and its effects on process performance are assessed while the other parameters remain unchanged. On the other hand, process optimisation consists of analysing the effect of a set of operating parameters on the process performance [214]. It was observed from Table 4 that very limited studies carried out process optimisation [208,212,213,215]. Most studies performed process analysis at system or component level by varying operating parameters, for example, temperature, pressure, flowrate and feed composition to evaluate their effects on the conversion and production efficiency. Furthermore, In-depth process analysis of microstructural properties was only reported for reforming [216,217] and SOEC [218,219] technologies probably due to the complexity of micro-modelling. Although considerable progress has been reported with individual parameter analysis, the net contribution to improving the underlying technology is still difficult to assess. Further studies on process optimisation are required to meaningfully evaluate the interaction among different operating parameters which cannot be obtained with the "one parameter at a time" approach.

5.4. Process intensification

Process intensification aims at reducing the equipment size of processing plants without compromising their production rates. This can be realised through improved and targeted mixing, heat and mass transfer rates resulting in enhanced product selectivity and better energy efficiency [220]. Some greater levels of intensification can be achieved by combining two or more conversion processes and/or combining the synergies of equipment and processes [221]. Therefore, if successfully implemented, intensified systems present the potential to lower capital costs as well as improve process safety, response times and in some cases be more environment-friendly [220,221]. Very limited studies on process intensification of CO_2 transformation technologies were found in the open literature. Some examples include CO_2 hydrogenation to methanol [53,222] and DMC synthesis via carboxylation [223,224] (modelling and simulation details are provided in Table 4).

To illustrate, the traditional CO_2 hydrogenation is a multi-stage process wherein H_2O is actively removed in-between stages to improve CO_2 conversion and product selectivity. A recent modelling study proposed a process intensification for CO_2 hydrogenation to methanol with in-situ water sorption [222]. By adding zeolite-A4 in the methanol reactor, the process operates without a distillation column for methanol recovery. Furthermore, the proposed model overcomes the severe thermodynamic limitations observed with the traditional process (Section 4.2.2) and achieved 99.98% CO_2 conversion and 97.76% methanol yield at 230°C and 50 bar. Al-Kalbani et al. [53] carried out heat integration on

CO_2 hydrogenation to methanol. Compared to the conventional method, the cooling and heating utilities of the integrated process are reduced by 59.7% and 67.3%, respectively. These studies demonstrated the potential of process intensification for CO_2 transformation technologies. However, further R&D on stable catalysts, reactor design and configuration that can withstand continuous operation and reaction is highly required.

Table 4: Examples of modelling and simulation studies for CO_2 transformation technologies.

Algae production				
Production system	**Model description**	**Software**	**Simulations performed**	**Ref.**
Open pond	Mechanistic and steady state model based on mass balance and kinetic of an open algal pond.	gPROMS®	Effect of pond depth, CO_2 mole fraction, gas flowrate and O_2 demand on algae growth.	[225]
Open pond	Dynamic and mechanistic model based on mass balance for gas-liquid transfer and light intensity to study algae production.	MATLAB®	1) Model validation for dissolved O_2, algae biomass, pH, inorganic N_2 and carbon. 2) Effects of O_2 demand, dilution and pond depth on algae growth.	[206]
PBR	Semi-empirical and dynamic modelling based on data and mass balance for prediction of algae productivity rate under varying light intensity and nutrients.	MATLAB®	Model validation in terms of algae, lipid, glucose and glycine concentration as a function of time.	[207]
PBR	Dynamic and mechanistic modelling based on mass transfer between gaseous and liquid phases for algae growth in photo-autotrophic and photo-mixotrophic environment.	Python and IPOPT	1) Dynamic model validation for algae concentration and pH. 2) Effects of nutrients, reactor thickness and light intensity on algae growth (Python)	[208]

			3) Process optimization (IPOPT): Variation of algae productivity with recycle ratio and dilution rate.	
PBR	A dynamic and semi-empirical model based on kinetics was developed to assess microalgae growth and describe the effects of photorespiration and photosynthesis.	COMSOL Multiphysics™	1) Model validation in term of algae growth and ammonium concentration. 2) Influence of pH, irradiance and temperature on algae growth.	[209]
PBR	Dynamic and mechanistic model based on mass balance equations and kinetics was used to evaluate the interaction between bacteria and algae during culture.	MATLAB®	1) Dynamic model validation for O_2, algae, bacteria, NO_3^- and NH_4^+ concentration. 2) Sensitivity analysis of O_2 mass transfer, NO_3^- and NH_4^+ concentration. 3) Calibration using Monte Carlo simulation.	[211]
PBR	Dynamic and mechanistic modelling of algae growth based on kinetics of nutrient consumption and light intensity.	Mathematica®	1) Model validation for NO_3^- and algae concentration, N_2 quota, fluorescence and FAME yield. 2) Sensitivity analysis of the above-mentioned parameters on the system efficiency	[210]
Non-Photosynthetic				
Cell type	**Model description**	**Software**	**Simulations performed**	**Ref.**
Abiotic anode cell	Dynamic and mechanistic model based on material balance equations	AQUASIM 2.1	Effect of applied voltage on CH_4 production, methanogen growth rate and pH of the digester.	[198]

	and growth rate kinetics to assess CO_2 fixation by anaerobic methanogens.			
Reforming				
Reactor	**Model description**	**Software**	**Simulations performed**	**Ref.**
Annular reactor	Mechanistic, steady state and micro model for analysis of DRM process based on reaction kinetics on Rh-based catalyst.	Not specified	1) Model validation for the outlet composition and conversion rate at different temperatures. 2) Sensitivity analysis of temperature and conversion rate.	[216]
Fire-steam reformer	1D, steady-state and mechanistic model for DRM process based on energy conservation and reaction kinetics.	Not specified	Effects of feed gas composition and temperature on the process conversion rate.	[226]
Contact-bubble reactor	Mechanistic, steady state and micro modelling of DRM process based on reaction kinetics Ni-based catalysts.	GRI-Mech 3.0	1) Model validation for CH_4 and CO_2 conversion at various temperature. 2) Effect of inlet flowrate, feed gas ratio, active surface area and residence time on CH_4 and CO_2 conversion.	[217]
Fixed-bed reactor	A mechanistic and steady state model based on mass/energy balance and kinetics was built to investigate the	UniSim and MATLAB®	1) Model validation for CO/H_2 ratio, CH_4 and CO_2 conversion (UniSim). 2) Effect of temperature, pressure and gas space velocity on CO/H_2 ratio, CH_4 and CO_2 conversion (UniSim).	[215]

	non-equilibrium behaviour of DRM using Ni- based catalyst.		3) Process optimization (MATLAB®): Evolution of CO rate and CO_2 conversion with temperature, inert fraction and gas space velocity.	
Not specified	Semi-empirical and steady state modelling based on experimental data and mass conservation principle of DRM process using solar energy.	Aspen Plus®	1) Model validation for CO and H_2 outlets and temperature. 2) Process analysis for different irradiations.	[227]
Hydrogenation				
Reactor	**Model description**	**Software**	**Simulations performed**	**Ref.**
Plug flow reactor	A mechanistic and steady state model was developed based on kinetics and mass/energy balance principle to study methanol synthesis using H_2 from chlor-alakali.	Aspen Plus®	1) Model validation for CO_2 conversion. 2) Sensitivity analysis of temperature, pressure, CO/H_2 ratio and GSV on CO and methanol yield.	[228]
Multi-tubular reactor	Mechanistic and steady state model of CO_2 and CO hydrogenation to methanol based on mass/energy balance and reaction kinetics using Cu catalyst.	Aspen Plus®	Influence of feed gas ratio on total CO_2 conversion and energy efficiency.	[229]
Lurgi-type reactor	1) 1D and mechanistic modelling of methanol synthesis based on kinetics, heat transfer energy balance and continuity principles.	Not specified	1) Dynamic model validation in term of methanol production. 2) Simultaneous and dynamic optimization of recycled CO_2 and shell temperature.	[212]

	2) Dynamic and empirical modelling of Lurgi-type reactor using genetic algorithm (GA).			
Lurgi-type reactor	Steady state and mechanistic model based on kinetic equations to investigate methanol synthesis using H_2 from water electrolysis.	Aspen HYSYS®	1) Heat integration between cold and hot streams for process intensification. 2) Comparison of energy requirement and climate impact.	[53]
Not specified	A mechanistic and steady state model based on minimization of Gibbs free energy was built to evaluate DME synthesis.	Aspen Plus®	Influence of H_2/CO_2 ratio, temperature and pressure on CO_2 conversion and DME selectivity.	[230]
Fixed-bed reactor	Mechanistic and steady state modelling of methanol synthesis based on mass balance and Gibbs free energy minimization	Aspen Plus®	1) Addition of water sorbent (zeolite-A4) in methanol reactor for process intensification. 2) Effect of temperature, pressure, feed ratio and sorbent volume on methanol yield. 3) Comparison between traditional and sorption-enhanced processes.	[222]
Electrochemical reduction				
Electrode material	**Model description**	**Software**	**Simulations performed**	**Ref.**
GDE	Mechanistic and steady state model based on gas transport, material	COMSOL Multiphysics™	1) Model validation for voltage versus current density at different feed flowrates.	[231]

	balance and charge transfer kinetics to study CO synthesis.		2) Effect of CO_2 concentration, flowrate, electrode porosity and channel length on cell performance.	
Cu and Ag	1) 1D, mechanistic and steady state modelling of CO synthesis based on mass conservation, charge transfer kinetics to study species transport and surface reactions. 2) Macro model based on Ohm's law and Butler-Volmer equation to assess polarization losses.	COMSOL Multiphysics^{TM}	1) Effect of current density on species concentration and polarisation losses. 2) Effect of pH, conductivity, buffer and boundary layer thickness on polarisation losses.	[232]
GDE	1D, macro, mechanistic and steady state model based on mass balance, charge transfer kinetics, Ohm's law and charge conservation was built for CO production	COMSOL Multiphysics^{TM}	1) Model validation for FE of CO Vs voltage and voltage Vs current density. 2) Analysis of electrode properties on local CO_2 concentrations and CO partial current density.	[233]
GDE	1D, macro, mechanistic and steady state model based on mass/charge conservation, charge transfer kinetics, Butler-Volmer equation, energy and gas transport to assess flooding and dehydration issue in membrane electrode assembly cell.	COMSOL Multiphysics^{TM}	1) Effect of current density on CO_2 conversion and utilisation efficiency. 2) Analysis of temperature and membrane thickness for water issue management.	[234]
Electrochemical Reduction – SOEC				

Cell Assembly	**Model description**	**Software**	**Simulations performed**	**Ref.**
Ni-YSZ/YSZ/LSM	A macro, steady state and mechanistic SOEC model was built based on mass/energy balances for chemical equilibrium and Faraday's law for O^{2-} flow.	UniSim	1) Model validation for outlet composition and temperature. 2) Evaluation of syngas production efficiency as a function of current density for various specific resistances.	[235]
Ni-YSZ/YSZ/LSM-YSZ	1) 2D, steady state and mechanistic model based on energy, mass and momentum conservation to study mass transfer and fluid flow between electrodes. 2) macro modelling based on Nernst potential, Ohm's law and Butler-Volmer equation to assess SOEC required voltage.	FLUENT	1) CFD, electrochemical and chemical model validation. 2) Influence of temperature, inlet gas composition and operating voltage on the SOEC performance.	[236]
Ni-YSZ/YSZ/LSM	Mechanistic and steady state model based on mass, momentum, charge and energy conservation was developed to analyse the surface electrolysis reactions.	COMSOL Multiphysics™	1) Model validation for voltage versus current density. 2) Effects of temperature, voltage and feed gas composition on gas distribution and adsorbed species within the electrodes.	[237]
	2D, mechanistic, steady state and micro modelling of SOEC based on		1) Model validation for voltage versus of current density at different CO_2/H_2O ratios and temperatures.	

Ni-YSZ/ScSZ/LSM-ScSZ	energy/mass balance, fluid flow, charge and momentum conservation principles.	COMSOL Multiphysics^{TM}	2) Sensitivity analysis of temperature, CO_2/H_2O ratio and gas flow velocity on polarisation distribution. 3) Effect of operating voltage on conversion ratio.	[218]
Ni-YSZ/YSZ/LSM	A quasi 2D, mechanistic, steady state and micro model was built based on Butler-Volmer equation, charge conservation and mass transfer	DETCHEM	1) Model validation for voltage versus current density using different feed compositions 2) Influence of temperature, inlet gas velocity and micro-structural properties on species distribution and electrochemical performance. 3) Flow analysis of surface reaction mechanism.	[219]
Ni-GDC/YSZ/LSM-YSZ	Dynamic, mechanistic and 3D model based on energy conservation, charge transport and kinetics to investigate SOEC scale up from lab to commercial scale.	DETCHEM	1) Model validation of voltage and outlet composition as a function of current density for different temperature and inlet feed composition. 2) Process optimisation: Variation of syngas efficiency with unit length and inlet gas velocity for different temperatures.	[213]
Photochemical reduction				
Photo-Reactor	**Model description**	**Software**	**Simulations performed**	**Ref.**

Optical fiber monolith reactor	2D, steady-state and mechanistic model based on mass transfer, reaction kinetics and species transport to study CH_3OH synthesis using TiO_2 with 1% $NiO/InTaO_4$.	COMSOL Multiphysics™	1) Model validation for outlet CH_3OH concentration. 2) Effect of H_2O content, gas inlet velocity and UV intensity on CH_3OH concentration. 3) Impact of optical fiber installation on light intensity distribution.	[238]
Double-skin sheet reactor	3D, steady-state and mechanistic model based on mass transfer, reaction kinetics and species transport to study CH_3OH synthesis using TiO_2 with 1% $NiO/InTaO_4$.	COMSOL Multiphysics™	1) Model validation for outlet CH_3OH concentration. 2) Analysis of CH_3OH concentration on X-Y and X-Z sections. 3) Effect of H_2O content, gas inlet velocity, reactor surface area and width/height ratio on CH_3OH concentration.	[239]
Bubbling twin reactor	3D, dynamic and mechanistic model based on mass transfer, reaction kinetics and species transport to assess CH_3OH synthesis using $Pt/CuAlGaO_4$ and $Pt/SrTiO_2$: Rh.	FLUENT and COMSOL Multiphysics™	1) Effect of inlet gas velocity, inlet gas number, diameter and pitch on CH_3OH concentration. 2) Performance comparison between tradition and bubbling twin reactors.	[240]
Optical fiber monolith	3D, steady-state and mechanistic model based on mass transfer, reaction kinetics and species transport	COMSOL Multiphysics™	1) Model validation for outlet CH_3OH concentration.	[241]

reactor with glass balls	to study CH_3OH synthesis using TiO_2 with 1% $NiO/InTaO_4$.		2) Effect of ball location and numbers, layer and circle number on CH_3OH concentration.	
Carboxylation				
Reactor type	**Model description**	**Software**	**Simulations performed**	**Ref.**
Plug-flow reactor	Steady-state and mechanistic model based on mass balance and thermal transfer principles was developed to study urea synthesis process.	Aspen Plus®	Integration of heat and steam recovery systems to improve process thermal balance.	[52]
Fixed-bed reactor	Dynamic and mechanistic model based on material and heat balance, mole fraction normalisation and kinetics was built to investigate process intensification of DMC synthesis.	gPROMS®	1) In-situ hydration of ethylene oxide and integrated gas-phase side distillation reactor for process intensification. 2) Effect of feed composition, pressure, column number of stages and temperature on process conversion and DMC selectivity.	[223]
Continuous Stirred-tank	Steady-state and mechanistic modelling of DMC synthesis based on mass/energy balance and reaction kinetics.	Aspen Plus®	1) Heat integration and addition of butylene oxide as dehydrating agent for process intensification. 2) Economic and net CO_2 emission analysis.	[224]
Mineralisation				
Reactor type	**Model description**	**Software**	**Simulations performed**	**Ref.**

Autoclave reactor	Mechanistic and steady state model based on reaction kinetics of indirect carbonation of red gypsum to calcium carbonate.	PHREEQC	1) Model validation in term of reaction rate and constant for different temperature, liquid-solid ratio, stirring rate and Ca dissolution. 2) Effect of temperature, stirring rate, Ca dissolution and liquid-solid ratio on the carbonation process. 3) Kinetic analysis of Ca dissolution.	[242]
Plasma catalysis				
Plasma reactor	**Model description**	**Software**	**Simulations performed**	**Ref.**
DBD reactor	Empirical and steady state model based on hybrid artificial neural network and genetic algorithms was built to investigate plasma reforming on CaO-MnO/CeO_2 catalyst.	MATLAB®	1) Model validation for H_2/CO ratio, CH_4 conversion, H_2 and C_{2+} selectivities. 2) Influence of flowrate, temperature, discharge voltage and CH_4/CO_2 ratio on the reactor performance.	[243]
Packed bed DBD reactor	A 2D, steady state and mechanistic model was developed based on continuity equations of electron energy and density to assess micro-	COMSOL Multiphysics™	1) Analysis of spatial distribution of electron ionization rate, electric field, plasma density and electron temperature for different voltages and pore sizes.	[244, 245]

	discharge formation inside the catalyst pores.		2) Effect of required voltage and pore size on the microdischarge behaviour.	

6. Comparison of CO_2 transformation technologies

Each CO_2 transformation technology has distinctive characteristics that make it more appropriate for a specific utilisation and help to identify the most suitable technology in any given circumstance. This section compares CO_2 transformation technologies in terms of maturity, cost, market and net CO_2 usage.

6.1. Technological maturity

The technology readiness level (TRL) tool is used to assess each CO_2 technological maturity as illustrated in Figure 14. TRL is a common tool used in EU and USA for measuring the maturity of any technology. Further explanation on TRL can be found here [246]. Plasma catalysis and photochemical reduction methods have been attributed TRL of 1-3 and 2-4, respectively as they are still being validated in a laboratory environment [22,247]. TRL of 3-5 has been allocated to electrochemical reduction and non-photosynthetic processes since they are tested at pilot scale in projects such as CELBICON and BioPower2Gas, respectively [248,249]. Details on these projects are given in Table 7. Reforming, photosynthetic and mineralisation technologies have higher TRLs of 4-6, 4-7 and 7-9, respectively [10,247,250].

Hydrogenation and carboxylation technologies have a broad-ranged TRL of 2-9 because they lead to a wide range of products with different TRLs (Table 5). For example, methanol and methane synthesis have achieved high TRL of 7-9 whilst CO_2 hydrogenation to formic acid and DME is still at an early stage with TRL of 3-5 and 2-3, respectively [250,251]. The FTS process operates at commercial scale in some plants, for instance, Pearl GTL plant in Qatar with a production of 140,000 GTL/day [252]. However, it has a TRL of 5-8 since sustainable FTS is usually integrated with lower maturity processes such as reforming and SOEC for syngas production [250]. Urea synthesis has achieved high TRL of 7-9 whilst production of polymers, cyclic carbonates and carboxylic acids through carboxylation have TRLs of 6-7, 5-7 and 2-4, respectively [250,253].

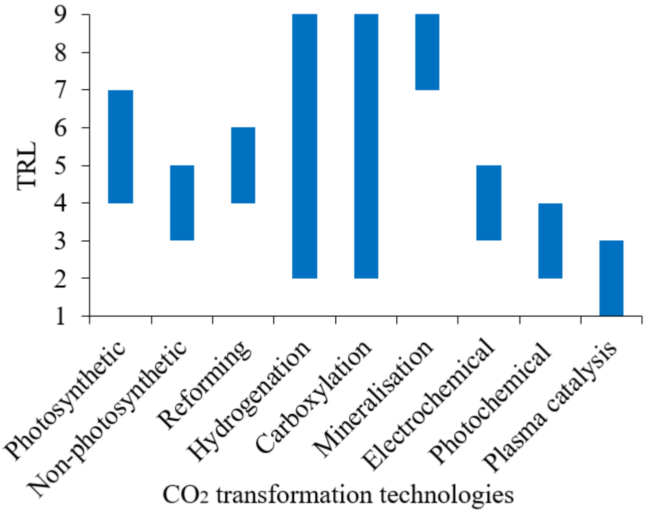


Figure 14: TRL of CO_2 transformation technologies.

Table 5: TRL of hydrogenation and carboxylation based on their products [10,250,253].

Technology	Product	TRL
Hydrogenation	Methanol	7-9
	Methane	7-9
	Liquid fuels via FTS	5-8
	Formic acid	3-5
	DME	2-3
	Formaldehyde	2-3
Carboxylation	Urea	7-9
	Polymers	6-7
	Cyclic carbonates	5-7
	Carboxylic acids	2-4

6.2. Cost considerations

One of the most important factors for commercial deployment is the cost. Assessment of total cost for a given CO_2 conversion technology should include both capital and operational expenditures

(CAPEX and OPEX). CAPEX corresponds to costs for designing, purchasing equipment and building the plant. OPEX includes fixed costs (for plant operation and maintenance) and variable costs (for raw materials, catalysts, utilities and disposal of by-products) [254]. Table 6 presents the normalized values of CAPEX and OPEX, together with the utility consumption for some CO_2 transformation technologies. The utility can be electricity, heating and/or cooling consumption. It should be noted that plasma catalysis, photochemical reduction and non-photosynthetic technologies are not included as no economic studies were found in the open literature.

Table 6: Key performance indicators of some CO_2 transformation technologies

CO_2 conversion technology	CAPEX	OPEX	Utility consumption	Net CO_2 used	Plant life (Year)	Source
Reforming	23.9 £/$t_{methanol}$	100.6 £/$t_{methanol}$	0.7 MWh/$t_{methanol}$	1.86 t_{CO2}/$t_{methanol}$	20	[10,255]
Hydrogenation	853 – 924 £/$t_{methane}$	6,854 – 10,281 £/$t_{methane}$	15.2 MWh/$t_{methane}$	1.0 t_{CO2}/$t_{methane}$	20	[10,256]
	93.2 – 206.3 £/$t_{liquid\ fuel}$	1304.3 – 2173.9 £/$t_{liquid\ fuel}$	11.93 MWh/$t_{liquid\ fuel}$	2.6 t_{CO2}/t liquid fuel	20	[199,257]
	22.0 £/$t_{methanol}$	586.1 £/$t_{methanol}$	1.5 MWh/$t_{methanol}$	1.23 t_{CO2}/$t_{methanol}$	20	[254]
	59.1 £/t_{FA}	1,335 £/t_{FA}	9.8 MWh/t_{FA}	0.67 t_{CO2}/t_{FA}	20	[251]
Carboxylation	9.5 £/t_{urea}	144.2 £/t_{urea}	0.02 – 0.16 MWh/t_{urea}	0.74 t_{CO2}/t_{urea}	20	[10]
	3.1 £/t_{polyol}	1,026.4 £/t_{polyol}	0.01 MWh/t_{polyol}	0.23 t_{CO2}/t_{polyol}	25	[258]
Mineralisation	7.5 – 11 £/$t_{CO2\ seq.}$	56.3 – 75.7 £/$t_{CO2\ seq.}$	0.001 – 0.17 MWh/$t_{CO2\ seq.}$	0.36 – 0.42 t_{CO2}/t_{CaCO3}	10	[259]

Electrochemical reduction	680.7 £/t_{FA}	858.4 £/t_{FA}	1.1 MWh/t_{FA}	0.5 t_{CO2}/t_{FA}	25	[10,260]
Photosynthetic	417.5 £/$t_{algal\ oil}$	1,457 – 2,217 £/$t_{algal\ oil}$	1.6 MWh/$t_{algal\ oil}$	2.24 t_{CO2}/$t_{algal\ oil}$	20	[261]

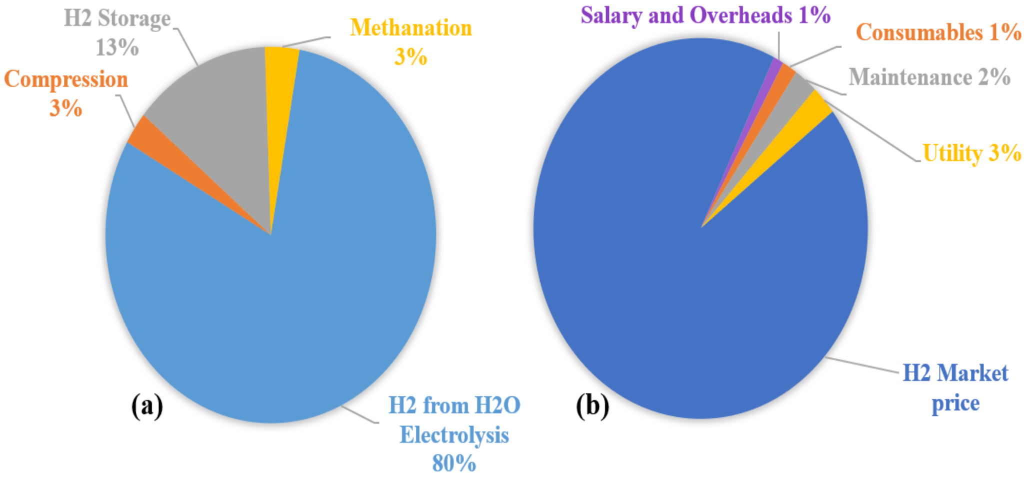


Figure 15: Cost breakdown for CO_2 hydrogenation to (a) methane and (b) methanol [254,256].

In terms of operating cost per ton of product, mineralisation technology depicts the lowest range with the least utility consumption. Likewise, the hydrogenation process presents the highest ranges for both OPEX and utility consumption. Götz et al. [256] evaluated the costs of CO_2 hydrogenation to methane at 35.8 €M for a production rate of 591 m^3/hr. Cost breakdown (Figure 15a) shows that 80% of costs account for H_2 production via water electrolysis. Hence, high OPEX of hydrogenation is directly related to its high electricity demand for H_2 synthesis. The utility demands for methanol synthesis via hydrogenation seems lower but still have a high OPEX. Cost breakdown analysis revealed that H_2 was purchased and represented 93% of OPEX (Figure 15b) [254]. On the other hand, raw materials for the reforming technology are fairly inexpensive with CO_2 sometimes negatively priced [10], this could explain its low OPEX. In addition to utility, high OPEX for algae production is also due to cost for nutrients, water and CO_2 supply [261]. Mature technologies such as mineralisation and carboxylation for urea synthesis which have undergone considerable development over the decades are in the low range for both operating costs and utility consumption.

Similarly, high OPEX of electrochemical reduction and hydrogenation to formic acid could be due to their low TRLs.

6.3. Market analysis

Another main difference among CO_2 transformation technologies is the value of products since they have different market values. CO_2-derived fuels (such as diesel, gasoline, methanol and methane) are already in use in today's market and mainly produced from fossil fuels. The market price for CO_2-derived fuels via hydrogenation are currently estimated 2-7 times higher than fossil fuel-routes mostly owing to intensive energy/electricity and cost for H_2 production [51]. Similarly, methane, ethylene and methanol synthesis via electrochemical reduction were respectively estimated 20, 7 and 3 times higher than the current market price [262]. In addition to electricity, high costs of electrochemical reduction could also be due to its low TRL (3-5). Therefore, CO_2-derived fuels may be competitive if low-cost feedstock and carbon-neutral energies are available.

On the other hand, the market for CO_2-derived polymers is competitive as they require relatively low energy. It was demonstrated that some polymers could be synthesized at 15-30% lower cost than the conventional methods if CO_2 used were cheaper than the conventional method-based feedstock [263]. Similar results were observed for CO_2-derived concrete and aggregates [51]. By volume, CO_2-derived fuels (hence hydrogenation, electrochemical reduction and biological technologies) have the greatest potential for CO_2 utilisation as their market demand is estimated above 5 GT/yr whereas, market demand for CO_2-derived concrete, aggregates, chemicals and polymers is between 1-5 GT/yr [51]. However, regarding the cost and TRL, the greatest potential would be CO_2-derived concrete and aggregates (mineralisation) followed by CO_2-derived polymers and chemicals (via carboxylation and hydrogenation). Market analysis for plasma catalysis and photochemical reduction is yet to be provided due to their very low TRL range (1-4).

6.4. Amount of CO_2 used

Table 6 also provides the net CO_2 used for some CO_2 transformation technologies. Algae production and hydrogenation to liquid fuels via FTS have the highest net CO_2 used of 2.24 t_{CO2}/t_{algal}

$_{oil}$ and 2.6 $t_{CO2}/t_{liquid\ fuel}$, respectively. The reforming, hydrogenation to methane and methanol consume a range of 1.0–0.86 $t_{CO2}/t_{product}$. By incorporating high amounts of CO_2 into products, these transformation technologies offer great potential for effectively contributing to CO_2 reduction targets. The remaining conversion processes present a net CO_2 utilisation rate between 0.23–0.74 $t_{CO2}/t_{product}$ with the lowest value for polyol synthesis via carboxylation. In comparison to the conventional methods, these conversion processes still have the advantage of consuming more CO_2 than they release. It is worth specifying that a full lifecycle analysis (including, for example, CO_2 emitted during transport and combustion of derived-products that were not taken into consideration in this paper) will be needed to provide a more accurate indication of each technology's environmental benefits.

7. Example of projects for CO_2 utilisation via transformation

In this section, the projects are divided into 4 groups according to their scale: laboratory, pilot, demonstration and commercial. Figure 16 illustrates the definition and capacity of each scale. Laboratory projects refer to as academic research programme whereas, pilot, demonstration and commercial projects are conducted in testing facilities at their corresponding scales [264]. Table 7 gives examples of laboratory, pilot, demonstration and commercial projects carried out worldwide for CO_2 utilisation via transformation. The Smart CO_2 Transformation (SCO_2T) database was launched in 2016 as part of the EU Seventh Framework Programme to gather research & innovation information on CO_2 biological and chemical transformations [264]. As of 2019, the SCO_2T database shows a total of 189 projects for CO_2 utilisation via transformation. A detailed analysis of the SCO_2T database reveals that 53% of projects are laboratory projects whilst pilot, demonstration and commercial projects account for 23%, 10% and 14%, respectively (Figure 17).

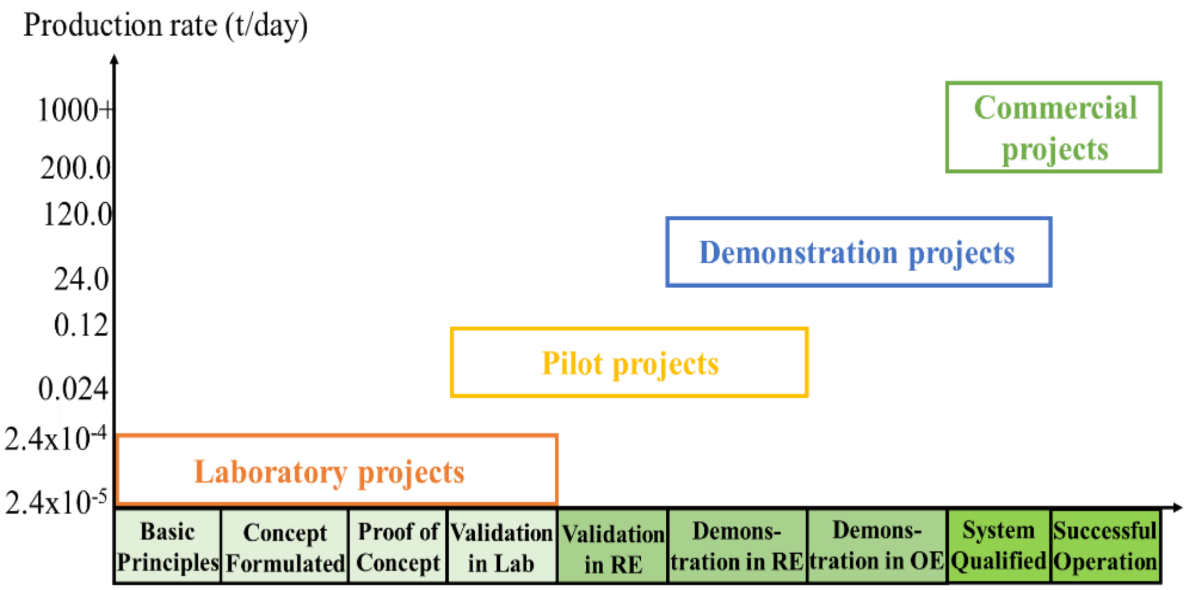


Figure 16: Definition of project types [265].

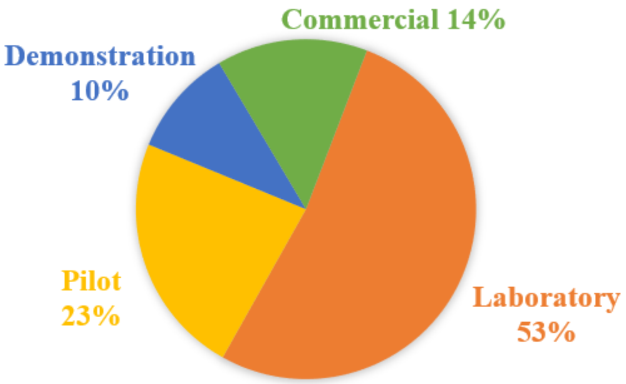


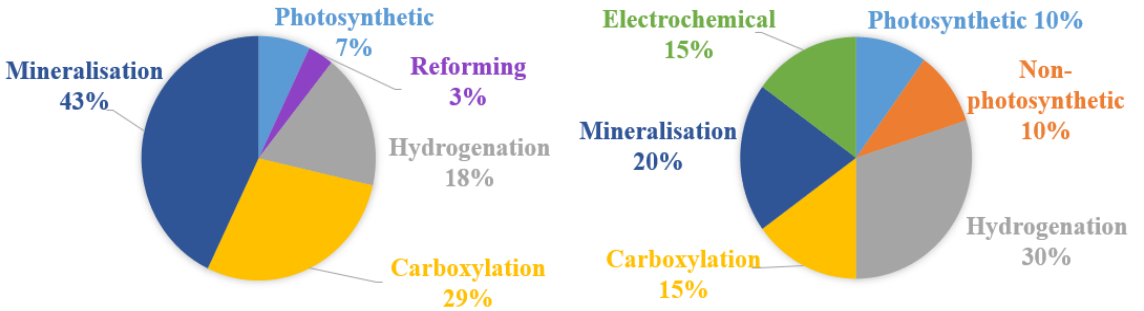
Figure 17: Repartition of projects for CO_2 transformation technologies according to their scales.

In terms of project scales, mineralisation technology accounts for 43% of commercial projects (Figure 18a). Hence, mineralisation seems to be the most favourable option among the technologies. The analysis shows that there is currently no commercial project for plasma catalysis, photochemical, electrochemical and non-photosynthetic technologies which is in good agreement with their low TRLs. Indeed, plasma catalysis and photochemical reduction are only laboratory projects (4 and 12, respectively) as shown in Figure 19. These technologies are still emerging and will likely have a better efficiency due to their lower operating conditions and diversity of accessible chemical and fuels.

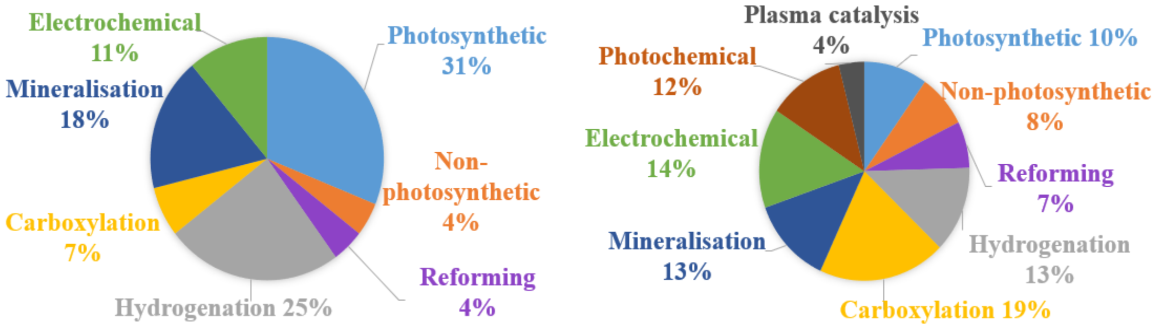
Table 7: Examples of projects for CO_2 utilisation via transformation

Technology	Project name	Location	Start year	Duration (year)	Products	Scale	Status	Source
Photosynthetic	ALGAENET	Madrid – Spain	2012	4	Microalgae, biogas	Laboratory	Completed	[266]
	PhotoFuel	Wolfsburg – Germany	2015	5	Algae, biofuels	Pilot	Ongoing	[267]
	Algenol IBR	Florida – US	2010	5	Algae, bioethanol	Demonstration	Operating	[268]
Non-photosynthetic	BioPower2Gas	Allendorf – Germany	2013	3	Methane	Pilot	Operating	[249]
Reforming	Shell-Sari-Lu'An joint	Shanxi Province - China	2011	n/s	Syngas	Demonstration	Ongoing	[269]
	Sunexus CO_2 reforming	California – USA	2010	1	Syngas, diesel	Laboratory	Completed	[270]
Hydrogenation	MefCO_2	Niederaussem – Germany	2014	7	Methanol	Pilot	Ongoing	[271]
	Methanol+	Alberta – Canada	2014	2	Methanol	Pilot	Completed	[264]
	Audi e-diesel	Dresden – Germany	2014	n/s	Diesel	Demonstration	Ongoing	[272]
	Chemical CO_2 immobilisation	Osaka – Japan	2008	n/s	Methanol, olefins	Pilot	n/s	[264]
Carboxylation	CyclicCO_2R	The Hague – Netherlands	2013	3	Cyclic carbonates	Pilot	Operating	[264]
	E^3Tec	Michigan – USA	2013	4	DMC	Pilot	Completed	[273]
	Carbon4PUR	Germany	2017	3	Polyols, polyurethane	Demonstration	Ongoing	[274]
	Carbon8 Aggregates	Brandon – UK	2012	n/s	Concrete	Commercial	Operating	[275]

Mineralisation	MCi	Newcastle – Australia	2013	5	Inorganic carbonates	Pilot	Completed	[276]
	SkyMine®	Texas – USA	2010	5	Sodium bicarbonate	Commercial	Completed	[264]
	SOLID Life	Weimar – Germany	2016	3	Cement, concrete	Demonstration	Ongoing	[277]
Electrochemical	CELBICON	Turin – Italy	2016	3.5	Syngas, formic acid	Pilot	Completed	[248]
	LOTER.CO2M	Cologne – Germany	2018	3	Methanol	Pilot	Ongoing	[278]
	Rheticus	Marl – Germany	2018	2	Butanol, hexanol	Laboratory	Ongoing	[279]
Photochemical	PROPHECY	Karlsruhe – Germany	2016	3	C_1 chemicals	Laboratory	Completed	[280]
Plasma catalysis	PIONEER	Sorbonne – France	2019	3	n/s	Laboratory	Ongoing	[281]



(a) Share of commercial projects (b) Share of demonstration projects



(c) Share of pilot projects (d) Share of laboratory projects

Figure 18: Repartition of project scales for different technologies.

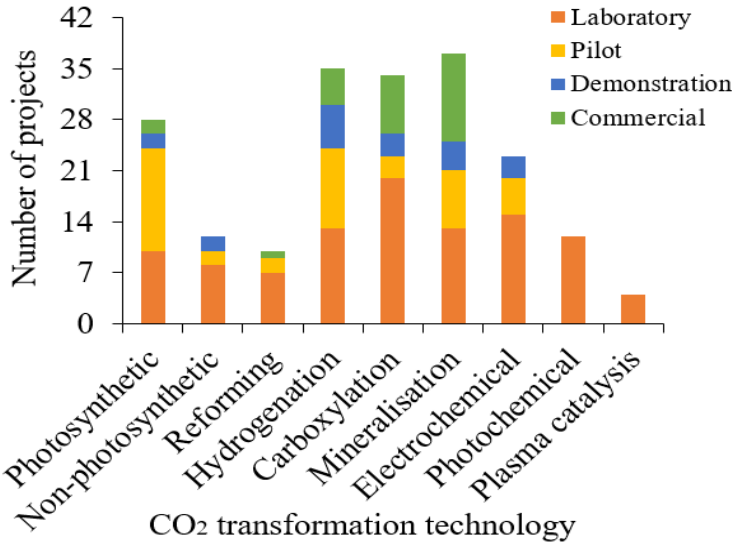


Figure 19: Number of projects for different CO_2 transformation technologies.

The highest number of projects was observed for mineralisation (37) closely followed by hydrogenation (35) and carboxylation (34) technologies (Figure 19). Hydrogenation and carboxylation technologies also represent respectively 18% and 29% of commercial projects with 45% cumulative share of demonstration projects (Figures 18a and b). Therefore, when fully mature these technologies will dominate the CO_2 utilisation sector due to high market demand for CO_2-

derived fuels, chemicals and materials. 28 projects were found for algae production. Despite its TRL of 4-7, algae production accounts for 7% of commercial projects with 10% and 31% share of demonstration and pilot projects, respectively (Figures 18a, 18b and 18c) confirming its suitability for large-scale deployment.

Analysis of projects for CO_2 transformation technologies in different continents (Figure 20) shows the highest share of projects in Europe (65%) followed by North America (29%). Asia and Australia only account for 4% and 2%, respectively. This percentage seems quite small knowing that Asia is responsible for more than 50% of the world's CO_2 emissions [4]. The latest roadmap for CCUS in China reported 23 key projects (divided into 5, 7 and 11 pilot, demonstration and commercial projects, respectively) that have been planned, operated and completed since 2006 [282]. However, these projects mostly focused on direct use of CO_2 via EOR while SCO_2T database gathers projects on CO_2 utilisation via transformation which may justify the low percentage found in Asian countries. USA leads the world in progressing CO_2 utilisation via transformation as it holds the highest number of 45 projects divided into 21, 10, 6 and 8 laboratory, pilot, demonstration and commercial projects, respectively (Figure 21). It is sensitive to believe that USA will continue in the first place since the USA Department of Energy has recently announced \$110 million for the deployment of various large-scale CCUS projects [283]. Germany, UK and Netherlands are also strong supporters of CO_2 utilisation with a cumulative of 78 projects divided into 43, 20, 10 and 10 laboratory, pilot, demonstration and commercial projects, respectively (Figure 21).

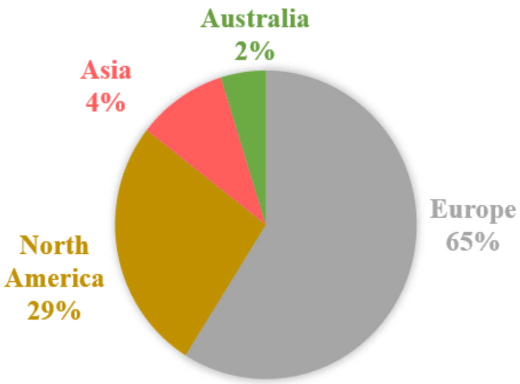


Figure 20: Repartition of projects for CO_2 transformation technologies in different continents.

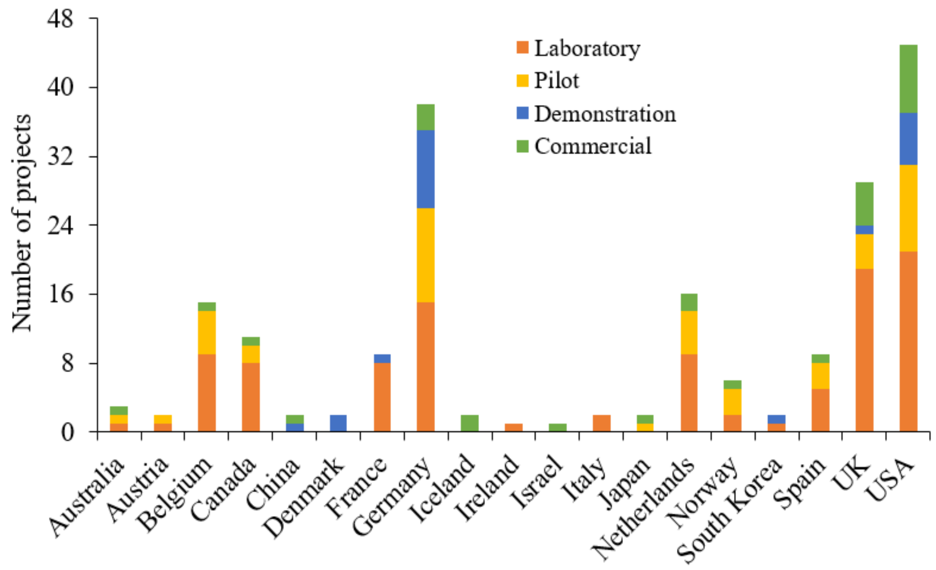


Figure 21: Number of projects for CO_2 transformation technologies in different countries.

8. Research trend, challenges and future prospects

8.1. The research trend

The increasing interest in CO_2 transformation into value-added products can be translated into the significant number of published papers in the area. Therefore, research papers found in literature is used as an indicator to investigate the research trend of CO_2 transformation technologies and evaluate where the focus has been devoted the most.

8.1.1. Methodology

ScienceDirect database (https://www.sciencedirect.com/search) was used to search for research articles on CO_2 utilisation via transformation. ScienceDirect is the world's leading database for medical and scientific research. It provides over 12 million contents from articles to books. The search for papers was conducted in January 2019 using keywords as indicated in Table 8.

8.1.2. Limitations

The search for research papers on CO_2 utilisation via transformation only covers a period of 10 years (2008 to 2018). Only the title, abstract and keywords were reviewed to identify articles relevant to CO_2 transformation technologies. Therefore, CO_2 technologies that were not mentioned in the title and abstract were not included. Also, research papers that were not in the ScienceDirect database were not included.

Table 8: Search technique

Technology	Keywords
Photosynthetic	“CO_2 + Photosynthetic biological fixation”
Non-Photosynthetic	“CO_2 + Non-Photosynthetic biological fixation”
Reforming	“CO_2 + Reforming + syngas”
Hydrogenation	“CO_2 + Fischer-Tropsch” AND “CO_2 + Hydrogenation”
Carboxylation	“CO_2 + Carbamate synthesis” AND “Carboxylation with CO_2” AND “CO_2 + Urea synthesis” AND “CO_2 + Cyclic carbonate synthesis” AND “CO_2 + Linear carbonate synthesis” AND “CO_2 + Polymer synthesis”
Mineralisation	“CO_2 + Mineral carbonation + carbonates”
Electrochemical reduction	“CO_2 + Electrolysis cell + Syngas” AND “CO_2 + Electrochemical reduction”
Photochemical reduction	“CO_2 + Photochemical reduction”
Plasma catalysis	“CO_2 + Plasma catalysis”

8.1.3. Analysis of research trend

A total of 34,329 papers were retrieved from the search. 31,941 papers were excluded as they were either review papers or not related to CO_2 utilisation (most of them discuss CO_2 capture from flue gas, CO_2 geological storage, CO_2 separation from mixtures like CO_2/N_2, electrochemistry for corrosion etc.). After evaluation, 2,389 research papers were relevant to CO_2 transformation technologies. Figure 22 illustrates the repartition of research papers for CO_2 transformation technologies. Hydrogenation is the most studied process with the highest percentage of 27% while non-photosynthetic and plasma catalysis have the lowest percentage of 1% and 2%, respectively. CO_2 reforming, electrochemical, mineralisation, carboxylation, photosynthetic fixation and photochemical technologies represent 17%, 16%, 15%, 10%, 7% and 5% of research papers, respectively.

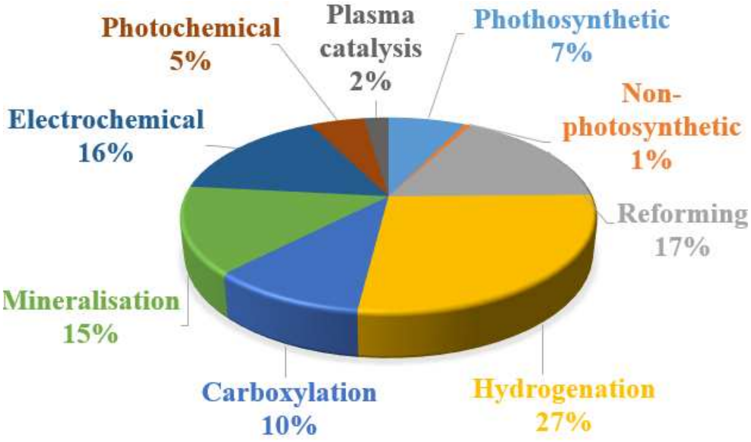


Figure 22: Repartition of research papers for CO_2 transformation technologies.

The overall trend shows a growing interest in CO_2 transformation technologies (Figure 23) with a significant increase in research papers from 70 papers published in 2008 to 548 papers in 2018. Furthermore, a previous study on the research trend for CO_2 utilisation via transformation reported 855 papers published between 1999–2009 [284]. In comparison, we report 2,389 research papers between 2008–2018. This clearly demonstrates the rapid growth in research and development for CO_2 utilisation via transformation which depicts the rising interest in overcoming climate change and global warming concerns by shifting towards more sustainable and environmentally friendly resources, processes and products.

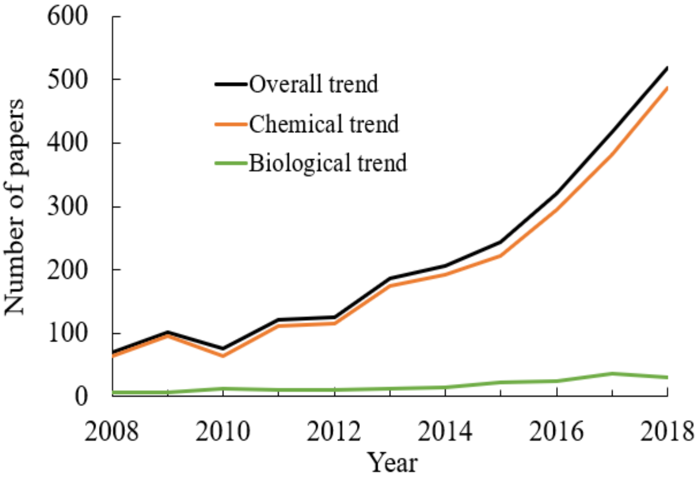


Figure 23: Research trend for CO_2 transformation technologies.

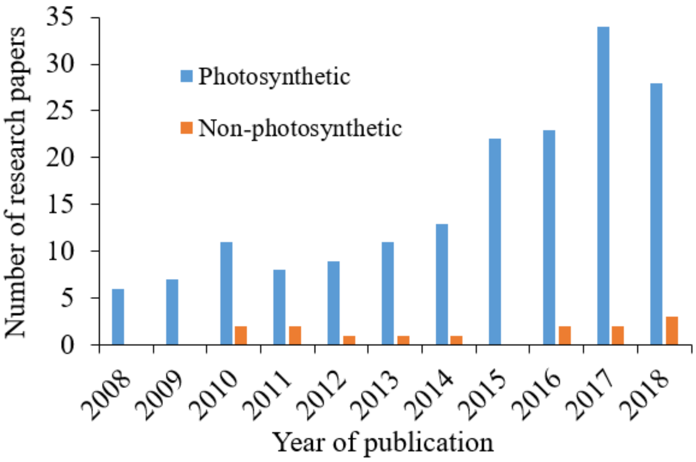


Figure 24: Research papers for CO_2 biological transformations.

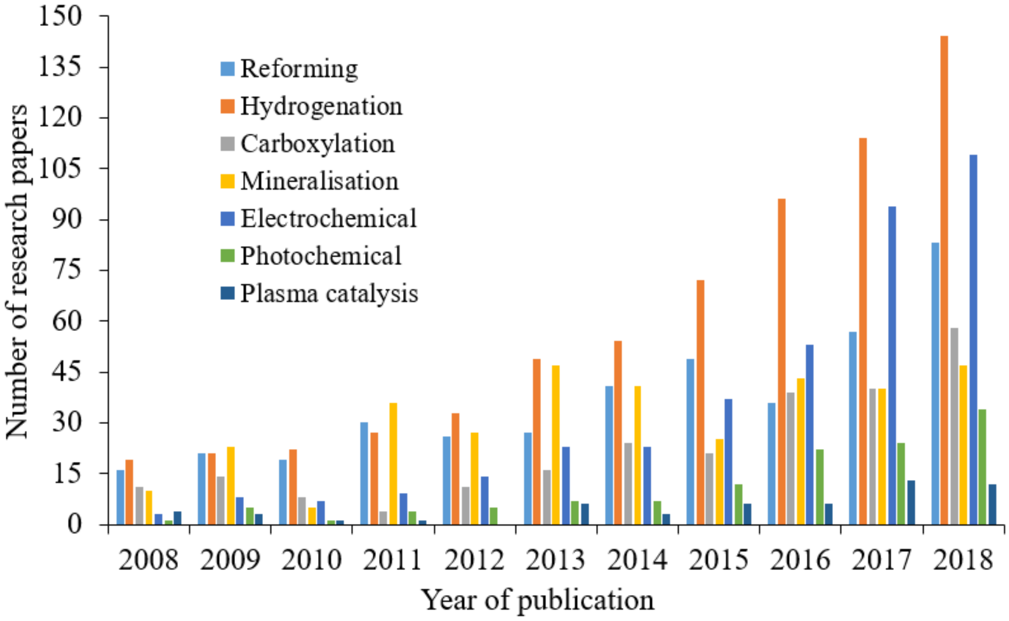


Figure 25: Research papers for CO_2 chemical transformations.

The high number of research papers (hence faster trend) observed for CO_2 chemical transformations (2,203 papers) compared to CO_2 biological transformations (186 papers) is mostly due to the higher number of available technologies and products via chemical conversion which may also explain why there are more projects for CO_2 chemical transformations (Figure 19). No paper was found for plasma catalysis in 2012 and non-photosynthetic in 2008, 2009 and 2015 (Figures 24 and 25). This does not necessarily mean that no research was conducted for these technologies on the specified years. It could be due to the limitations of the search for papers as specified in Section 8.1.2. Figure 25 indicates that hydrogenation and electrochemical reduction are the most studied technologies since 2016. Besides their variety of products, a possible explanation might be the increased availability of renewable energies which now represent the third of the global power capacity [285].

8.2. Challenges and future prospects

It is no doubt that CO_2 utilisation via transformation can help to mitigate CO_2 emissions and secure a wide range of chemicals and fuels. Although considerable progress was achieved in the past decades, CO_2 transformation technologies are still facing several challenges hindering their commercial implementation.

8.2.1. Technical barriers

(1) CO_2 activation/conversion

Achieving high CO_2 conversion is still an open challenge for most CO_2 transformation technologies due to the thermodynamic stability of C=O bonds and rapid catalyst deactivation. Though good conversion efficiency was reported ($\geq$60%) for reforming, hydrogenation, carboxylation and electrochemical technologies, the processes were operating either under high temperatures/pressures, excess overpotentials or using catalysts with low availability and high costs (e.g. noble metals and ionic liquids). Therefore, further research is required to find novel catalysts with improved stability and activity at lower operating conditions and costs. Clarifying the mechanisms of CO_2 activation and/or electron transfer during CO_2 conversion processes (especially for plasma catalysis, photochemical reduction, non-photosynthetic and electrochemical reduction) are also needed to identify and control the different steps in elementary reactions thus overcome CO_2 conversion limitations.

(2) Product selectivity

Theoretically, a wide range of value-added products can be obtained from CO_2 conversion. However, there is a clear gap between the quality and quantity of reported products. By comparison, plasma catalysis, electrochemical and photochemical methods have poor selectivity to C_{2+} products whereas, the non-photosynthetic CO_2 fixation mostly forms methane and acetate via the W-L pathway. Although selectivity above 75% was achieved via electrochemical reduction, high overpotentials were also required. Synthesis of most organic acids through carboxylation has not yet achieved satisfactory results, DMC still suffers from low yield and acceptable selectivity was only observed for cyclic carbonates and polymers. Except for methanol, CO_2 hydrogenation suffers from low selectivity to oxygenate compounds (mostly formic acid and DME). Exploring novel catalytic materials and microorganisms will play an important role in addressing the aforementioned issues. Research into reactor design with better mass/liquid transfer and cell construction with high active surface areas can help to enhance CO_2 conversion efficiency and improve product selectivity.

(3) Energy requirement

All CO_2 conversion processes require considerable energy input. Most studies demonstrated that increasing the energy input (light, heat or electricity) leads to better CO_2 conversion and product yield efficiencies. However, the use of energy comes with costs and CO_2 emissions depending on the energy source. Therefore,

- Further research is needed to enhance CO_2 transformation technologies which use a free natural energy source (such as photosynthetic and photochemical CO_2 reduction) as they have the potential to be less expensive.
- More studies integrating the use of renewable electricity for electrochemical reduction, non-photosynthetic CO_2 fixation and H_2 production for CO_2 hydrogenation are highly needed to assess their full potential for CO_2 conversion.
- Further studies are also required to achieve high energy efficiency without decreasing the CO_2 conversion rate during plasma catalysis.
- Research into heat integration techniques is also highly required for further optimization of energy efficiency and management.

8.2.2. Cost reduction

Cost assessment of CO_2 transformation technologies is very difficult as they are affected by varying parameters including type of CO_2 transformation technology, desired product, type of energy and raw material required, product price, plant location etc. Compared to conventional methods, most CO_2 transformation technologies are still quite expensive with some that have not been economically evaluated yet. It is paramount to reduce the cost of CO_2 transformation technologies for CO_2-derived products to be competitive in today's market. Cost reduction can be achieved through process intensification and development of better catalysts that can lower the energy requirements. Cost minimization also varies from one technology to another. For instance, hydrogenation cost would significantly reduce if the cost of H_2 production was halved [254]. Cost reduction for algae production would require cheaper nutrients/fertilizers, water recirculation systems and shorter distance to water [27]. More general considerations such as the cost of CO_2 capture should also be assessed. Further research in reducing costs for energy-intensive CO_2 capture processes will greatly promote the deployment of CO_2 transformation technologies.

8.2.3. Modelling and simulation

There are limited modelling and simulation studies on CO_2 conversion processes possibly due to lack of experimental data. Indeed, process modelling and simulation would require detailed information about reaction kinetics and catalysts for accurate process designs. However, reaction mechanisms involved in CO_2 conversion processes are still being verified, not well understood and search for effective catalysts is still ongoing which limit the availability of required data. This is particularly true for CO_2 transformation technologies with low TRLs including carboxylation and hydrogenation to some products (Table 5), plasma catalysis, photochemical reduction, non-photosynthetic and electrochemical reduction. Future research could use basic knowledge on thermodynamics, mass/heat transfer, preliminary assumptions and simplified models for initial modelling and design to evaluate the process performance. Most studies reported steady-state models indicating the early development stage for CO_2 transformation technologies. Further studies on dynamic modelling, steady-state and dynamic model validation are required to gain further insights into the actual operation and control design of CO_2 conversion processes at transient conditions. More studies on process intensification and optimisation techniques are also needed to address the current challenges encountered in CO_2 conversion to value-added products.

8.2.4. Suggested research directions

- Future research directions should focus on long-term operation and economic feasibility of the most promising technologies (such as mineralisation, hydrogenation, carboxylation to polymers and organic carbonates and photosynthetic) so that effective commercial scale-up can be implemented.
- Priority should also be given to the least studied technologies with low TRLs including non-photosynthetic, plasma catalysis and photochemical reduction (research percentage ≤ 5%) so that early good practices and effective techniques can be achieved. These technologies have the main advantage of operating at ambient conditions. Furthermore, the non-photosynthetic CO_2 fixation could lead to several biochemicals/fuels using H_2 as an energy source and by-pass the high operating conditions of CO_2 hydrogenation which could result in considerable cost reduction.
- Studies on process optimisation and process intensification of CO_2 transformation technologies are highly needed to assess the interaction among different operating parameters, enhance process efficiency and lower costs.
- Flue gas temperature at the furnace outlet is quite high (typically around 1200°C) and must be cooled down to roughly 40-50°C for CO_2 capture [220]. On the other hand, most CO_2 conversion processes require heat as energy input which is usually provided by external sources. Therefore, future studies should investigate the process integration of CO_2 capture and CO_2 utilisation to assess the synergy between the two processes.

- Direct use of flue gas for some CO_2 conversion processes (such as reforming, mineralisation, algae production and carboxylation for polymer synthesis) should also be explored as it could eliminate the cost of energy-intensive CO_2 capture processes.

It is worth specifying that CO_2 transformation technologies do not have to be used alone, the combination of biological and chemical transformation (for instance, microbially enhanced mineralisation [286,287]) could provide a highly efficient hybrid system which would possibly surpass any CO_2 chemical or biological process alone.

8.2.5. Policy impact

Although policies were not explicitly examined in this review, it is worth emphasizing that policy improvements can support the deployment of CO_2 transformation technologies. They can be applied in the following areas: (1) market regulation for the commercial activity of CO_2 utilisation, (2) financial support for early development to assist participants who cannot afford costs of early-stage projects and (3) incentives and guidance for commercial deployment when business propositions have not reached commercial maturity [288].

9. Conclusion

In this review paper, CO_2 transformation technologies were defined and grouped into biological (photosynthetic and non-photosynthetic) and chemical (reforming, hydrogenation, carboxylation, mineralisation, electrochemical reduction, photochemical reduction and plasma catalysis) processes, the typical operating conditions and the diversity of products from CO_2 conversion were carefully outlined, the recent progress in experimental and modelling/simulation studies were reviewed, the different technologies were compared in terms of maturity, cost, market and amount of CO_2 used, a detailed analysis of CO_2 utilisation projects worldwide and research trends were provided and finally, the challenges and future research directions were discussed. The following conclusions were reached: (1) Due to the diversity of products, hydrogenation and carboxylation technologies will have a large share of commercial deployment when fully mature; (2) The development of available and low-cost catalysts is of great importance for large-scale applications of CO_2 transformation technologies; (3) Process optimisation and process intensification can help to decrease costs and improve process efficiency; (4) The non-photosynthetic CO_2 fixation has the great potential to overcome high operating conditions encountered with hydrogenation technology; (5) Large-scale demonstrations are required for emerging technologies such as reforming and algae production to gain confidence and improve technologies to reach commercial-scale; (6) Finally, the research trend analysis demonstrated that more research will be carried out in CO_2 utilisation via transformation in the years to come.

Conflicts of interest

There are no conflicts to declare.

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