

Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

ISSN: (Print) (Online) Journal homepage: <https://www.tandfonline.com/loi/ueso20>

Carbon capture and utilization technologies: a literature review and recent advances

Francisco M. Baena-Moreno, Mónica Rodríguez-Galán, Fernando Vega, Bernabé Alonso-Fariñas, Luis F. Vilches Arenas & Benito Navarrete

To cite this article: Francisco M. Baena-Moreno, Mónica Rodríguez-Galán, Fernando Vega, Bernabé Alonso-Fariñas, Luis F. Vilches Arenas & Benito Navarrete (2019) Carbon capture and utilization technologies: a literature review and recent advances, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 41:12, 1403-1433, DOI: [10.1080/15567036.2018.1548518](https://doi.org/10.1080/15567036.2018.1548518)

To link to this article: <https://doi.org/10.1080/15567036.2018.1548518>



Published online: 21 Nov 2018.



Submit your article to this journal [↗](#)



Article views: 4057



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 93 View citing articles [↗](#)



Carbon capture and utilization technologies: a literature review and recent advances

Francisco M. Baena-Moreno, Mónica Rodríguez-Galán, Fernando Vega, Bernabé Alonso-Fariñas, Luis F. Vilches Arenas, and Benito Navarrete

Department of Chemical and Environmental Engineering, School of Engineering, University of Seville, Sevilla, Spain

ABSTRACT

This paper presents a comprehensive list of Carbon Capture and Utilization technologies and applications, ranging from lab-scale R&D activities reported in academic papers to commercially established uses of carbon dioxide. Carbon dioxide, as a source of carbon, has the potential to be used as a solvent, as a raw material in the manufacturing of fuels, carbonates, polymers, and chemicals, or as a recovery agent in techniques such as enhanced oil recovery or enhanced coal bed methane. In this paper, a literature review and recent advances of each technology are explained. To finish, most relevant Life Cycle Assessment studies carried out by experts in this field are included. Among the different alternatives studied for the use of carbon dioxide, the processes of carboxylation, consisting the synthesis of carbonates and carboxylates, have stood out. Both the production of salicylic acid as well as that of dimethyl carbonate and mineral carbonation are presented as the most likely applications of carbon dioxide, at least, in the short term.

ARTICLE HISTORY

Received 7 July 2018
Revised 26 September 2018
Accepted 14 October 2018

KEYWORDS

Carbon capture and utilization; CO₂ as feedstock; life cycle assessment; environmental impacts; mineral carbonation

Introduction

The concern for climate change is one of the key agendas stated by world leaders and experts on the subject, as well as in the daily conversations or the media every day. Carbon dioxide (CO₂) emissions are considered the main cause of this concern. Therefore, it is logical to think that the solution to this problem lies in the reduction of these emissions (Aresta 2010; European Commission 2016; Hatzigeorgiou, Polatidis, and Haralambopoulos 2010). Figure 1 represents monthly CO₂ concentration values.

As can be seen in Figure 1, CO₂ emissions have increased by approximately 2 parts per million per year. Currently, the direct reduction of the aforementioned emissions is complicated in the short term, due to the established technologies in different industries, based mainly on the use of fossil fuels. As a consequence, the concept of Carbon Capture and Storage (CCS) emerges as an attractive idea for the reduction of emissions, where, among others, absorption has been proved as an efficient technology to achieve a high capture yield with different solvents, such as monoethanolamine (MEA) or piperazine (PZ) (Li and Zhang 2018; Vega et al. 2017; Zhang 2016; Zhang et al. 2018a), but with certain technical and economic limitations like, for instance, the high energy penalty mainly due to the thermal regeneration of the mentioned solvents (Bilgen 2016; Zhang et al. 2018b). On the other hand, a common issue for all CCS technologies is the high requirement of CO₂ gas storage capacity (IPCC 2005).

Carbon Capture and Utilization (CCU) seeks not only to reduce the volume of emissions to the atmosphere but also to obtain a benefit through the use of CO₂ in different types of industrial processes, replacing conventional raw materials (Aresta 2010; Bilgen 2016). These methods will not be enough to achieve the desired objective, but they could be the key to complement the use of carbon-free renewable technologies, together with the awareness of the population (Princeton University 2015). This paper

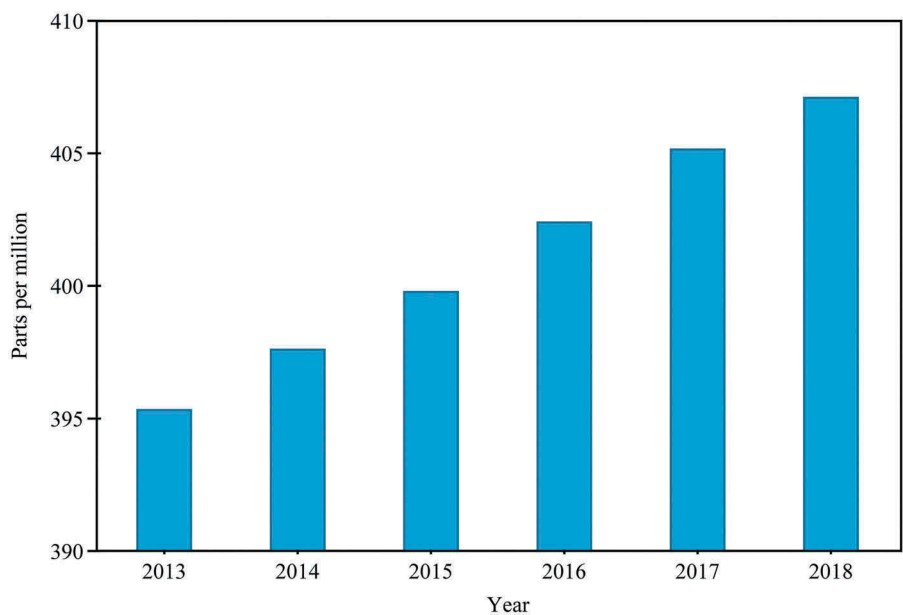


Figure 1. Monthly record of the concentration of CO₂ in the atmosphere. Adapted from Scripps Institution of Oceanography (2018).

analyzes the main available CCU technologies, as well as the innovative studies carried out so far by experts in this area. Finally, some Life Cycle Assessments (LCA) that have been done by other authors for promising CCU options are presented. The studied technologies have been grouped in four categories as shown in **Figure 2**: CO₂ as a solvent, Chemicals from CO₂, Fuels from CO₂, and Enhanced Oil Recovery (EOR) & Enhanced Coal Bed Methane (ECBM).

CCU technologies

The use of CO₂ can be technological, biological or chemical, and all of them seek to improve or replace traditional processes with the incentive of contributing doubly to curb climate change: it would reduce CO₂ emissions into the atmosphere and could lead to a reduction in the extraction of

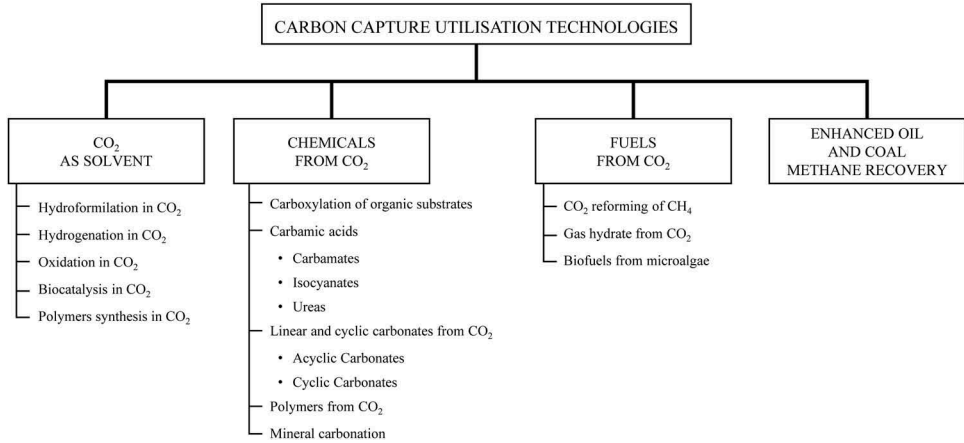


Figure 2. CCU technologies included in this study.

CO₂ from fossil fuels, as well as an economic saving for companies that consider their use (Abdeen et al. 2016a; Aresta 2010; Aydin 2014; Cuéllar-Franca and Azapagic 2015). On the one hand, the direct or technological use of CO₂ includes applications such as the extraction of compounds with supercritical CO₂ (scCO₂), dry cleaning, water treatment, and food industry uses, among others. In the case of the food industry, CO₂ is utilized as a replacement for the toxic elements used for food disinfection (e.g. n-hexane) as well as a replacement of the organic solvents in the extraction of compounds and finally replacing dangerous acidic species in water treatment (Aresta 2010). On the other hand, for the biological use, it is worth mentioning the direct fixation of CO₂ in fast-growing biomass. This can help to reduce the accumulation of CO₂ in the atmosphere much quicker than would naturally occur. This procedure can be used both for the manufacture of chemical products and for the production of energy, for example, converting that biomass into gaseous or liquid fuels instead of directly burning the biomass. A clear example of this fast-growing biomass is photosynthetic microorganisms or microalgae (Aresta 2010; Cuéllar-Franca and Azapagic 2015). Finally, the chemical use consists of the conversion of CO₂ into other products, such as methanol, acetic acid, carbonates, and polymers, among others (Aresta 2010).

CO₂ as a solvent

The use of solvents in the chemical industry involves large costs, both environmental and economic. The use and separation of solvents entail the use of many unit operations in the manufacturing of chemical products, representing a high percentage of the energy consumption of the process. From the environmental point of view, the organic solvents used in the chemical industry generate a negative impact, due to its flammability, smog formation, its toxicity, and the risk of inhalation, also affecting human health. This is why a considerable amount of research in the field of sustainable chemistry revolves around the development of new ecological solvents. The ideal solvent would be non-flammable, non-toxic for both humans and the environment, abundant, renewable, highly stable, low cost, easy to prepare, and separate from the final product (Albo et al. 2013; Aresta 2010; Lee et al. 2017; Marriott, Jessop, and Barnes 2014; Wang et al. 2016a). Under these conditions, CO₂ appears as a possible candidate, which seems to meet all the criteria, except that related to global warming. Even so, this CO₂ does not generate this effect directly, since it is a recycled material obtained from a waste. However, the contribution to global warming would be generated by the use of the energy necessary to compress the CO₂ to a liquid or supercritical state. This operation involves a generally high cost, which must be taken into account when comparing it with the energy consumption of conventional solvents (Beckman 2004; Boyère, Jérôme, and Debuigne 2014; Cuéllar-Franca and Azapagic 2015; Marriott, Jessop, and Barnes 2014).

CO₂ can be used as a solvent in both liquid (lCO₂) and scCO₂ states. A pure gaseous component is considered in a supercritical state when its temperature and pressure exceeds its critical values, for CO₂ these are 304.1 K and 7.4 MPa, respectively (Boyère, Jérôme, and Debuigne 2014). Its easily accessible critical point, high diffusivity, low viscosity, and surface tension make CO₂ even more attractive as a solvent (Albo et al. 2013; Aresta 2010; Boyère, Jérôme, and Debuigne 2014; Lee et al. 2017; Linstrom and Mallard 2014; Marriott, Jessop, and Barnes 2014; Wang et al. 2016b). Properties of the solvents can be expressed through different parameters such as dipole moment, dielectric constant, refractive index or solubility degree. ScCO₂ has characteristic properties of non-polar solvents, such as n-hexane. Table 1 shows some properties of lCO₂ and scCO₂.

Table 1. lCO₂ and scCO₂ physical properties. (Hyatt 1984; Marriott, Jessop, and Barnes 2014).

Solvent	Density (kg/L)	Viscosity (Pa·s)	C _p (25°C) (kJ/kg·K)	Reichardt Scale Polarity	Dielectric Constant (F/m)
scCO ₂	0.956 ^a	1.060 × 10 ⁻⁴ ^c	0.846 ^c	0.090 (Var)	1.10–1.50
lCO ₂	1.000 ^b	1.200 × 10 ⁻⁴ ^e	3.140 ^d	0.090 (Var)	1.50

^a 40°C and 400 bar ^b 20°C and 65 bar ^c 40°C ^d 10°C ^e 25°C

Dielectric constant of scCO_2 and lCO_2 is similar to n-hexane (2.00 F/m) (Mopsik 1967). However, the solvency power measured on the Reichardt scale suggests that scCO_2 and lCO_2 are more polar than n-hexane (0.09 vs 0.009 presented by n-hexane) (Marriott, Jessop, and Barnes 2014; Ren et al. 1999). Initially, scCO_2 was proposed for extractions and fractionation in the field of natural product processing. Some of the commercial processes that began to be performed with CO_2 were the extraction of hops, decaffeination of coffee and tea, and the extraction of flavors, spices, and essential oils from botanical material. Even so, it has not been until the last twenty-five years when there has been an increasing interest in the use of this unconventional solvent as a substitute for liquid organic solvents (Aresta 2010; King and Bott 1993). One of the most important studies related to this subject focused on the extraction of various natural aromatic raw materials through different procedures, namely, solid/liquid extraction and solid/ scCO_2 extraction (Pellerin 2003). One of the reported advantages of the use of CO_2 is that the amount of scCO_2 needed is relatively small and typically in the same order as the amount of raw material whereas the amount of conventional solvent needed are values from 3 (continuous reactor) (Aresta 2010) up to between 10 and 20 (batch reactor) (Marriot, Jessop, and Barnes 2014) times the amount of raw material. In addition, the elimination of waste with the use of conventional solvents cost up to € 380 per ton of waste (Marriot, Jessop and Barnes, 2014), while in the case of CO_2 , if the waste has not been in contact with organic solvents, it can be re-used for other purposes. Finally, it was estimated that the equipment cost would be higher using CO_2 rather than conventional process, but, due to energy savings, environmental safety, and impact parameters, the use of scCO_2 was a better option in this comparison. The presence of scCO_2 in reactions with gaseous reagents makes it possible to operate in single-phase conditions, thus increasing the kinetics of mass transfer. This is due to the fact that the existing gas-liquid interface when using liquid solvents is avoided and the supercritical media have properties that favor the matter transport (Aresta 2010). The reactions where the use of scCO_2 has been most developed are hydroformylation, hydrogenation, oxidation, biocatalysis, and polymers synthesis (Aresta 2010).

Hydroformylation in CO_2

Hydroformylation is an industrial process of great importance in the manufacturing of aldehydes, obtained from olefins and syngas. This process involves the addition of CO and H_2 to a carbon-carbon double bond, forming the aldehyde that contains a number of carbons greater than the starting olefin. Hydroformylation can be carried out by both homogeneous and heterogeneous catalysis, the latter being easy to recycle (Bektesevic et al. 2006). Most investigations on the hydroformylation of olefins or alkenes in scCO_2 have been carried out in homogeneous catalytic systems, where the solvent is used to recover the catalyst after the reaction, what involves a great effort and a significant expense when traditional solvents are used. The results obtained with high molecular weight olefins have been quite satisfactory (85% yield) since these cannot be hydroformylated in aqueous bases with rhodium catalyst due to their low solubility in water (Aresta 2010; Bektesevic et al. 2006; Marriott, Jessop, and Barnes 2014).

Hydrogenation in CO_2

Hydrogenation in scCO_2 is one of the few processes that have been successfully developed on an industrial scale, taking place in both fluid and gaseous phases. While the biphasic hydrogenation reactions use a homogeneous catalyst, the three-phase ones use a heterogeneous catalyst in addition to the reactive liquid and hydrogen gas. Some hydrogenation reactions in scCO_2 are listed in Table 2.

It can be seen that the main advantages of using scCO_2 are the high yields and selectivity obtained in the different hydrogenation reactions. Other studies have been conducted in which the use of CO_2 as a solvent favors hydrogenation. For example, in the hydrogenation of nitrile to primary amines, undesired dialkylamines are usually generated, but in expanded CO_2 media, the primary amines are stabilized through a reaction easily reversible with CO_2 , obtaining carbamate salts. On the other hand, the hydrogenation of the oleic acid catalyzed by platinum at 35°C stops at a conversion of 90% even with long reaction times of more than 25 h. However, at the conditions of 55 bar of expanded CO_2 , the reaction achieves a 97% conversion after only one hour (An et al. 2009; Anastas and Zimmerman 2013; Devetta et al. 1997; Marriott, Jessop, and Barnes 2014; Mayadevi 2012; Wang et al. 2018).

Table 2. Hydrogenation reactions in scCO₂. Modified from Mayadevi (2012).

Reaction	Catalyst	scCO ₂ Advantage
Biphenyl Hydrogenation	Rh/C, Ru/C	Yield > 99%
Furfural Hydrogenation	Pd/C	Switchable selectivity of 5 different products varying the operating conditions
2-butylene-1,4-diol Hydrogenation	5% mass Pd/C	100% selectivity for butane-5,6-diol
Styrene oxide to 2-phenyl-ethanol	Pd/Cu encapsulated with polyurea	100% selectivity and yield

Oxidation in CO₂

Another reaction that has been the target of several investigations, is the selective oxidation of organic substrates in dense CO₂. One of the key aspects that CO₂ presents as a good solvent for this type of reaction is that it cannot be oxidized. This means that it will not lead to the formation of byproducts or unwanted compounds while generating a solvent consumption that would have to be replaced which is the case for most organic solvents (Aresta 2010; Marriott, Jessop, and Barnes 2014).

Some of the most recent studies (Ribeiro et al. 2017a; Sutradhar et al. 2017) have analyzed the results obtained from the oxidation of cyclohexane using different catalytic complexes in different solvents. For example, comparing the action of molybdenum complexes in acetonitrile, ionic liquid, and scCO₂ has concluded that cyclohexanol has the highest selectivity in scCO₂ (98%) (Sutradhar et al. 2017). However, using Fe (II) scorpionate complexes, the highest selectivity of the cyclohexanone was given for a mixed solvent medium of scCO₂ and an ionic liquid ([bmim] [PF₆]), reaching values up to 96%, while the maximum obtained in pure solvents was 77% (Ribeiro et al. 2017b). The partial oxidation of alcohols to obtain carbonyls or carboxylic compounds are of high industrial interest. Thus, scCO₂ was investigated as a reaction medium for the partial oxidation of aliphatic, unsaturated, aromatic, and benzylic acids with different catalytic systems based on noble metals, both in continuous and discontinuous reactors. The results obtained using palladium and gold catalysts for the oxidation of benzyl alcohol to benzaldehyde were very promising, achieving selectivities greater than 90% (Aresta 2010; Hou, Theyssen, and Leitner 2007; Wang et al. 2014).

Biocatalysis in CO₂

Another field in which scCO₂ can be used as a solvent is biocatalysis. The capability of being adjusted in its properties and its previously mentioned characteristics make the scCO₂ especially suitable for use in organic synthesis. The attractive idea of combining natural catalysts such as enzymes with a natural solvent such as CO₂ has been an incentive for research in this field, since it seems to be the perfect union between a highly selective and active sustainable catalytic system, and an ecological solvent with excellent transport properties. Thus, scCO₂ is presented as an alternative solvent for biocatalysis under non-aqueous conditions, which allows an easy recovery of the products and the enzyme, in addition to providing a similar yield to that observed in organic solvents such as n-hexane and cyclohexane. Although theoretically, this technology seems to have a high potential, the use of biocatalysts in scCO₂ has tried to be avoided due to the interactions between the solvent and the catalyst, which lead to the generation of carbamates (Du et al. 2008; Marriott, Jessop, and Barnes 2014; Matsuda 2013).

Polymers synthesis in CO₂

ScCO₂ is the main candidate to replace traditional solvents in the synthesis of polymers due to its environmental advantages that have been exposed previously. However, the use of scCO₂ as a solvent in polymerization reactions has a drawback, since high molecular weight compounds, especially polymers, are generally poorly soluble in scCO₂ under relatively soft conditions ($T < 373$ K, $P < 35$ MPa) (Boyère, Jérôme, and Debuigne 2014; Jo et al. 2017; Vert et al. 2009; Zhang et al. 2015a). Polytetrafluoroethylene (PTFE) was synthesized in a heterogeneous CO₂ medium, using a water-soluble persulfate initiator, achieving rapid polymerization kinetics, yield values of up to 90% and

high molecular weight. PTFE was also produced in a medium based on dry scCO_2 , both in the absence and in the presence of stabilizers, obtaining morphology of fibrillated PTFE, which could be particularly interesting for the manufacture of hydrophobic microporous membranes without solvents (Giaconia et al. 2008; Romack, DeSimone, and Treat 1995).

Chemicals from CO_2

As can be seen below, CO_2 could also be employed to produce chemicals. This can be achieved through carboxylation reactions where CO_2 plays a fundamental role as a precursor for organic compounds.

Carboxylation of organic substrates with CO_2

The reaction of CO_2 with organic substances can lead to the formation of carbon-carbon bonds for the production of carboxylic acids or the formation of carbon-heteroatom bonds for the production of carbonates or carbamates in which the first type is called carboxylation reaction (Senboku and Katayama 2017; Yuan et al. 2017; Zhang and Hou 2017). Carboxylic acids are organic compounds in which a carbon atom is linked to an oxygen atom by a double bond and a hydroxyl group by a single bond, forming the carboxyl group ($-\text{COOH}$). They are widely used in food, chemical, and pharmaceutical industries. Its applications include the production of detergents, pharmaceuticals, antibacterials, plastics, dyes, textiles, perfumes, and animal feed. Currently, other advanced applications of carboxylic acids can be found, such as in the production of biopolymers, being additives for lubricating oils, in drug administration, and in tissue engineering. Most carboxylic acids are produced on an industrial scale by chemical synthesis (Djas and Henczka 2018). The synthesis of aromatic hydroxycarboxylic acids with CO_2 turns out to be one of the most studied industrial syntheses. Since the carboxylation reaction of Kolbe-Schmitt is the traditionally used process, it is also currently a standard commercial method for the preparation of said aromatic acids (Lindsey and Jeskey 1957). Subsequently, this sparked research into variations of this reaction such as Iijima and Yamaguchi (2008a). They carried out several studies proposing different promoters of the reaction to obtain salicylic acid from phenol and scCO_2 . In the first place, the direct synthesis of hydroxybenzoic acid (HBA) was carried out under optimal conditions, at 473 K and 8 MPa of CO_2 , using several types of basic metal oxides as catalysts, such as γ -alumina, zirconia, and ceria. They were also tested with Lewis acids such as SiO_2 and ZrO-SO_4^{2-} which were identified to be ineffective catalysts for the reaction. Other basic oxides such as CaO and MgO were equally unsuitable for this type of reaction. When investigating the effect of various carbonates of alkali and alkaline earth metals on the synthesis of this acid, it was observed that the catalytic activity of K_2CO_3 was the highest among the catalysts studied, followed by that of KHCO_3 , having yields of 36% and 17%, respectively. Table 3 represents an extract of the results produced in two studies for HBA obtaining.

As can be seen in Table 3, except for K_2CO_3 , none of the catalysts result in the formation of 4-hydroxybenzoic acid (p-HBA). An increase in salicylic acid formation was observed up to a yield of 68% with the use of 30 mmol of K_2CO_3 , although an optimum amount of K_2CO_3 of 10 mmol was

Table 3. Extract of results obtained for the two studies on the direct synthesis of HBA (Iijima and Yamaguchi 2008b, 2008a).

Catalyst	Yield (% mol)	o-HBA yield (% mol)	p-HBA yield (% mol)	o- HBA selectivity (%)
Study: Direct synthesis of salicylic acid from phenol and supercritical CO_2 with K_2CO_3 as a catalyst (Iijima and Yamaguchi 2008b)				
K_2CO_3	36.57	36.02	0.55	98.5
Rb_2CO_3	0.54	0.54	0.00	100.0
CaCO_3	0.39	0.39	0.00	100.0
KHCO_3	17.06	17.06	0.00	100.0
Study: Effective regioselective carboxylation of phenol to salicylic acid with supercritical CO_2 in the presence of aluminum bromide (Iijima and Yamaguchi 2008a)				
ZnCl_2	5.20	5.20	0.00	100.0
ZnBr_2	12.90	12.90	0.00	100.0
AlCl_3	2.70	2.70	0.00	100.0
AlBr_3	55.90	55.90	0.00	100.0

suggested, since the greatest increase in HBA formation occurs at this amount (Iijima and Yamaguchi 2008b). Although the traditional method previously explained has been widely used, some of the pioneering studies in the synthesis of carboxylic acids are taking place in the field of electrochemistry. One of the advantages of the organic compounds reduction in presence of CO_2 is the efficient fixation of CO_2 to organic molecules, forming C-C bonds under soft conditions. CO_2 electroreduction could be presented as a worthy alternative to these processes that involve intensive use of energy as well as the replacement of toxic reducing agents by electrons. It has been shown that the resulting carboxylic acid is obtained with high efficiency by using reactive metals such as magnesium or aluminum galvanic or sacrificial anode, which also has its drawbacks, which will be discussed later (Matthessen et al. 2014; Senboku and Katayama 2017). Some authors studied the electrolysis by divergent pairs of diacid precursors and diol, from the cathodic carboxylation and the simultaneous anodic acetoxylation of conjugated dienes (Matthessen et al. 2015, 2014; Senboku et al. 2015; Tateno et al. 2015). In their studies, an innovative methodology is defined that allows a conversion of CO_2 using a durable and inert anode. This process results in the formation of dicarboxylate salts and diacetate esters, from cathodic carboxylation and anodic acetoxylation, respectively. Trifluoroacetate (TFA) and tetraethylammonium (TEA) were used both as supporting electrolytes and as reagents for acetoxylation, forming their corresponding salts in the solution. The electrolysis of other diene substrates was also carried out under the same conditions as in the previous case. It should be mentioned that in the case of 1,3-butadiene, the CO_2 pressure was 10 bar. It can be observed that by carrying out the electrolysis of 1,3-cyclohexadiene with nickel cathode and graphite anode, in a solution of CH_3CN with TEA and TFA, under a pressure of 1 bar of CO_2 , a carboxylation yield of 35% and an acetoxylation yield of 49% were obtained (Matthessen et al. 2015).

Another application of electrochemistry is ionic liquids. Since the compatibility of ionic liquids with scCO_2 is known, they have been frequently used in the electrochemical carboxylation of both supporting electrolyte and reaction medium. One of the examples reported consisted in the electrocarboxylation of a wide range of halogenated aromatic hydrocarbons, such as bromobenzene, iodobenzene, or chloronaphthalene, using a platinum cathode and a magnesium anode in the ionic liquid DEME-TFSI reacting with scCO_2 . Moderate yields of approximately 50% were obtained, which leaves a considerable range for improvement in these processes. In spite of the obtained yields, it turns out to be an alternative more respectful towards the environment and simpler in terms of being able to purify the products by means of simple column chromatography. Therefore, it is a field still under study (Kathiresan and Velayutham 2015; Senboku and Katayama 2017; Tommasi and Sorrentino 2009, 2006, Zhao et al. 2014).

It is concluded that the use of CO_2 in carboxylation processes is interesting to meet the economic and environmental requirements, and provides an alternative to traditional CO_2 coupling reactions that require organometallic reagents, with a great future of electrocarboxylation, and especially, that is free of sacrificial anodes (Luo and Larrosa 2017; Senboku and Katayama 2017).

Carbamic acids from CO_2

CO_2 has a particular affinity for interacting with various nitrogen nucleophiles, such as ammonia or amines. This fact is of great synthetic relevance since it is a key step towards the carbonylation of the said nucleophile and the synthesis of N-carbonyl compounds. The fixation of CO_2 by amines can produce carbamic acids, carriers of the carbamate group ($\text{RR}'\text{NCO}_2$). Nowadays, the interest in the reaction between amines and CO_2 continues, since in addition to its traditional uses, such as in the Solvay process or in the synthesis of urea from ammonia and CO_2 , new applications with synthetic relevance have emerged, such as the synthesis of esters from carbamates, isocyanates, and ureas (Quaranta and Aresta 2010).

Carbamates. The carbamate esters (urethanes) are fundamental structural elements for the development and obtaining of therapeutic agents, such as drugs or agrochemicals (Vessally et al. 2018). One of the most important methodologies for the preparation of organic acyclic carbamates from CO_2 involves the reaction of three components: amines, alkyl halides, and CO_2 . Firstly, the tri-

component reaction of amines with alkyl halides and CO₂ is a highly known synthetic route for the synthesis of acyclic carbamates, being the object of several investigations. Salvatore et al. have proved the treatment of several aliphatic, aromatic, and heteroaromatic amines with alkyl halides in the presence of Cs₂CO₃ as a base, tetrabutylammonium iodide as an additive, and Dimethylformamide (DMF) as a solvent, under a CO₂ atmosphere, obtaining the corresponding carbamates with yields of up to 98%. This same research group extended its methodology with the use of benzyl chloride, observing reasonable results, with yields from 60% to 96% (An et al. 2014; Salvatore et al. 2002, 2001).

Hooker et al. (2009) demonstrated that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can efficiently catalyze the carboxylate coupling of amines with alkyl halides and CO₂. Various radio-labeled carbamates were obtained by the treatment of [¹¹C] CO₂ with a mixture of amines and alkyl chlorides in the presence of DBU as a base, in DMF. The reactions were carried out with amine, alkyl chloride, and DBU at a concentration of 100 mM each, in 300 ml of DMF, with yields from 60% to 77%. Kong et al. (2011) have demonstrated that a range of carbamate esters can be obtained from the reaction of the corresponding aliphatic and aromatic amines with a variety of alkyl and CO₂ halides in very soft conditions, at atmospheric pressure of CO₂ and at room temperature, using K₂CO₃ as a base in polyethylene glycol 400 (PEG 400) as solvent and catalyst while considering a more ecological procedure for the production of organic carbamates. The obtained yields from this process varied from 29% to 93%. Xiong et al. (2015) developed a methodology for obtaining O-aryl carbamates from the reaction between aliphatic amine, diaryliodonium salts, and CO₂. Under the right conditions, the reaction was carried out for a wide variety of functional groups on the aryl ring of the diaryliodonium salts, such as fluorine, chlorine, bromine, and nitrile. The yields obtained were 63%, 38%, 20%, and 75%, respectively. With asymmetric salts of aryl-(phenyl)-iodonium as functional groups, yields of up to 91% were reported. More recently, Riemer et al. (2016) were able to synthesize different amino acids protected with carboxybenzyl (Cbz) from amino acids with benzyl bromide and CO₂ at atmospheric pressure, using Cs₂CO₃ as a base in Dimethyl sulfoxide (DMSO). The reaction provided the carbamates corresponding to the said amino acids in favorable yields, between 70% and 90%. Yang et al. (2017) developed a generation of aniline carbamates with nitrile, reacting aniline with 2-ethylbenzo-nitrile bromides and CO₂ under soft basic conditions, obtaining yields of 80–86%. New substituents were obtained that turned out to be excellent guiding groups for the activation of anilines with C-H meta-bonds for the construction of new C-C and C-O bonds in metal-catalyzed reactions.

There are also studies on the synthesis of carbamate esters promoted electrochemically (Feroci et al. 2003, 2007). Some of the conclusions were that the aliphatic amines gave better yields than the aromatic amines and that the secondary aliphatic amines are more reactive than the primary amines. Thus, it is concluded that carboxylate coupling of amines with alkyl halides and CO₂ is one of the most useful synthetic routes for the biologically and synthetically most important carbamate esters. The key features of this procedure are that the raw materials turn out to be cheap and easily accessible, non-toxic byproducts, reasonable yields, and their production from common bases under very soft operating conditions. These results clearly show the possible application of this chemical fixation of CO₂ at an industrial level. Despite this, the number of studies reported on this subject continues to be limited, making this field of research still open.

Isocyanates. The second key point of this section is the isocyanates, carriers of the RNCO group. Isocyanates are compounds of great industrial importance, since their application reaches various fields. They are used as raw material for the manufacture of phytosanitary agents, pesticides, dyes, resins and plastics, textile waterproofing agents, detergents, bleaches, and adhesives (Germain et al. 2016; Quaranta and Aresta 2010; Wang, Liu, and Deng 2017). One of the phosgene-free alternatives for the synthesis of isocyanates consists of two steps: first, a catalytic synthesis of carbamates from nitrile or amino compounds and CO₂, followed by a thermal cracking that provides the corresponding isocyanates. There is no chloride involved in this specific route, leading to the simplification of the separation and purification operations, hence increasing the quality of the products. Despite its apparent advantages, few studies were reported on the direct synthesis of isocyanates from CO₂, amines, and alcohols (Wang, Liu, and Deng 2017).

Table 4. Summary of studies on the synthesis of carbamates to obtain isocyanates from CO₂ (Ammar et al. 2017; Choi et al. 2002; Wang, Liu, and Deng 2017; Yan et al. 2011).

Catalyst	Operating Conditions	Yield (%)
Bu ₂ SnO	200 °C, 24 h, 30 MPa CO ₂	14
Bu ₂ SnO	Me ₂ C(OEt) ₂ , 200 °C, 24 h, 30 MPa CO ₂	84
Ni(OAc) ₂ -bipiridina	200 °C, 24 h, 30 MPa CO ₂	67
Cs ₂ CO ₃	200 °C, 24 h, 2.5 MPa CO ₂	44
CeO ₂	150 °C, 12 h, 5 MPa CO ₂	91
MnO _x (0,03)-CeO ₂	150 °C, 12 h, 5 MPa CO ₂	82

The synthesis of carbamates by reacting CO₂, amines, and alcohols were tested in Abila, Choi, and Sakakura (2004)'s work. Initially, they used tin-based catalysts at pressures of 30 MPa of CO₂ and 200°C. After 24 h of reaction, the conversion of n-butylamine was only 16%, which could be improved to 100% using acetal in large excess as a dehydrating agent. Due to the toxicity of tin, they used nickel-based catalysts, less harmful and more active, but this methodology was unsatisfactory by industrial standards (Abila, Choi, and Sakakura 2001, 2004). Honda et al. (2011) used commercial CeO₂ as a heterogeneous catalyst to synthesize methyl benzyl carbamate in one step from CO₂, benzylamine, and methanol. Under a pressure and temperature of CO₂ of 5 MPa and 150°C, after 12 h of reaction, a greater conversion of 99% of benzylamide was obtained, with the selectivity of the methyl-benzylcarbamate of 92%, obtained without using dehydrating agents. In addition, it had the advantage that the catalyst could be reused after calcination at 600°C for 3 h. More recently, a catalyst of cerium and manganese (MnO_x-CeO₂) was prepared, which showed high activity in the synthesis of aliphatic carbamates from CO₂, aliphatic amines and methanol, reaching carbamate yields of up to 82% and the catalyst can be reused up to four times for a simple recycling process (Zhang et al. 2015a). Although there have been several studies conducted in recent years regarding the use of CO₂ for the synthesis of isocyanates which are also summarized in Table 4, most are still in pilot scale (Wang, Liu, and Deng 2017).

Undoubtedly, phosgene is the most effective carbonylation agent and its technology is too established to be replaced, due to its high efficiency and profitability. Even so, its environmental and health risk makes it increasingly necessary to search for alternative routes for the synthesis of phosgene-free isocyanates. The key to finding the methodology that increases the performance of isocyanates lies in three points. Firstly, choose a suitable carbonyl source, for example, CO₂; although it represents a great challenge. Secondly, develop an efficient catalytic system and finally, search for an integrated production system that takes advantage of the resources used.

Ureas. In this section, the manufacturing of urea from CO₂ will be looked into. The synthesis of urea is currently the main consumer of CO₂ in organic synthesis. Urea, (CO(NH₂)₂), is the most widely produced nitrogen fertilizer and is commonly marketed. It is produced at industrial level via the reaction of ammonia with CO₂, a two-stage process where ammonia and CO₂ react to form ammonium carbamate, which is then dehydrated producing urea. This industrial method is based on the Bosch-Meiser urea process, developed in 1922. This reaction is exothermic and the process requires operating conditions between 150°C and 250°C with pressures of 5–25 MPa (Wang, Xin, and Li 2017; Xiang et al. 2012).

The apparent need to employ high pressure and temperature is what led Xiang et al. (2012) to investigate a way based on a negative corona discharge. They demonstrated for the first time that, although the reduction of CO₂ by NH₃ in urea at environmental conditions was not feasible through conventional processes, by making these gases available under said discharge urea could be synthesized at room temperature and pressure. Thus, without using any metallic catalyst, they achieved a conversion of 82% under a pressure of 1 atm and at 20°C. They observed that the yields of the solid mixture of urea and ammonium carbamate increased with the reduction of temperature and with the increase of the molar ratio NH₃/CO₂ and the frequency of discharge. Recently, the use of metal salts of oxalates as catalysts for

the synthesis of N, N'-dialkylureas from CO₂ and amines was described (Sun et al. 2016). They compared the use of metal salts of sodium oxalates, nickel, manganese, iodine, cesium, and zirconium, in addition to other salts of yttrium of borate, carbonate and citrate, and yttrium oxide, resulting in Y₂(C₂O₄)₃ being the catalyst that provided higher yields. Under the optimal conditions, which were found to be 20 atm of CO₂, 10 atm of NH₃ and at a temperature of 150°C, in N-methyl-2-pyrrolidone (NMP), high conversions of 71–86% were obtained. However, the secondary amines and aromatics showed to be incompatible with this carbonylation reaction. In addition to the target product, byproducts were also formed: N, N'-dialkylamide, N-alkynylcyanate, and N-N'-dialkyl carbodiimide. A recent method for the production of ureas in which primary amines and CO₂ were used in the absence of additives and solvents was described. Research on temperature and pressure revealed that there is a point of equilibrium of both factors. At more than 180°C the yield gradually decreased, which could be attributed to the reversibility of the reaction. The inclusion of additional additives in the system did not improve the performance considerably. Under the optimal reaction conditions (180°C and 10 MPa of CO₂), the aliphatic primary amines react gently with CO₂ to give ureas of different types, with a selectivity of 100% and yields that in some cases reached up to 97% after 24 h of operation (Wu et al. 2010). From the point of view of profitability and green chemistry, the use of a cheap, stable, and recyclable catalyst without a stoichiometric excess of dehydrators in the synthesis of urea is very attractive. This implies that researchers must still look for new concepts and technologies of dehydration for the synthesis of urea, especially based on the new mode of activation for CO₂, amines or carbamates so to be able to take them as soon as possible on a large scale.

Linear and cyclic carbonates from CO₂

Among the various chemical conversion processes that involve the transformation and consumption of CO₂, an actively investigated field is the production of organic carbonates, of linear, acyclic, and cyclic type, in addition to their use for the synthesis of polycarbonates. This synthesis of carbonates, which is environmentally friendly, could be an exit from the conventional use of toxic chemicals such as phosgene (COCl₂) and carbon monoxide (CO) (Lim, Lee, and Jang 2014; Martín, Fiorani, and Kleij 2015).

Acyclic carbonates. In recent decades, the synthesis of CO₂ based acyclic carbonates such as dimethyl carbonate (DMC), diethylene carbonate (DEC), and diphenyl carbonate (DPC) has attracted attention in various studies. Especially, the DMC has been one of the most active focuses in this field, since it represents a molecule with a wide variety of applications such as apolar solvent, fuel additive, electrolyte in lithium-ion batteries and carbonylation reagent, methylation, and methoxycarbonylation (Prat et al. 2016; Pyo et al. 2017). More than 90,000 tons of DMC are consumed worldwide annually, being destined to the production of polycarbonates, approximately 50%, and up to 25% of its total use is as a solvent. Traditionally, DMC has been produced from the reaction between methanol and phosgene, a method that has led to disuse being replaced by less toxic routes that involve the oxidative carbonylation of methanol (Garcia-Herrero et al. 2016; Kindermann, Jose, and Kleij 2017). Most acyclic carbonates are synthesized from alcohols and CO₂ by heterogeneous catalysis using metal oxides, zeolites, and metal complexes. Although in comparison with many effective homogeneous catalysts, heterogeneous catalysts have the advantage of being superior in stability and reuse. However, they also have deficiencies: the catalytic activity is usually unsatisfactory, so it is necessary to use solvents to improve the activity and selectivity, in addition to require dehydrating or efficient drying to obtain carbonates with high yields (Honda et al. 2014a; Dai et al. 2009).

Some of the studies carried out on homogeneous catalytic systems for the formation of DMC from methanol and CO₂ investigated the use of titanium, zirconium and nionium compounds, as well as complexes of tin and other organometallic compounds, whose efficiency was quite low (Kizlink and Pastucha 1995). Furthermore, using ortho-esters as a dehydrating agent and [Bu₂Sn(OMe)₂] as a catalyst, a yield and selectivity of the DMC of 48% and 85%, respectively, were obtained. This was achieved under high pressures of approximately 300 atm of CO₂ and 180°C,

resulting in a problem concerning ortho-esters including difficult recycling (Sakakura et al. 2000). The use of acetal as a drying agent was also studied, since it was considered more sustainable when regenerating, achieving higher yields in DMC (58%) in the presence of the tin catalyst (Sakakura et al. 1999). Organic desiccants were also used, which made zeolites, considered inefficient at high temperatures, achieved yields of up to 45% in DMC from methanol (Choi et al. 2002). Despite the different options studied, significant advances were achieved only with the addition of desiccant or dehydrating agents. The use of nitriles, compounds capable of regeneration through the formation of amides and subsequent conversion to nitriles, was proposed. The results were not expected when using acetonitrile as a desiccant for the synthesis of DMC from methanol and CO₂ with CeO₂ as a catalyst, since at 0.5 MPa of CO₂ and 150°C, the yield of DMC after 48 h reached only 9%, with a selectivity of 65%. Improved results were obtained when using benzonitrile, increasing the yield and selectivity of the DMC up to values of 47% and 75%, respectively, after 86 h of operation under a pressure of 1 MPa and at 150°C (Honda et al. 2011).

After making a classification of different dehydrators based on nitrile, it was concluded that 2-cyanopyridine was the nitrile that produced the best results when used with cerium oxide. The yield (94%) and the selectivity (96%) of the DMC reported in this system after 12 h of reaction at 5 MPa of CO₂ and 120°C were surprisingly high. In addition, the use of 2-cyanopyridine as a desiccant had the advantage that its dehydration by Na₂O and SiO₂ was feasible, although its efficiency could be improved (Honda et al. 2013; Honda et al. 2014b). Due to the excellent results in performance and selectivity registered when combining CeO₂ with 2-cyanopyridine, this system appears as a promising candidate for its application in the industrial and commercial field. In 2014, the first continuous flow process with fixed bed reactors was developed by means of this system, represented in Figure 3.

Briefly, in this process, a system capable of carrying out reactions from atmospheric pressure to 400 bar was used. Pumps were used both for the feed of the methanol and 2-cyanopyridine mixture and for the supply of liquid CO₂, while the CO₂ gas was introduced into the system by means of a thermal mass flow controller. In addition, the lines after the reactor were maintained at temperatures above 180°C to avoid the formation of solids. Tests at various temperature and pressure conditions were made presented in Table 5.

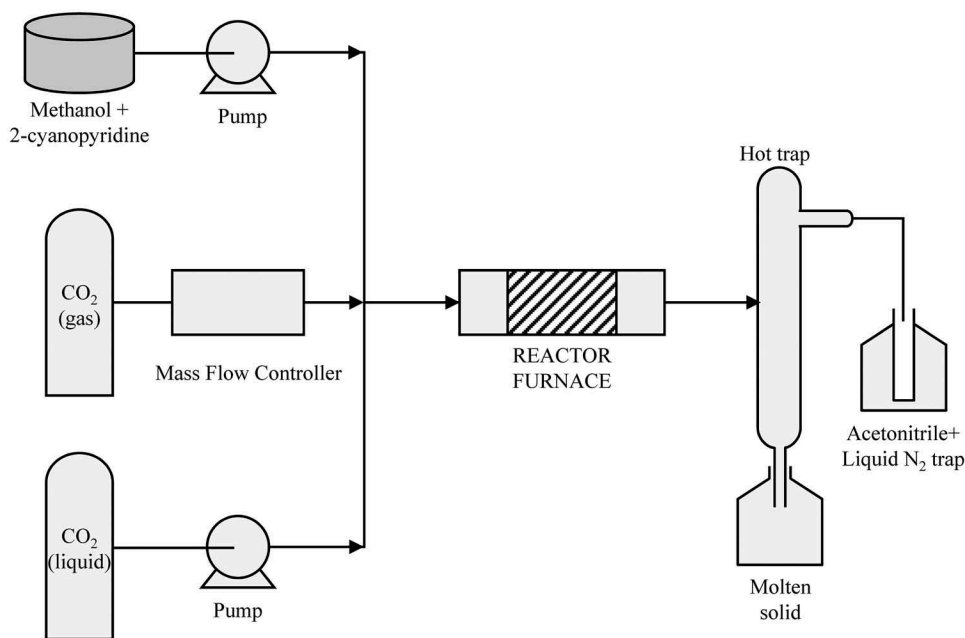


Figure 3. Flowchart of the continuous process for the production of DMC. Adapted from Bansode and Urakawa (2014).

Table 5. Results of the analysis of the effects of temperature and pressure in the continuous production process of DMC from CO₂ and methanol, with 300 mg of catalyst. (Bansode and Urakawa 2014).

Study	T (°C)	P (bar)	Methanol Yield (%)	DMC Selectivity (%)
Pressure Effect	120	1	27	96,5
		30	92	>99
		>30	92	>99
Temperature Effect	80	200	17	>99
	120		92,4	>99
	140		94	98
	160		90	93

It was concluded that the efficiency of the reaction reached a maximum and remained practically constant from 30 bar of CO₂, and that the optimum operating temperature was 120°C, as presented in Table 5. A key finding reached in a previous study was the existence of a delicate balance between temperature, pressure, and residence time required to achieve an excellent catalytic performance leading to the appearance of new opportunities in heterogeneous catalysis that promotes the investigation of the possibility of transforming traditional discontinuity in continuous processes, since batch processes are especially limited by the balance and the presence of water (Bansode and Urakawa 2014). Given its good results, it is not surprising that research has intensified in this field. Alongside this, the reuse of the cerium oxide catalyst has been studied, which is eventually deactivated by adsorption of the amide formed by 2-cyanopyridine. Furthermore, this system is not only limited to the formation of acyclic carbonates, but also for the synthesis of cyclic carbonates, carbamates, cyclic and acyclic urea derivatives, and even for the preparation of polymeric materials from CO₂ and diols (Tamura et al. 2016; Honda et al. 2014c). The synthesis of acyclic carbonates free of metals has also been reported through the use of organic promoters. To avoid the problem of dehydration and promote an effective and direct coupling of alcohols and CO₂, the Mitsunobu reagent was introduced, through which it was possible to convert primary, secondary, and even tertiary alcohols into acyclic carbonates. The product yields are from 70% to 98% in less than 8 h of operation, working between 90°C and 100°C (Chaturvedi, Mishra, and Mishra 2007). Moreover, the use of DBU was studied for the synthesis of organic carbonates, both acyclic and cyclic. Through this method, moderate performance (48%) was achieved at relatively soft conditions (70°C and 10 bar CO₂) for the DMC. In these same conditions, it was possible to obtain a yield of 69% for the synthesis of dibenzyl carbonate, another acyclic carbonate (Lim, Lee, and Jang 2014). Another method reported for the manufacture of DMC is the electrochemical synthesis from methanol, CO₂ and propylene oxide in an ionic liquid (bmimBr). Under optimum conditions; temperature of 30°C, atmospheric pressure of CO₂, with a molar ratio of methanol/propylene oxide of 11.5:1 and after 48 h of reaction, 97% conversion of methanol as well as the yield of the DMC of 75.5% was obtained (Yan et al. 2011).

Cyclic carbonates. The production of cyclic carbonates from CO₂ synthesis is a well-established field. One of the most investigated reactions in this field is the addition of CO₂ to epoxides which has also been used on an industrial scale for the manufacture of cyclic carbonates and polycarbonates (PC) (Martín, Fiorani, and Kleij 2015). For the reaction of epoxides with CO₂, catalysts have been developed based on alkali metal salts, metal oxides, transition metal complexes, organic bases, and ionic liquids. Studies are still emerging that raise other alternative procurement systems, such as, for example, the use of proteins for the catalysis of this reaction. It was demonstrated that amino acids can become a reaction catalyst for cycloaddition of CO₂ with epoxides. Relatively adverse conditions, more than 6 MPa of CO₂ at 130°C for 48 h, were necessary to obtain satisfactory results from the use of amino acids (Saptal and Bhanage 2017). Even so, when combining alkaline metal salts with amino acids, excellent results were reported, reaching a propylene oxide conversion of 99% after one hour of operation at a temperature of 120 °C and 2 MPa of CO₂ (Yang et al. 2014).

Table 6. Results of PC synthesis from different catalysts. Modified from Chang et al. (2018).

SwithOut WP		WITH WP	
CO-CATALYST	PC YIELD (%)	CO-CATALYST	PC YIELD (%)
KI	7	KI	94
KBr	3	KBr	29
KCl	Traces	KCl	13
DBU	6	DBU	20
DMAP	Traces	DMAP	15
TBAI	30	TBAI	81

Chang et al. (2018) recently proposed the use of wool powder (WP) as a catalyst for the coupling of epoxides with CO₂. By having hydroxyl, carboxyl and sulfonic acid groups, which turn out to be activators of epoxides while amino groups are the activator of the CO₂ molecule, it seems to be a good candidate to catalyze this type of reactions. Using CO₂ with a purity of 99.99% and propylene oxide as reagents, PC synthesis was studied using WP alone and with other co-catalysts: potassium iodide (KI), potassium bromide (KBr), potassium chloride (KCl), tetrabutylammonium (TBAI), DBU, and N, N-dimethylaminopyridine (DMAP). After 3 h of operation at 120°C and 1.5 MPa of CO₂, and without the use of any solvent, the results obtained are shown in Table 6.

When WP was exclusively used, PC performance was only 12%, while as can be seen in presented Table 6, using KI had the performance of 7%. Surprisingly, the combination of both in the same reaction gave a yield of 94% of the desired product. The dependency of the yield with the reaction time was studied, observing that it increased rapidly in the first 3 h, reaching its maximum in 94%, practically constant even when the operating time increased (Chang et al. 2018).

The direct carbonylation of glycerol and CO₂ to obtain glycerol carbonate (GC) is a very interesting and challenging route, since it would involve converting two materials considered as waste into valuable products for the chemical industry (Mohd et al. 2017). One of the most recent studies about the synthesis of GC, deals with the carbonylation of glycerol with CO₂ on cerium oxide catalysts, using as a desiccant agent of 2-cyanopyridine. Under optimized operating conditions of 150°C, 4 MPa of CO₂, 10 mmol of glycerol, 30 mmol of 2-cyano-ridin and 10 mmol of CeO₂ producing GC with the yield of approximately 79% after 5 h of reaction (Liu et al. 2016). Using the same system of CeO₂ and 2-cyanopyridine, PC synthesis was developed from propylene glycol (PG). The influence of 2-pridine turned out to be decisive due to the fact that the yield of PC produced went from less than 0.3% to more than 99% by the addition of 100 mmol of 2-cyanopyridine and only one hour of operation, at a temperature of 130 °C and 5 MPa of CO₂ while using 20% molar of catalyst (Honda et al. 2014a).

Given the current situation in the field of the synthesis of carbonates, both acyclic and cyclic, certain points can be concluded. One of the crucial characteristics for the optimization of these processes continues to be the regeneration of the desiccant species since, if it can be regenerated efficiently, the process would have a greater potential for its large-scale application and commercial exploitation. On the other hand, although the systems that use organic catalysts are more attractive for the environment, the activity shown by the metal complexes is considerably greater, so it is necessary to continue developing organometallic systems capable of equaling and even exceeding the activity promoted by the catalysts based on metals. As mentioned, the study of catalysts capable of facilitating high conversions of epoxides and alcohols at low CO₂ pressures is a field of great interest. It is worth mentioning that the research alongside the different routes reported in the last twenty years about the synthesis of the carbonates has made it possible to use more ecological and sustainable catalytic methods in pharmaceutical production and bulk chemistry.

Polymers from CO₂: polycarbonates and polyurethanes

The use of CO₂ to obtain polymers would not imply a substantial reduction in emissions, since the emission from the consumption of fossil energy is several orders of magnitude higher compared to

the reduction that would be produced through the use of CO₂ in this industry. Even so, its use would make this sector meet the requirements of sustainable development through the utilization of versatile raw materials in the synthesis of polymers. It is important to note that the polymers generated from CO₂ are biodegradable (Qin and Wang 2010; Trott, Saini, and Williams 2016). Polycarbonates obtained from CO₂ and epoxides copolymerization, usually show inferior mechanical properties, in addition to a moderate chemical and thermal stability in comparison with the polycarbonates produced from bisphenol. Although these characteristics limit their industrial application as plastics, the biodegradability and sustainability of the synthesis of these polymers stimulated both the search for new applications and research to improve their properties and the efficiency of their synthesis (Taherimehr and Pescarmona 2014).

The most widely studied CO₂-based copolymers are propylene polycarbonate (PPC) and cyclohexene polycarbonate (PCHC), synthesized from propylene oxide (PO) and cyclohexene oxide (CHO), respectively (Engels et al. 2013). Different investigations have focused on the search for catalysts that increase the efficiency and selectivity of the desired product, as in most fields where the use of CO₂ is treated, due to its high stability (Xu, Feng, and Song 2014). Much of the catalytic systems investigated are homogeneous complexes based on metals combined with a nucleophile, which is often an organic salt. Since this reaction produces both cyclic carbonates and polycarbonates, the selectivity of these will be determined by the operating conditions, taking into account different factors. On the one hand, depending on the type of epoxide used, the formation of the polymer product will be more or less favored. Obviously, the operating temperature will also have an influence, favoring the high temperatures the synthesis of the cyclic product, since it is the thermodynamic product. On the other hand, due to intermolecular reactions, the higher the ratio between the nucleophile and the metal, the greater the selectivity of the cyclic product (Machado, Nunes, and Da Ponte 2018). The homogeneous catalysts can be classified into two types: bicomponent catalysts, which consist of the use of metal (III) complexes with other co-catalysts and dinuclear or bimetallic catalysts, which are metal complexes (II/III). Catalysts of the first type are usually metal complexes of Co (III), Cr (III), Mn (III) or Al (III), coordinated with ligands such as salicilimine or porphyrins. The co-catalysts employed are typically ionic salts, such as bis(triphenylphosphine)iminium chloride (PPNCl) or Lewis bases such as 4-dimethylaminopyridine (DMAP) (Trott, Saini, and Williams 2016). Some of the highest activities in the synthesis of PPC were reported using bifunctional catalysts substituted with ionic groups, reaching a conversion frequency (TOF) of up to 26,000 h⁻¹ with low catalyst loads (ratio [catalyst]/[PO] = 1: 25000) (Na et al. 2009). Lee et al. (2005) were pioneers in the use of a series of complexes of bis(anilido-alimine) and Zn (III), which showed considerably high activities (TOF = 2860 h⁻¹) with very low catalyst loads (ratio Zn/Epoxide = 1:50000). Kember et al. (2012) prepared a series of di-cobalt halide catalysts with several neutral co-ligands, such as pyridine, methylimidazole, and DMAP. They were used at a moderate temperature and at 1 atm of CO₂ for the synthesis of PCHC from CHO. In many cases, the registered activities were from good to excellent (TOF from 16 to 480 h⁻¹), taking into account the low pressures under which the reaction was executed.

Heterogeneous catalysts have also been reported in this area of study, such as zinc glutarate or other carboxylates, and double metal cyanides, highlighting Zn₃(CoCN₆)₂. In some cases, they are used industrially as epoxide homopolymerization catalysts, although for their use in CO₂ copolymerization much stronger conditions are required than for homogeneous catalysts. They need high CO₂ pressures and generally produce polyether carbonates instead of polycarbonates (Sebastian and Srinivas 2013; Trott, Saini, and Williams 2016). The disadvantage of this type of catalysts is their implicit toxicity when containing metals, whose use is strictly restricted, as well as the fact that their presence should not be detected in the final biodegradable polymers. It is for this reason that several efforts have been made to achieve metal complexes that are more respectful with the environment, but with high catalytic activity. Some of these metals are Fe, Zn, Mg, and Ti. For example, Wang et al. (2015) designed a binary complex of titanium salts for the synthesis of PCHC, which compared its tetravalent counterpart and increased its activity from 41 to 557 h⁻¹. Although all these systems

showed polymer formation from CO_2 and CHO , in the CO_2/PO system the corresponding cyclic carbonate is produced and the propylene polycarbonate has a very low activity, this polymer being one of the most used industrial level (Liu and Wang 2017).

The synthesis of polyurethane (PU) has been another field of study during the last years. PU currently has multiple applications: elastomer, foam, adhesive, packaging, and sealant. This last generation polymer is synthesized on the basis of the reaction between isocyanates and polyols. Due to the decrease in the price of isocyanate in recent years (less than 2000 \$/ton since March 2015) (Liu and Wang 2017), the challenge to reduce the cost associated with the synthesis of PU is focused on the price of polyols, which initially were cheap. This is where polyether carbonate polyols or CO_2 polyols come into play providing a promising way to lower costs of raw material, which is a substitute for polyols from polyether or polyester. Some of the main advantages have already been analyzed: polyether carbonate polyols with a CO_2 content of 20% mass reduce greenhouse gas emissions by 11–19%, with the saving of fossil resources that implies (13–16%) (von der Niklas and Bardow 2014). In addition, the PU synthesized from these polyols presents an improved resistance to oxidation and hydrolysis with respect to that based on polyether polyol (Wang et al. 2016b). Thus, both from the economic and technical point of view, the CO_2 polyols are presented as a substituent with great potential of conventional polyols, whose overall production in 2016 was approximately 9.4 Mt.

The initiator of the reaction is another important parameter to determine the characteristics of the polyols of synthesized CO_2 . Thus, when employing oligomeric alcohol initiators, the required copolymerization time will be higher and producing polyols with low average molecular mass (MN) and high content of carbonate units (CU) will be difficult (Trott, Saini, and Williams 2016). To reduce this problem, the use of organic dicarboxylic acids as initiators has begun to be carried out. Using sebacic acid as an initiator, a controlled synthesis of CO_2 -diol was achieved, with a catalyst activity of 1 kg of polymer/g of catalyst, a controllable MN below 2000 g/mol was achieved, although the content in CU could modify between 40% and 75% (Gao et al. 2012). The CO_2 -triol was synthesized in a similar way using 1,3,5-benzene tricarboxylic acid (TMA) as an initiator, providing an MN between 1400 and 3800 g/mol and a content of CU somewhat lower than for the CO_2 -diol (20–54%) (Liu et al. 2014). When the initiator represents approximately 10% of the total weight of the raw material for the copolymerization reaction to take place, its cost must be considered when choosing which initiator to use (Trott, Saini, and Williams 2016). That is why oxalic acid has been selected as the initiator, since it turns out to be the cheapest organic dicarboxylic acid. One of the most recent studies has reported the synthesis of CO_2 -diol as a flame retardant from the use of bisphenol A as an initiator. The resulting polyol was obtained with a content in CU of 42% and an MN of 2400 g/mol, with a productivity of 2.4 kg of polymer/g of the catalyst after 6 h of operation at 2 MPa of CO_2 and 75°C (Ma et al. 2016). Due to the great improvement of the efficiency of these systems, a production line of 10000 tons per year of CO_2 polyols have been built in the city of Nantong, Jiangsu province, located in China, carried out by the company Huasheng Polymer Co. On the other hand, Covestro invested up to 17 million dollars for the configuration of a factory of CO_2 polyols with a capacity of 5000 tons per year, becoming doubly awarded in 2017 for the use of CO_2 for the synthesis of polyurethane foams, generating sustainable material and even reducing the use of fossil raw materials consumed previously by up to 20% (Alex 2015; Covestro 2017).

As it has been observed, this field of research is continuously active with much still to be improved however, studies are progressing in the right direction. Another addition to the study of these reactions would be the substitution of reactive epoxides for ones that are bio-derived, and not generated on the basis of fossils. Thus, the production of polycarbonates could be totally renewable. The main drawback is that these bio-derived species are generally highly substituted epoxies, so they are more challenging to present a more complex structure and considerably less reactivity.

Mineral carbonation

Mineral carbonation will be treated in this section, a chemical process in which CO_2 reacts with a metal oxide, such as magnesium, calcium or iron for the formation of stable carbonates such as

calcite (CaCO_3) and magnesite (MgCO_3). Both calcite and magnesite are of great interest for their wide variety of applications in the pharmaceutical, cosmetic, explosives, paints, inks, resins, rubber, detergents, construction industries, and in particular, CaCO_3 is used for the surface treatment of plastics (Cuéllar-Franca and Azapagic 2015; Gao et al. 2018).

The great potential of using this type of processes can be easily understood when analyzing that the amount of carbon in the atmosphere currently involves around 870 Gt (NOAA/ESRL 2017), while approximately 39 million Gt of carbon is present in the carbonated rocks of the earth's crust, such as marble, limestone or chalk (Abdeen et al. 2016b; Oelkers and Cole 2008). Thus, to generate this reaction of mineral carbonation, the use of silicates based on magnesium seems to be indicated due to its availability in large quantities throughout the world, being the main sources of these natural magnesium silicates the olivine, the forsterite, and the serpentine. In the case of calcium silicates, wollastonite and anortite are usually employed (Oelkers and Cole 2008; Olajire 2013). There are also alternative resources as a source of calcium and to a lesser extent, magnesium which is an industrial alkaline waste. Its main advantages are its availability at low cost, high reactivity compared to that of natural minerals, proximity to CO_2 sources, and the possibility of improving environmental quality by encapsulating potentially toxic elements. However, these wastes are usually available in smaller quantities than minerals, making their use feasible at the individual plant level only. Some of the alkaline residues studied for use in mineral carbonation since 2008 are shown in Table 7 (Gao et al. 2018; Olajire 2013).

Wastes with the highest CaO/MgO content were ashes from coal-fired power plants and stainless steel slag, due to the industrial process from which they come. This carbonation process can be carried out *ex situ* in a chemical processing plant after the extraction and processing of the silicates or in situ, by injecting CO_2 directly into geological formations rich in silicates or alkaline aquifers (Olajire 2013). When dealing with this project of using CO_2 to obtain useful chemical products, only *ex situ* carbonation will be developed (Figure 4) (Mazzotti et al. 2005).

As can be observed in Figure 4, in *ex-situ* mineral carbonation the CO_2 generated is sent to a mineral carbonation plant, where resulted carbonated compounds are stored for its re-use or final disposal. The routes of the mineral carbonation process are a combination of the treatment of minerals and the CO_2 capture in them. The pretreatment usually consists of the extraction, crushing, and grinding of minerals before carbonation. The main objective of these actions is to increase the reactive surface, thus increasing the reaction rate of carbonation. Thus, mineral carbonation methods can be divided into direct and indirect (Helwani et al. 2016). In the direct methods the mineral is carbonated in a single step, while in the indirect, the reactive metal oxides are first extracted from the ore matrix to be carbonated in a later step, obtaining in this way high purity carbonates (IPCC 2005; Mazzotti et al. 2005; Olajire 2013). Within the direct routes, initially, the gas-solid route can be found, where gaseous CO_2 directly affects the mineral or alkaline solids. This method is simple, but the reaction rates were very low, that is why its development has not continued. There is also direct aqueous carbonation, which involves three phases coexisting in a single reactor. Firstly, the CO_2 dissolves in an aqueous solution obtaining a slightly acidic medium with HCO_3^- . On the other hand, there are the leachates of Ca or Mg from the mineral matrix that, together with the solution, cause the carbonate to precipitate. A lot of studies have been developed in this area (Baciorchi et al. 2013, 2011; Lombardi et al. 2012, 2011; Olajire 2013). Regarding indirect routes, there have been many proposed methods with different minerals. First of all, the multistage gas-solid method stands out. In this method, the Ca/Mg silicates are converted into hydroxides or oxides (Ca/Mg(OH)_2 and Ca/MgO) which will be transformed into the corresponding carbonates by its dry carbonation with CO_2 (Wang et al. 2017). Regarding the carbonation of minerals, despite being thermodynamically favorable, it is not easy to carry on an industrial scale. The main challenges to be faced in this type of reactions lie in the gigantic scale needed to reduce real CO_2 emissions and be able to carry out this mineralization, in addition to the need to accelerate the formation of carbonate to make it more efficient. The question whether this process would significantly affect the reduction of emissions has to take into account two opposite aspects: treatments such as transport, heating or cooling

Table 7. Industrial waste suitable for mineral carbonation (Gao et al. 2018; Olajire 2013).

INDUSTRIAL WASTE	CaO – MgO PRESENCE
Ashes from coal-fired power plants	65% mass CaO
Bottom ash from solid waste incinerators	20% mass CaO
Fly ash from solid waste incinerators	35% mass CaO
Paper recycling ash	35% mass CaO
Stainless steel slag	65% mass CaO+ MgO

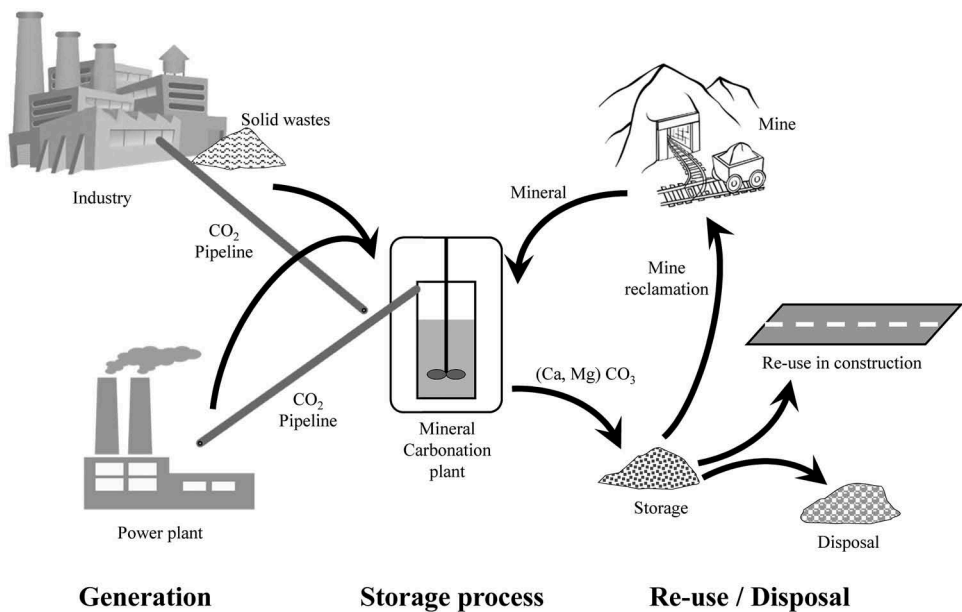


Figure 4. Ex situ mineral carbonation process. Adapted from Mazzotti et al. (2005).

of CO₂ would not be entirely necessary, since carbonation would take place around the emitting plant of this gas. On the other hand, the extraction, transport, and preparation of minerals also consume energy, but this is something that could be solved with the use of alternative raw materials such as wastes from different industries. Thus, the main advantage of mineral carbonation is the formation of stable carbonates capable of storing CO₂ for long periods of time, without the risk of leakage as in other CCS. Due to these qualities, it is presented as one of the most interesting and favorable technologies for the reduction of CO₂ emissions on a large scale.

Fuels from CO₂

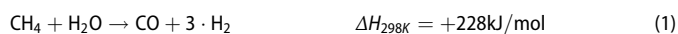
Converting CO₂ into fuels generally requires a reforming reaction, typically, hydrocarbon and carbon reforming reactions and hydrogen reforming reactions (hydrogenation) (Jiang et al. 2010; Styring et al. 2011). The main processes to obtain fuels from CO₂ are syngas from reforming of CH₄, gas hydrates, and biofuels from microalgae.

CO₂ reforming of CH₄

Three different processes have been proposed to obtain syngas via reforming of methane used for the synthesis of syngas: steam reforming (SRM), partial oxidation (PO) and dry reforming (DRM). The SRM is the conventional technology used for the production of hydrogen from hydrocarbon fuels

(Abdullah, Ghani, and Vo 2017). Approximately 75% of the hydrogen produced is obtained by this process, due to its higher performance compared to the other two alternatives (Fan et al. 2016). The differences among SRM, PO, and DRM for syngas production are based on the kinetics and energy of reaction, the ratio of synthesis gas produced (H_2/CO) and the used oxidant: water in SRM (1), oxygen in PO (2) and CO_2 in DRM (3) (Abdullah, Ghani, and Vo 2017; Ebrahimi, Sarrafi, and Tahmooreesi 2017).

Thus, of all these technologies, DRM is the most promising since it uses two abundant greenhouse gases for the manufacture of a useful product and of great importance in the industry, at the same time that it is presented as a possible method to reduce the net emission of these gases into the environment (Selvarajah et al. 2016). This process is also more economical than others, since it



eliminates the gas separation process of the final products. Additionally, biogas (CO_2 , CO , and CH_4) can be reformed through this process and the synthesis gas product is even considered as a storage of solar and nuclear energy. The use of catalysts in the dry methane reforming process is of great importance to maximize the production of syngas by altering and improving the reaction rate. Being an endothermic reaction, high temperatures are required to be carried out effectively, which can be lowered due to the presence of catalysts (Aramouni et al. 2018; Egawa 2018).

Among the numerous possible materials to be used as catalysts for CH_4 reforming with CO_2 , it has been found that the catalysts supported by noble metals show a promising performance in terms of conversion and selectivity towards the synthesis gas. Particularly Ru, Rh, and Ni are classified as active metals. Most of the catalysts used in this synthesis are based on nickel, which has reported long-term deactivation problem due to the deposition of coke, causing the conversion of reagents to decrease (Abdullah, Ghani, and Vo 2017; Aramouni et al. 2018; Egawa 2018). Several authors concluded that the main and desired reaction of the dry reformat is favored thermodynamically at temperatures above 730°C , although to achieve an $H_2/CO = 1:1$ mixture ratio of the synthesis gas obtained with a minimum formation of coke and a CO_2/CH_4 feed-rate of the unit, temperatures higher than 900°C are required (Abdullah, Ghani, and Vo 2017; Egawa 2018; Nikoo and Amin 2011; Selvarajah et al. 2016). At this high temperature, secondary reactions responsible for the formation of coke were not favored, except for the decomposition of methane to be endothermic. Thus, the maximum carbon formation usually occurs at temperatures between 100 and 300°C , which is favored by a CO_2/CH_4 ratio greater than unity, due to the presence of H_2 (Aramouni et al. 2018). Recently, Hassani et al. conducted a study where they showed, among other effects, the H_2/CO ratios produced in the DRM reaction at different temperatures under a pressure of 1 atm , using a Ni/Al_2O_3 nanocatalyst and with a $CO_2/CH_4 = \text{feed ratio of } 1$. They observed that as the temperature increased, the H_2/CO ratio increased with it, which is due to the endothermic nature. Under the conditions specified to obtain an H_2/CO ratio of the unit in the synthesis gas produced, temperatures higher than 850°C were necessary, thus giving the greatest conversion of reagents and the best performance (Hassani et al. 2016). Another very recent study analyzed the activity and selectivity of Ni catalysts with natural clay base for the DRM reaction. The effectiveness of catalysts with natural clay support ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), clay modified with Fe and clay modified with Cu were checked. The methane and CO_2 conversions recorded were greater than 75% at temperatures above 800°C for

all catalysts, except for the clay modified with Fe, which reached a maximum conversion at this temperature of 50% and 55% for CH₄ and CO₂, respectively (Liu et al. 2018a).

Despite its great environmental potential, DRM is not considered an industrially mature process. The extremely high endothermic reaction requires a lot of energy, along with the rapid carbon formation that ultimately leads to the deactivation of the catalyst, long reaction time, and the requirement of pure CO₂. These disadvantages make the DRM an impractical process that still needs additional developments. Future research in this field will probably revolve around catalysts based on bimetallic nickel like the Co-Ni catalyst. This is due to the fact that these catalysts have shown stable activity and high resistance to deactivation, even though carbon deposition is generated. The combined reforming reactions, such as DRM and partial oxidation, should also be considered and studied in greater depth, since the heat released by partial oxidation may be the heat supplied for DRM, which may lead to minimizing the operating cost.

Gas hydrates from CO₂

Gas hydrates are non-stoichiometric crystalline forms of water that are filled with small-sized gas molecules in its molecular cavities via hydrogen bonding at low temperatures and high pressures. Among the gases that could form a hydrate compound (methane, ethane, carbon dioxide, and nitrogen), CH₄ hydrates are expected to be an important energy resource in the near future, due to the fact that it is estimated that there are about 20,000 trillion m³ of CH₄ hydrate below the ocean, which is more than all of the current fuel sources combined (Collett 2002; Pan et al. 2018). Many researchers in the past decades have studied the recovery of CH₄ hydrate from the ocean floor at various conditions (Fujioka et al. 2003; Collett 2002; Pan et al. 2018; Liu et al. 2018a), and more recently the idea of the replacement of CH₄ in the hydrate with high-pressure CO₂ emerges as a long-term storage of this gas and a way to keep the ocean floor stabilized after recovering CH₄ gas (Ota et al. 2005). Also, the direct use of CO₂ hydrate in oil production pipelines has been reported by some authors, as well as CO₂ hydrate-technology which is growing in relative to transportation processes (Jiang et al. 2016; Sabil, Azmi, and Mukhtar 2011; Veluswamy et al. 2018; Yu et al. 2008).

The advantages of CO₂ hydrate as a way of capturing are numerous. Firstly, the main chemical compound needed for CO₂ formation is water, which makes the process cheap and green since a solvent such as MEA or sodium hydroxide is not required. Secondly, it has been studied that the reduction of energy requirements for hydrate formation is possible by employing some chemicals in low concentrations (Liu et al. 2018b; Mooijer-Van Den Heuvel, Witteman, and Peters 2001). Among their uses, the feasibility of seawater desalination via hydrates was developed industrially and demonstrated that could be economically beneficial with the use of a promoter (Englezos 1993; Javanmardi and Moshfeghian 2003). Studies have been conducted where the feasibility of employing eutectic freeze crystallization with CO₂ hydrates for the separation of highly soluble salts from aqueous solutions has been shown (Güner 2015; Sabil, Azmi, and Mukhtar 2011; Vaessen, Ham, and Witkamp 2006). Also, CO₂ hydrates have been studied as cold distribution agent and phase-change material, due to the fact that the melting temperatures are consistent with the temperature needed in these applications and the dissociation heat is suitable for refrigeration application as well as easily regenerable. CO₂ hydrate based process can also be a good alternative to freeze-crystallization processes to concentrate water-rich streams which require relatively low temperatures (Sabil, Azmi, and Mukhtar 2011). Another usage of CO₂ hydrate is to increase CO₂ concentration in culturing algae, where its addition to algal culture systems can increase algal biomass effectively (Nakano et al. 2014).

Biofuels from microalgae

Microalgae cultivation can be carried out in submerged areas, infertile lands, and seawater (Mashayekhi et al. 2017; Singh, Nigam, and Murphy 2011). The cultivation of algal biomass, apart from providing biofuel feedstock, has a favorable environmental impact by reducing the concentration of greenhouse gases because it uses large amounts of CO₂ (Demirbaş 2009; El-Sheekh et al.

2017). To choose a desired type of microalgae, a selection strategy should be considered based on various criteria such as growth rate, quantity of lipids that can be produced and its quality, response to external changes in the environment, temperature variations, nutrient input and light source, absorption speed, and affinity for nutrients, and particularly CO₂, nitrogen, and phosphorus (Amaro, Guedes, and Malcata 2011; Singh, Nigam, and Murphy 2011; Ugwu, Aoyagi, and Uchiyama 2008).

There are three different sources of CO₂ for microalgae: atmospheric CO₂, industries emissions of CO₂ and CO₂ from soluble carbonates (Wang et al. 2008). Moreover, there are two kinds of possible ways to carry out microalgae cultivation: in open raceway ponds or photo-bioreactors (flat-plate, annular or tubular) (Brentner, Eckelman, and Zimmerman 2011; Styring et al. 2011). Economically, bioreactors are more expensive than open-bond systems and recent research have tried to make this process cheaper in terms of capital cost and energy requirements (Brentner, Eckelman, and Zimmerman 2011). The main problem of microalgae cultivation is that a large land area is required. Also, process control is difficult, what makes the productivity to be limited (Cuéllar-Franca and Azapagic 2015). Microalgae cultivation does not compete to food markets that makes them especially interesting for futures researches. This research should be lead towards a reduction of the cultivated area needed and a reduction of general costs (Tan et al. 2018). Figure 5 presents a block diagram of the process needed to convert microalgae to biofuels. In this process, after converting a carbon source in a flue gas, a microalgae cultivation stage is employed to obtain a wastewater biomass that will be dry before its transformation into biofuels.

Enhanced oil and coalbed methane recovery

Throughout the life of an oil production field, there are three stages. Firstly, at the beginning of production, the oil flows naturally to the surface due to the pressure difference existing alongside the deposit. In the second phase, when the pressure in the reservoir falls, water is typically used to increase it while displacing the crude and continuing extracting it. Finally, in a third stage, the remaining oil can be recovered through various technologies with the injection of either steam or

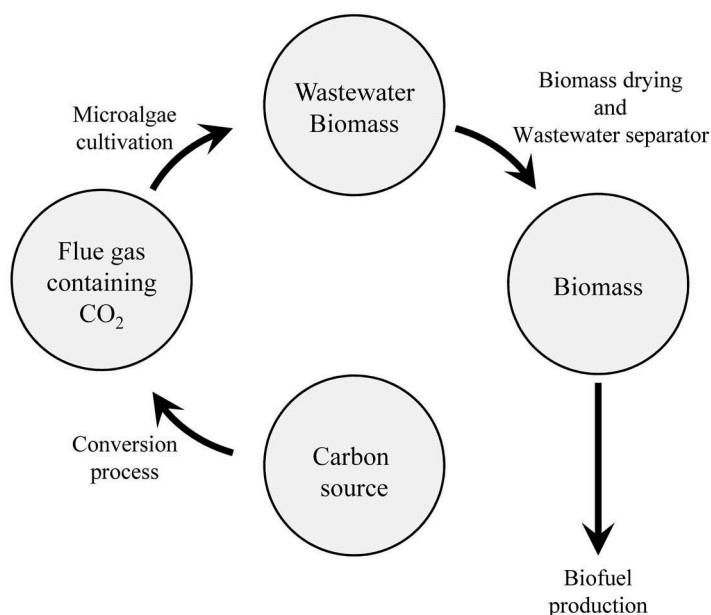


Figure 5. Biofuels from microalgae process. Modified from Tan et al. (2018).

CO₂ being the most common (Ghoodjani and Bolouri 2015). The use of CO₂ as an oil or natural gas recovery agent in techniques such as EOR and ECBM, respectively, has been investigated for many years. Outcomes from both laboratory scale and industrial studies show that CO₂ is an efficient agent displacing oil and natural gas (Panwar et al. 2017).

EOR with CO₂ injection is the second most improved hydrocarbon recovery technique after water injection according to the International Energy Agency (IEA 2015). Its application is preferable in oil fields with a depth greater than 800 m that have at least between 20% and 30% of the original oil, in which there have been previously applied secondary recovery methods (Godec, Kuuskraa, and Dipietro 2013). The injection of CO₂ is not only valid for specific gravities of medium or light oils, but it has also been increasing its application year after year for the recovery of heavy oils. The flexibility of the CO₂ injection process allows it to be used in a miscible or immiscible manner, depending on the existing conditions (pressure, temperature, and composition of the oil in the deposit) (Hertwich et al. 2008; Sweatman, Parker, and Crookshank 2009). Lately, EOR studies assessed the impact of various methods for allocating CO₂ system emissions and the benefits of sequestration under a number of different scenarios (Godec, Kuuskraa, and Dipietro 2013; Jaramillo, Griffin, and McCoy 2009). Also, some studies developed some methodologies for the identification and screening of oil reservoirs that are suitable for CO₂ flooding (Bachu, Shaw, and Pearson 2004; Dai et al. 2014). Moreover, Li et al. (2016) modified these applications for estimating CO₂ sequestration capacity at depletion as well as under enhanced oil recovery.

Regarding ECBM process, studies focused on economic issues as well as potential storage in mixed gas while studying the best places to apply this during these recent years (Saghafi 2010; Jikich et al. 2004; Busch and Gensterblum 2011; BarBaran et al. 2014; Hamelinck et al. 2002). EOR has been practiced for long periods of time in countries such as the United States or Canada. However, ECBM is under test phase (IPCC 2005). The information collected in this section argues that CO₂-EOR deserves to be a major part of a worldwide carbon management strategy. According to IEA, growth in production from CO₂-EOR is now limited by the price of CO₂ (IEA 2015).

LCA studies for CCU techniques

Subsequently, a comparison of the environmental impact of some CCU technologies studied based on LCA found in the literature, summarized in Table 8, will be made. LCA is a quantitative tool that allows collecting and evaluating the inputs and outputs of matter and energy and the potential impacts of a product, service, process or activity throughout the life of the product. Thus, in a complete LCA, all the environmental effects derived from the consumption of raw materials and energy necessary for production, emissions and waste generated during the productive activity as well as the environmental effects of its transportation, use, and consumption are attributed to the final product. The prerequisites that are generally important for a CCU technique to really reduce this environmental impact are the availability and use of clean energies as well as the use of raw materials that do not imply a negative environmental effect including CO₂ capture (Cuéllar-Franca and Azapagic 2015; Kressirer et al. 2013).

Conclusions and future prospect

This study confirms that a range of CCU technologies are available for use in several applications. From direct utilization of CO₂ as a solvent or for chemicals production, to obtain fuels or improve EOR techniques, with the potential for meaningful cuts in CO₂ emissions and associated benefits in the industry globally. Among the different alternatives studied, the processes of carboxylation have stood out, that is the synthesis of carbonates and carboxylates. The production of salicylic acid, DMC, and mineral carbonation are presented as the most likely applications of CO₂, at least in the short term. Along with the production of urea, the synthesis of salicylic acid and DMC has been carried out on an



Table 8. LCA studies for some CCU options.

REFERENCE	CCU OPTION	PROCESS	SCOPE	CO ₂ CAPTURE METHOD	FUNCTIONAL UNIT (kg of CO ₂ per item indicated)
EPA-7 2015	Carboxylation	Production of salicylic acid	LCA comparison of different methods of synthesis of salicylic acid from resorcinol by K-S reaction. LCA includes initial and processing processes, waste disposal, isolation and purification of the final product. Comparing different reaction media and heating methods for continuous and discontinuous process.	Post-combustion capture via MEA	Production of 1 kg of salicylic acid
Honda et al. 2014b	Acydic carbonates	Production of dimethyl carbonate	LCA comparison of different methods for the synthesis of DMC from methanol. The environmental impact of the most widespread commercial methods (Eni and Ube) is compared with a process that involves the electrochemical reaction of methanol with CO ₂ in potassium methoxide.	Post-combustion capture via MEA	Production of 1 kg of DMC
Khoo et al. 2011	Mineral carbonation	Serpentine mineral carbonation	LCA from a mineral carbonation plant in Singapore, comparing 4 scenarios. It is considered CO ₂ capture, mineral carbonation, the exploitation and the transport of the serpentine. CO ₂ is captured from a natural gas combined cycle power plant (NGCC), analyzing capture LCA with MEA or direct use of combustion gases. Two possible yields of carbonation are distinguished.	Post-combustion capture via MEA/Direct use of combustion gases	Production of 1 MWh of electricity in NGCC
Nduagu, Bergerson, and Zevenhoven (2012)	Mineral carbonation	MgCO ₃ production from CO ₂	LCA from a coal power plant located in Canada. This study includes coal and serpentine mining and transport, CO ₂ capture, transport and mineralization.	Post-combustion capture via MEA	Sequestration of 1 tonne of CO ₂
Wang et al. 2016b	Polymerization	Synthesis of polyols based on CO ₂ for use in polyurethane	LCA comparison of polyols based on CO ₂ with the conventional method for its synthesis, to use it for the production of polyurethane. The LCA includes all the energy supply for obtaining the raw materials, as well as the CO ₂ capture of a lignite power plant.	Post-combustion capture via MEA	Production of 1 kg of polyols and 0.36 kWh of lignite power plant electricity
Elbashir et al. (2018)	CO ₂ reforming of CH ₄	CO ₂ reforming of CH ₄	LCA comparison of different synthesis gas production methods. Problem when comparing LCA since the ratio of synthesis gas produced by each method is very different.	Post-combustion capture via MEA	Production of 1 kg of synthesis gas
Campbell, Beer, and Batten (2011)	Biofuels from microalgae	Production of biodiesel	Comparative LCA of biodiesel production from microalgae between canola and ultra-low sulphur diesel.	Direct injection/Post-combustion capture via MEA	Tonne kilometer
Jaramillo, Michael Griffin, and McCoy 2009	Enhanced oil recovery	IGCC and EOR	LCA comparison among five IGCC plants including capture, compression, transport and use for EOR.	Pre-combustion capture via selexol	The total amount of electricity production during the project lifetime
Viebahn et al. (2007)	CO ₂ pure for multiple uses	Could be applied to multiple processes	LCA comparison of CCS to obtain a pure CO ₂ applied to PC, CCGT and IGCC power plants in Germany.	Pre-combustion via rectisol and oxy-fuel combustion	1 kWh of electricity

industrial scale with success. Although at the moment, mineral carbonation has been the technology whose analysis of life cycle has reflected the most positive result on global warming prevention by reducing the net emission of CO₂ into the atmosphere. As it is gathered in this paper, technological advances in this field are being a slow but constant process. The number of studies on CCU continues to increase, achieving satisfactory results and, in some cases, better than expected.

Future work should be aimed at the economic improvement of the processes mentioned above, which could allow its implementation on an industrial scale, as well as at technological improvement in the development of processes to achieve a greater added value such as, for example, the synthesis of methanol, the use of CO₂ consuming microalgae for the generation of ethanol and the use of electrochemical reactions that are showing initial results of great interest. The main objective will be to improve the processes already studied, increasing the activity of the catalysts and the performance of the final products.

Funding

This work was supported by University of Seville through its V PPIT-US.

References

- Abdeen, F. R. H., M. Mel, M. S. Jami, S. I. Ihsan, and A. F. Ismail. 2016a. A review of chemical absorption of carbon dioxide for biogas upgrading. *Chinese Journal of Chemical Engineering*. doi:10.1016/j.cjche.2016.05.006.
- Abdeen, F. R. H., M. Mel, M. S. Jami, S. I. Ihsan, and A. F. Ismail. 2016b. A review of chemical absorption of carbon dioxide for biogas upgrading. *Chinese Journal of Chemical Engineering* 24 (6):693–702. doi:10.1016/j.cjche.2016.05.006.
- Abdullah, B., N. A. A. Ghani, and D. V. N. Vo. 2017. Recent advances in dry reforming of methane over ni-based catalysts. *Journal of Cleaner Production*. doi:10.1016/j.jclepro.2017.05.176.
- Abla, M., J. C. Choi, and T. Sakakura. 2001. Halogen-free process for the conversion of carbon dioxide to urethanes by homogeneous catalysis. *Chemical Communications* 2238–39. doi:10.1039/b106201h.
- Abla, M., J.-C. Choi, and T. Sakakura. 2004. Nickel-Catalyzed Dehydrative Transformation of CO₂ to Urethanes. *Green Chemistry*. doi:10.1039/b408429b.
- Albo, J., L. A. Alvarez, J. M. Andres, C. Bartolome, S. Burgos, and P. Castro. 2013. Usos Del CO₂: un camino hacia la sostenibilidad. *Journal of Chemical Information and Modeling*, Vol. 1. doi: 10.1017/CBO9781107415324.004.
- Alex, S. 2015. Learning to Love CO₂. *Chemical Engineering News* 93 (45):11–16.
- Amaro, H. M., A. Catarina Guedes, and F. Xavier Malcata. 2011. Advances and perspectives in using microalgae to produce biodiesel. *Applied Energy* 88 (10):3402–10. doi:10.1016/j.apenergy.2010.12.014.
- Ammar, M., Y. Cao, H. Peng, L. G. Wang, J. Q. Chen, and H. Q. Li. 2017. Zn-co bimetallic supported zsm-5 catalyst for phosgene-free synthesis of hexamethylene-1,6-diisocyanate by thermal decomposition of hexamethylene-1,6-dicarbamate. *Chinese Chemical Letters*. doi:10.1016/j.cclet.2017.03.015.
- An, H., L. Zhang, B. Yuan, X. Zhao, and Y. Wang. 2014. Influence of solvent on reaction path to synthesis of methyl n-phenyl carbamate from aniline, CO₂ and methanol. *Chinese Journal of Chemical Engineering* 22 (5):607–10. doi:10.1016/S1004-9541(14)60097-5.
- An, X., Y. Zuo, Q. Zhang, and J. Wang. 2009. Methanol synthesis from co₂hydrogenation with a Cu/Zn/Al/Zr fibrous catalyst. *Chinese Journal of Chemical Engineering* 17(1):88–94. Chemical Industry and Engineering Society of China (CIESC) and Chemical Industry Press (CIP). doi: 10.1016/S1004-9541(09)60038-0.
- Anastas, P. T., and J. B. Zimmerman. 2013. *Innovations in Green Chemistry and Green Engineering*. Berlin, Germany: Springer.
- Aramouni, N., J. G. Abdel Karim, B. Touma, A. Tarboush, J. Zeaiter, and M. N. Ahmad. 2018. Catalyst design for dry reforming of methane: analysis review. *Renewable and Sustainable Energy Reviews*. doi:10.1016/j.rser.2017.09.076.
- Aresta, M. 2010. *Carbon Dioxide as Chemical Feedstock*. Carbon Dioxide as Chemical Feedstock. New Jersey: Wiley. doi: 10.1002/9783527629916.
- Aydin, G. 2014. The modeling of coal-related co₂ emissions and projections into future planning. *Energy Sources Part A: Recovery, Utilization & Environmental Effects*. doi:10.1080/15567036.2012.760018.
- Bachu, S., J. C. Shaw, and R. M. Pearson. 2004. Estimation of Oil Recovery and CO₂ Storage Capacity in CO₂ EOR Incorporating the Effect of Underlying Aquifers. In *SPE/DOE Symposium on Improved Oil Recovery*, Society of Petroleum Engineers. doi: 10.2118/89340-MS.

- Baciacchi, R., A. Corti, G. Costa, L. Lombardi, and D. Zingaretti. 2011. Storage of carbon dioxide captured in a pilot-scale biogas upgrading plant by accelerated carbonation of industrial residues. *Energy Procedia* 4:4985–92. Elsevier. doi:10.1016/j.egypro.2011.02.469.
- Baciacchi, R., E. Carnevale, G. Costa, R. Gavasci, L. Lombardi, T. Olivieri, L. Zanchi, and D. Zingaretti. 2013. Performance of a biogas upgrading process based on alkali absorption with regeneration using air pollution control residues. *Waste Management* 33 (12):2694–705. doi:10.1016/j.wasman.2013.08.022.
- Bansode, A., and A. Urakawa. 2014. Continuous DMC Synthesis from CO₂ and methanol over a CeO₂ catalyst in a fixed bed reactor in the presence of a dehydrating agent. *ACS Catalysis* 4 (11):3877–80. doi:10.1021/cs501221q.
- Baran, P., K. Zarębska, P. Krzystolik, J. Hadro, and A. Nunn. 2014. CO₂-ECBM and CO₂ sequestration in polish coal seam – experimental study. *Journal of Sustainable Mining* 13 (2):22–29. doi:10.7424/jsm.140204.
- Beckman, E. J. 2004. Supercritical and near-critical CO₂ in green chemical synthesis and processing. *The Journal of Supercritical Fluids* 28 (2–3):121–91. doi:10.1016/S0896-8446(03)00029-9.
- Bektesevic, S., A. M. Kleman, A. E. Marteel-Parrish, and M. A. Abraham. 2006. Hydroformylation in supercritical carbon dioxide: catalysis and benign solvents. *Journal of Supercritical Fluids* 38 (2):232–41. doi:10.1016/j.supflu.2006.01.019.
- Bilgen, S. 2016. Pollution control techniques and technologies for cleaner coal. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2016.1152327.
- Boyre, C., C. Jérôme, and A. Debuigne. 2014. Input of supercritical carbon dioxide to polymer synthesis: an overview. *European Polymer Journal*. doi:10.1016/j.eurpolymj.2014.07.019.
- Brentner, L. B., M. J. Eckelman, and J. B. Zimmerman. 2011. Combinatorial life cycle assessment to inform process design of industrial production of algal biodiesel. *Environmental Science and Technology* 45 (16):7060–67. doi:10.1021/es2006995.
- Busch, A., and Y. Gensterblum. 2011. CBM and CO₂-ECBM Related Sorption Processes in Coal: A Review. *International Journal of Coal Geology*. doi:10.1016/j.coal.2011.04.011.
- Campbell, P. K., T. Beer, and D. Batten. 2011. Life cycle assessment of biodiesel production from microalgae in ponds. *Bioresource Technology* 102 (1):50–56. doi:10.1016/j.biortech.2010.06.048.
- Chang, H., L. Qingshuo, X. Cui, H. Wang, B. Zhanwei, C. Qiao, and T. Lin. 2018. Conversion of carbon dioxide into cyclic carbonates using wool powder-ki as catalyst. *Journal of CO₂ Utilization* 24:174–79. doi:10.1016/j.jcou.2017.12.017.
- Chaturvedi, D., N. Mishra, and V. Mishra. 2007. A high yielding, one-pot synthesis of dialkyl carbonates from alcohols using mitsunobu's reagent. *Tetrahedron Letters* 48 (29):5043–45. doi:10.1016/j.tetlet.2007.05.103.
- Choi, J. C., L. N. He, H. Yasuda, and T. Sakakura. 2002. Selective and High Yield Synthesis of Dimethyl Carbonate Directly from Carbon Dioxide and Methanol. *Green Chemistry* 4 (3):230–34. doi:10.1039/b200623p.
- Collett, T. S. 2002. Energy resource potential of natural gas hydrates. *AAPG Bulletin*. doi:10.1306/61EEDDD2-173E-11D7-8645000102C1865D.
- Covestro. 2017. "Award-winning solutions with polyurethane foam." <http://press.covestro.com/news.nsf/id/Award-winning-solutions-with-polyurethane-foam>.
- Cuellar-Franca, R. M., and A. Azapagic. 2015. Carbon capture, storage and utilisation technologies: a critical analysis and comparison of their life cycle environmental impacts. *Journal of CO₂ Utilization*. doi:10.1016/j.jcou.2014.12.001.
- Dai, W. L., S. L. Luo, S. F. Yin, and C. T. Au. 2009. The direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts. *Applied Catalysis A: General*. doi:10.1016/j.apcata.2009.06.045.
- Dai, Z., R. Middleton, H. Viswanathan, J. Fessenden-Rahn, J. Bauman, R. Pawar, S.-Y. Lee, and B. Mcpherson. 2014. An integrated framework for optimizing CO₂ sequestration and enhanced oil recovery. *Environmental Science & Technology Letters* 1:49–54. doi:10.1021/ez4001033.
- Demirbaş, A. 2009. Production of biodiesel from algae oils. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects* 31 (2):163–68. doi:10.1080/15567030701521775.
- Devetta, L., P. Canu, A. Bertucco, and K. Steiner. 1997. Modelling of a trickle-bed reactor for a catalytic hydrogenation in supercritical CO₂. *Chemical Engineering Science* 52 (21–22):4163–69. doi:10.1016/S0009-2509(97)00258-3.
- Djas, M., and M. Henczka. 2018. Reactive extraction of carboxylic acids using organic solvents and supercritical fluids: a review. *Separation and Purification Technology* 201 (September 2017):106–19. doi:10.1016/j.seppur.2018.02.010.
- Du, Z., L. Qinghai, M. Tong, L. Shaohua, and L. Haoran. 2008. Electricity generation using membrane-less microbial fuel cell during wastewater treatment. *Chinese Journal of Chemical Engineering* 16 (5):772–77. doi:10.1016/S1004-9541(08)60154-8.
- Ebrahimi, A., A. Sarrafi, and M. Tahmooreesi. 2017. Methane and hydrogen production from carbon dioxide by ZnS, CuS, and CuS Doped ZnS nanophotocatalyst deposited on montmorillonite. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2016.1255678.
- Egawa, C. 2018. Methane Dry Reforming Reaction on Ru(0 0 1) Surfaces. *Journal of Catalysis* 358:35–42. doi:10.1016/j.jcat.2017.11.010.
- Elbashir, N., S. Afzal, D. Sengupta, and M. El-Halwagi. 2018. CO₂ Utilization through Dry Reforming of Methane Process. ARC 18. *Energy and Environment - Paper Presentation*. doi: 10.5339/qfarc.2018.EEPP1093

- El-Sheekh, M. M., A. El-Gamal, A. E. Bastawess, and A. El-Bokhomy. 2017. Production and characterization of biodiesel from the unicellular green alga *scenedesmus obliquus*. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*. doi:10.1080/15567036.2016.1263257.
- Engels, H. W., H. G. Pirkel, R. W. Reinhard Albers, J. K. Albach, A. Hoffmann, H. Casselmann, and J. Dormish. 2013. Polyurethanes: versatile materials and sustainable problem solvers for today's challenges. *Angewandte Chemie - International Edition*. doi:10.1002/anie.201302766.
- Englezos, P. 1993. Clathrate Hydrates. *Industrial & Engineering Chemistry Research*. doi:10.1021/ie00019a001.
- European Commission. 2016. "European Commission on Reducing Emissions from Aviation." *EU Commission Report*.
- Fan, J., L. Zhu, P. Jiang, L. Luling, and H. Liu. 2016. Comparative exergy analysis of chemical looping combustion thermally coupled and conventional steam methane reforming for hydrogen production. *Journal of Cleaner Production* 131:247–58. doi:10.1016/j.jclepro.2016.05.040.
- Feroci, M., M. Orsini, L. Rossi, G. Sotgiu, and A. Inesi. 2007. Electrochemically promoted C–N bond formation from amines and CO₂ in ionic liquid BMIm-BF₄: synthesis of carbamates. *Journal of Organic Chemistry* 72 (1):200–03. doi:10.1021/jo061997c.
- Feroci, M., M. A. Casadei, M. Orsini, L. Palombi, and A. Inesi. 2003. Cyanomethyl anion/carbon dioxide system: an electrogenerated carboxylating reagent. synthesis of carbamates under mild and safe conditions. *Journal of Organic Chemistry* 68 (4):1548–51. doi:10.1021/jo0266036.
- Fujioka, T., K. Jyosui, H. Nishimura, and K. Tei. 2003. Extraction of Methane from Methane Hydrate Using Lasers. *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers*. doi:10.1143/JJAP.42.5648.
- Gao, J., L. Chun, L. Weizao, H. Jinpeng, W. Lin, and L. Qiang. 2018. Process simulation and energy integration in the mineral carbonation of blast furnace slag. *Chinese Journal of Chemical Engineering*. doi: 10.1016/j.cjche.2018.04.012.
- Gao, Y., G. Lin, Y. Qin, X. Wang, and F. Wang. 2012. Dicarboxylic acid promoted immortal copolymerization for controllable synthesis of low-molecular weight oligo(carbonate-ether) diols with tunable carbonate unit content. *Journal of Polymer Science, Part A: Polymer Chemistry* 50 (24):5177–84. doi:10.1002/pola.26366.
- García-Herrero, I., R. Marisa, C. Franca, V. M. Enríquez-Gutiérrez, M. Alvarez-Guerra, A. Irabien, and A. Azapagic. 2016. Environmental assessment of dimethyl carbonate production: comparison of a novel electrosynthesis route utilizing CO₂ with a commercial oxidative carbonylation process. *ACS Sustainable Chemistry and Engineering* 4 (4):2088–97. doi:10.1021/acssuschemeng.5b01515.
- Germain, N., I. Müller, R. A. Matthias Hanaauer, R. B. Paciello, O. Trapp, and T. Schaub. 2016. Synthesis of Industrially Relevant Carbamates towards Isocyanates Using Carbon Dioxide and Organotin(IV) Alkoxides. *ChemSusChem* 9 (13):1586–90. doi:10.1002/cssc.201600580.
- Ghoojani, E., and S. H. Bolouri. 2015. Green balance software: an integrated model for screening of CO₂-EOR and CCS projects. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2011.631965.
- Giaconia, A., O. Scialdone, M. Apostolo, G. Filardo, and A. Galia. 2008. Surfactant assisted polymerization of tetrafluoroethylene in supercritical carbon dioxide with a pilot scale batch reactor. *Journal of Polymer Science, Part A: Polymer Chemistry* 46 (1):257–66. doi:10.1002/pola.22377.
- Godec, M. L., V. A. Kuuskraa, and P. Dipietro. 2013. Opportunities for using anthropogenic CO₂ for enhanced oil recovery and CO₂ storage. *Energy & Fuels* 27 (8):4183–89. doi:10.1021/ef302040u.
- Güner, F., and E. Genceli. 2015. Feasibility Study of MgSO₄ hydrate Production by Eutectic CO₂ clathrate Crystallization. *Chemical Engineering Research and Design*. doi:10.1016/j.cherd.2014.10.019.
- Hamelinck, C. N., A. P. C. Faaij, W. C. Turkenburg, F. Van Bergen, H. J. M. Pagnier, O. H. M. Barzandji, K. H. A. A. Wolf, and G. J. Ruijg. 2002. CO₂ enhanced coalbed methane production in the Netherlands. *Energy* 27 (7):647–74. doi:10.1016/S0360-5442(02)00012-9.
- Hassani, R., S. Jamal, M. Haghighi, A. A. Eslami, F. Rahmani, and N. Rahemi. 2016. Sol–Gel vs. Impregnation Preparation of MgO and CeO₂ Doped Ni/Al₂O₃ Nanocatalysts Used in Dry Reforming of Methane: Effect of Process Conditions, Synthesis Method and Support Composition. *International Journal of Hydrogen Energy* 41 (11):5335–50. doi:10.1016/j.ijhydene.2016.02.002.
- Hatzigeorgiou, E., H. Polatidis, and D. Haralambopoulos. 2010. Energy CO₂ emissions for 1990–2020: a decomposition analysis for EU-25 and Greece. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567030902937101.
- Helwani, Z., A. D. Wiheeb, J. Kim, and M. R. Othman. 2016. In-situ mineralization of carbon dioxide in a coal-fired power plant. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2013.813991.
- Hertwich, E. G., M. Aaberg, B. Singh, and A. H. Strømman. 2008. Life-cycle assessment of carbon dioxide capture for enhanced oil recovery. *Chinese Journal of Chemical Engineering* 16 (3):343–53. doi:10.1016/S1004-9541(08)60085-3.
- Honda, M., M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, and K. Tomishige. 2014c. Direct cyclic carbonate synthesis from CO₂ and diol over carboxylation/hydration cascade catalyst of CeO₂ with 2-cyanopyridine. *ACS Catalysis*. doi:10.1021/cs500301d.

- Honda, M., M. Tamura, Y. Nakagawa, K. Nakao, K. Suzuki, and K. Tomishige. 2014a. Organic Carbonate Synthesis from CO₂ and Alcohol over CeO₂ with 2-Cyanopyridine: Scope and Mechanistic Studies. *Journal of Catalysis* 318:95–107. doi:10.1016/j.jcat.2014.07.022.
- Honda, M., M. Tamura, Y. Nakagawa, and K. Tomishige. 2014b. Catalytic CO₂ conversion to organic carbonates with alcohols in combination with dehydration system. *Catalysis Science & Technology* 4 (9):2830–45. doi:10.1039/C4CY00557K.
- Honda, M., M. Tamura, Y. Nakagawa, S. Sonehara, K. Suzuki, K. I. Fujimoto, and K. Tomishige. 2013. Ceria-catalyzed conversion of carbon dioxide into dimethyl carbonate with 2-cyanopyridine. *ChemSusChem* 6 (8):1341–44. doi:10.1002/cssc.201300229.
- Honda, M., S. Kuno, S. Sonehara, K. I. Fujimoto, K. Suzuki, Y. Nakagawa, and K. Tomishige. 2011. Tandem Carboxylation-Hydration Reaction System from Methanol, CO₂ and Benzonitrile to Dimethyl Carbonate and Benzamide Catalyzed by CeO₂. *ChemCatChem* 3 (2):365–70. doi:10.1002/cctc.201000339.
- Hooker, J. M., A. T. Reibel, S. M. Hill, M. J. Schueller, and J. S. Fowler. 2009. One-pot, direct incorporation of [11C] CO₂ into carbamates. *Angewandte Chemie International Edition* 48 (19):3482–3485. doi:10.1002/anie.v48:19.
- Hou, Z., N. Theyssen, and W. Leitner. 2007. Palladium nanoparticles stabilised on PEG-modified silica as catalysts for the aerobic alcohol oxidation in supercritical carbon dioxide. *Green Chemistry: an International Journal and Green Chemistry Resource: GC* 9 (2):127–32. doi:10.1039/B606740A.
- Hyatt, J. A. 1984. Liquid and supercritical carbon dioxide as organic solvents. *The Journal of Organic Chemistry*. doi:10.1021/jo00200a016.
- IEA. 2015. “Storing CO₂ through enhanced oil recovery.” *International Energy Agency, Paris, France*. http://www.iea.org/publications/insights/insightpublications/Storing_CO2_through_Enhanced_Oil_Recovery.pdf%5Cnhttp://www.iea.org/publications/insights/insightpublications/CO2EOR_3Nov2015.pdf.
- Iijima, T., and T. Yamaguchi. 2008a. Efficient regioselective carboxylation of phenol to salicylic acid with supercritical CO₂ in the presence of aluminium bromide. *Journal of Molecular Catalysis A: Chemical* 295 (1–2):52–56. doi:10.1016/j.molcata.2008.07.017.
- Iijima, T., and T. Yamaguchi. 2008b. K₂CO₃-catalyzed direct synthesis of salicylic acid from phenol and supercritical CO₂. *Applied Catalysis A: General* 345 (1):12–17. doi:10.1016/j.apcata.2008.03.037.
- IPCC 2005. IPCC special report on carbon dioxide capture and storage. prepared by working group iii of the intergovernmental panel on climate change. In *IPCC Special Report on Carbon Dioxide Capture and Storage* 2:442. doi: 10.1002/anie.201000431.
- Jaramillo, P., W. Michael Griffin, and S. T. McCoy. 2009. Life cycle inventory of CO₂ in an enhanced oil recovery system. *Environmental Science & Technology* 43 (21):8027–32. doi:10.1021/es902006h.
- Javanmardi, J., and M. Moshfeghian. 2003. Energy Consumption and Economic Evaluation of Water Desalination by Hydrate Phenomenon. *Applied Thermal Engineering*. doi:10.1016/S1359-4311(03)00023-1.
- Jiang, L. L., A. R. Li, J. F. Xu, and Y. J. Liu. 2016. Effects of SDS and SDBS on CO₂ Hydrate Formation, Induction Time, Storage Capacity and Stability at 274.15 K and 5.0 MPa. *ChemistrySelect*. doi:10.1002/slct.201601038.
- Jiang, Z., T. Xiao, V. L. Kuznetsov, and P. P. Edwards. 2010. Turning carbon dioxide into fuel. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 368 (1923):3343–64. doi:10.1098/rsta.2010.0119.
- Jikich, S. A., G. S. Bromhal, W. N. Sams, F. B. Gorucu, T. Ertekin, and D. H. Smith. 2004. Economics for Enhanced Coalbed Methane (ECBM) and CO₂ Sequestration with Horizontal Wells. In *Proceedings - Society of Petroleum Engineers Eastern Regional Meeting*.
- Jo, E. S., A. Xinghai, P. G. Ingole, W. K. Choi, Y. S. Park, and H. K. Lee. 2017. CO₂/CH₄ separation using inside coated thin film composite hollow fiber membranes prepared by interfacial polymerization. *Chinese Journal of Chemical Engineering* 25(3):278–87. Elsevier B.V. doi: 10.1016/j.cjche.2016.07.010.
- Kathiresan, M., and D. Velayutham. 2015. Ionic liquids as an electrolyte for the electro synthesis of organic compounds. *Chemical Communications* 51 (99):17499–516. doi:10.1039/C5CC06961K.
- Kember, M. R., F. Jutz, A. Buchard, A. J. P. White, and C. K. Williams. 2012. Di-cobalt(ii) catalysts for the copolymerisation of CO₂ and cyclohexene oxide: support for a dinuclear mechanism? *Chemical Science* 3 (4):1245.
- Khoo, H. H., J. Bu, R. L. Wong, S. Y. Kuan, and P. N. Sharratt. 2011. Carbon capture and utilization: preliminary life cycle CO₂, energy, and cost results of potential mineral carbonation. *Energy Procedia* 4 (2011):2494–2501. doi:10.1016/j.egypro.2011.02.145.
- Khoshtinat, N. M., and N. A. S. Amin. 2011. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation. *Fuel Processing Technology* 92 (3):678–91. doi:10.1016/j.fuproc.2010.11.027.
- Kindermann, N., T. Jose, and A. W. Kleij. 2017. Synthesis of carbonates from alcohols and CO₂. *Topics in Current Chemistry*. doi:10.1007/s41061-016-0101-8.
- King, M. B., and T. R. Bott. 1993. *Extraction of Natural Products Using Near-Critical Solvents*. Berlin, Germany: Springer.
- Kizlink, J., and I. Pastucha. 1995. Preparation of dimethyl carbonate from methanol and carbon dioxide in the presence of sn(IV) and ti(IV) alkoxides and metal acetates. *Collection of Czechoslovak Chemical Communications* 60 (4):687–92. doi:10.1135/cccc19950687.

- Kong, D. -L., L. -N. He, and J. -Q. Wang. 2011. Polyethylene glycol-enhanced chemoselective synthesis of organic carbamates from amines, CO₂, and alkyl halides. *Synthetic Communications* 41 (22):3298–3307. doi:10.1080/00397911.2010.517890
- Kressirer, S., D. Kralisch, A. Stark, U. Krtschil, and V. Hessel. 2013. Agile green process design for the intensified Kolbe-Schmitt synthesis by accompanying (simplified) life cycle assessment. *Environmental Science and Technology* 47 (10):5362–71. doi:10.1021/es400085y.
- Lee, B. Y., H. Y. Kwon, S. Y. Lee, S. J. Na, S.-I. Han, H. Yun, H. Lee, and Y.-W. Park. 2005. Bimetallic anilido-alimine zinc complexes for epoxide/CO₂ copolymerization. *Journal of the American Chemical Society* 127 (9):3031–37. doi:10.1021/ja0435135.
- Lee, W. J., C. P. Tan, R. Sulaiman, and G. H. Chong. 2017. Solubility of red palm oil in supercritical carbon dioxide: measurement and modelling. *Chinese Journal of Chemical Engineering* Elsevier B.V. doi: 10.1016/j.cjche.2017.09.024.
- Li, H., and Z. Zhang. 2018. Mining the intrinsic trends of CO₂ solubility in blended solutions. *Journal of CO₂ Utilization*. doi:10.1016/j.jcou.2018.06.008.
- Li, Y., J. Li, S. Ding, and H. Zhang. 2016. Co-Optimization of CO₂ sequestration and enhanced oil recovery in extra-low permeability reservoir in Shanbei. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2012.724148.
- Lim, Y. N., C. Lee, and H. Y. Jang. 2014. Metal-free synthesis of cyclic and acyclic carbonates from CO₂ and alcohols. *European Journal of Organic Chemistry* 2014 (9):1823–26. doi:10.1002/ejoc.201400031.
- Lindsey, A. S., and H. Jeskey. 1957. The Kolbe-Schmitt reaction. *Chemical Reviews* 57 (4):583–620. doi:10.1021/cr50016a001.
- Linstrom, P. J., and W. G. Mallard. 2014. NIST chemistry webbook, NIST standard reference database number 69. *National Institute of Standards and Technology* 69:20899.
- Liu, H., L. Yao, H. B. H. Taief, M. Benzina, P. Da Costa, and M. E. Gálvez. 2018a. Natural clay-based Ni-catalysts for dry reforming of methane at moderate temperatures. *Catalysis Today* 306:51–57. doi:10.1016/j.cattod.2016.12.017.
- Liu, J., L. Yuming, J. Zhang, and H. Dehua. 2016. Glycerol carbonylation with CO₂ to glycerol carbonate over CeO₂ catalyst and the influence of CeO₂ preparation methods and reaction parameters. *Applied Catalysis A: General* 513:9–18. doi:10.1016/j.apcata.2015.12.030.
- Liu, S., and X. Wang. 2017. Polymers from carbon dioxide: polycarbonates, polyurethanes. *Current Opinion in Green and Sustainable Chemistry*. doi:10.1016/j.cogsc.2016.08.003.
- Liu, S., Y. Qin, X. Chen, X. Wang, and F. Wang. 2014. One-pot controllable synthesis of oligo(carbonate-ether) triol using a Zn-co-dmc catalyst: the special role of trimethylsilyl acid as an initiation-transfer agent. *Polymer Chemistry* 5 (21):6171–79. doi:10.1039/C4PY00578C.
- Liu, Z., Z. Pan, Z. Zhang, P. Liu, L. Shang, and B. Li. 2018b. Effect of porous media and sodium dodecyl sulphate complex system on methane hydrate formation. *Energy and Fuels*. doi:10.1021/acs.energyfuels.8b00041.
- Lombardi, L., A. Corti, E. Carnevale, R. Baciocchi, and D. Zingaretti. 2011. Carbon dioxide removal and capture for landfill gas up-grading. *Energy Procedia* 4:465–72. doi:10.1016/j.egypro.2011.01.076.
- Lombardi, L., R. Baciocchi, E. Carnevale, and A. Corti. 2012. “Investigation of an innovative process for biogas up-grading – pilot plant preliminary results.” *Proceedings of ECOS 2012- the 25th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems*, June 26–29, Perugia, Italy, 1–12.
- Luo, J., and I. Larrosa. 2017. C–H carboxylation of aromatic compounds through CO₂ fixation. *ChemSusChem*. doi:10.1002/cssc.201701058.
- Ma, K., Q. Bai, L. Zhang, and B. Liu. 2016. Synthesis of flame-retarding oligo(carbonate-ether) diols via double metal cyanide complex-catalyzed copolymerization of PO and CO₂ using bisphenol A as a chain transfer agent. *RSC Advances* 6 (54):48405–10. doi:10.1039/C6RA07325E.
- Machado, A. S. R., A. V. M. Nunes, and M. N. Da Ponte. 2018. Carbon dioxide utilization—electrochemical reduction to fuels and synthesis of polycarbonates. *Journal of Supercritical Fluids* 134:150–56. doi:10.1016/j.supflu.2017.12.023.
- Marriott, R., P. Jessop, and M. Barnes. 2014. CO₂-Based Solvents. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle 1st ed.*, 73–96. Amsterdam, Netherlands: Elsevier. doi:10.1016/B978-0-444-62746-9.00006-2.
- Martin, C., G. Fiorani, and A. W. Kleij. 2015. Recent advances in the catalytic preparation of cyclic organic carbonates. *ACS Catalysis* 5 (2):1353–70. doi:10.1021/cs5018997.
- Mashayekhi Mazar, F., M. Alijanianzadeh, Z. Jamshidi Nia, and A. M. Rad. 2017. Introduction to biofuel cells: a biological source of energy. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2016.1219794.
- Matsuda, T. 2013. Recent progress in biocatalysis using supercritical carbon dioxide. *Journal of Bioscience and Bioengineering* 115 (3):233–41. doi:10.1016/j.jbiosc.2012.10.002.
- Matthessen, R., J. Fransær, K. Binnemans, and D. E. De Vos. 2014. Electrocarboxylation: towards sustainable and efficient synthesis of valuable carboxylic acids. *Beilstein Journal of Organic Chemistry*. doi:10.3762/bjoc.10.260.

- Matthessen, R., J. Fransaer, K. Binnemans, and D. E. De Vos. 2015. Paired electrosynthesis of diacid and diol precursors using dienes and CO₂ as the carbon source. *Chemical Electrochemistry* 2 (1):73–76. doi:10.1002/celc.201402299.
- Mayadevi, S. 2012. Reactions in Supercritical Carbon Dioxide. *Indian Journal of Chemistry* 51A:1298–305. doi:10.1002/047084289X.
- Mazzotti, M., J. Carlos, R. Allam, K. S. Lackner, F. Meunier, E. M. Rubin, J. C. Sanchez, K. Yogo, and R. Zevenhoven. 2005. Mineral carbonation and industrial uses of carbon dioxide. *IPCC Special Report on Carbon Dioxide Capture and Storage* (October):319–38. http://www.ipcc.ch/pdf/special-reports/srrcs/srrcs_chapter7.pdf.
- Mohd, A., N. Nabillah, N. Harun, N. M. Yunus, N. Dai Viet, M. Vo, T. Azizan, and S. Z. Abidin. 2017. Reforming of glycerol for hydrogen production over ni based catalysts: effect of support type. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2016.1244580.
- Mooijer-Van Den, H. M., M., R. Witteman, and C. J. Peters. 2001. Phase Behaviour of Gas Hydrates of Carbon Dioxide in the Presence of Tetrahydropyran, Cyclobutanone, Cyclohexane and Methylcyclohexane. In *Fluid Phase Equilibria*. Amsterdam, Netherlands: Elsevier. doi:10.1016/S0378-3812(01)00384-3.
- Mopsik, F. I. 1967. Dielectric Constant of N-Hexane as a Function of Temperature, Pressure, and Density. *Journal of Research of the National Bureau of Standards Section A: Physics and Chemistry*. doi:10.6028/jres.071A.035.
- Na, S. J., S. Sujith, A. Cyriac, B. E. Kim, Y. K. Jina Yoo, S. Kang, J. Han, C. Lee, and B. Y. Lee. 2009. Elucidation of the structure of a highly active catalytic system for co₂/epoxide copolymerization: a salen-cobaltate complex of an unusual binding mode. *Inorganic Chemistry* 48 (21):10455–65. doi:10.1021/ic901584u.
- Nakano, S., K. H. Chang, A. Shijima, H. Miyamoto, Y. Sato, Y. Noto, J. Y. Ha, and M. Sakamoto. 2014. A usage of CO₂ hydrate: convenient method to increase co₂ concentration in culturing algae. *Bioresource Technology*. doi:10.1016/j.biortech.2014.09.019.
- Nduagu, E., J. Bergerson, and R. Zevenhoven. 2012. Life cycle assessment of co₂ sequestration in magnesium silicate rock – a comparative study. *Energy Conversion and Management* 55 (2012):116–126. doi:10.1016/j.enconman.2011.10.026.
- NOAA/ESRL. 2017. “NOAA/ESRL.” *Scripps Institution of Oceanography (Scrippsco2.Ucsd.Edu)*.
- Oelkers, E. H., and D. R. Cole. 2008. Carbon dioxide sequestration: a solution to a global problem. *Elements* 4 (5):305–10. doi:10.2113/gselements.4.5.305.
- Olajire, A. A. 2013. A review of mineral carbonation technology in sequestration of CO₂. *Journal of Petroleum Science and Engineering* 109:364–92. doi:10.1016/j.petrol.2013.03.013.
- Ota, M., K. Morohashi, Y. Abe, M. Watanabe, R. L. Smith Jr., and H. Inomata. 2005. Replacement of CH₄ in the Hydrate by Use of Liquid CO₂. *Energy Conversion and Management*. doi:10.1016/j.enconman.2004.10.002.
- Pan, Z., Z. Liu, Z. Zhang, L. Shang, and M. Shihui. 2018. Effect of silica sand size and saturation on methane hydrate formation in the presence of SDS. *Journal of Natural Gas Science and Engineering*. doi:10.1016/j.jngse.2018.06.018.
- Panwar, D. S., V. K. Saxena, S. Suman, V. Kumar, and A. K. Singh. 2017. Physicochemical study of coal for cbm extraction in raniganj coal field, India. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2017.1314394.
- Pellerin, P. 2003. Comparing Extraction by Traditional Solvents with Supercritical Extraction from an Economic and Environmental Standpoint. In *6th International Symposium on Supercritical Fluids*. Versailles.
- Prat, D., A. Wells, J. Hayler, C. Helen Sneddon, R. McElroy, S. Abou-Shehade, and P. J. Dunn. 2016. CHEM21 selection guide of classical- and less classical-solvents. *Green Chemistry : an International Journal and Green Chemistry Resource* : GC 18 (1):288–96. doi:10.1039/C5GC01008J.
- Princeton University. 2015. *Carbon Mitigation Initiative*.
- Pyo, S.-H., J. H. Park, T.-S. Chang, and R. Hatti-Kaul. 2017. Dimethyl Carbonate as a Green Chemical. *Current Opinion in Green and Sustainable Chemistry* 5:61–66. doi:10.1016/j.cogsc.2017.03.012.
- Qin, Y., and X. Wang. 2010. Carbon Dioxide-Based Copolymers: Environmental Benefits of PPC, an Industrially Viable Catalyst. *Biotechnology Journal*. doi:10.1002/biot.201000134.
- Quaranta, E., and M. Aresta. 2010. The Chemistry of N- CO₂ Bonds: Synthesis of Carbamic Acids and Their Derivatives, Isocyanates, and Ureas. In *Carbon Dioxide as Chemical Feedstock*, 121–67. New Jersey: Wiley. doi:10.1002/9783527629916.ch6.
- Ren, B., F. Gao, Z. Tong, and Y. Yan. 1999. Solvent polarity scale on the fluorescence spectra of a dansyl monomer copolymerizable in aqueous media. *Chemical Physics Letters*. doi:10.1016/S0009-2614(99)00495-9.
- Ribeiro, A., L. Martins, E. Alegria, I. Matias, T. Duarte, and A. Pombeiro. 2017a. Catalytic Performance of Fe(II)-Scorpionate Complexes towards Cyclohexane Oxidation in Organic, Ionic Liquid and/or Supercritical CO₂ Media: A Comparative Study. *Catalysts* 7 (8):230. doi:10.3390/catal7080230.
- Ribeiro, A. P. C., L. M. Martins, E. C. B. A. Alegria, I. A. S. Matias, T. A. G. Duarte, and A. J. L. Pombeiro. 2017b. Catalytic performance of fe(ii)-scorpionate complexes towards cyclohexane oxidation in organic, ionic liquid and/or supercritical co₂ media: a comparative study. *Molecular Catalysis*.
- Riemer, D., P. Hirapara, and S. Das. 2016. Chemoselective synthesis of carbamates using CO₂ as carbon source. *Chemsuschem* 7 (230):1916–1920 :2455–1920. 2455–1920. doi:10.1002/cssc.v9.15.

- Romack, T. J., J. M. DeSimone, and T. A. Treat. 1995. Synthesis of tetrafluoroethylene-based, nonaqueous fluoropolymers in supercritical carbon dioxide. *Macromolecules* 28 (24):8429–31. doi:10.1021/ma00128a065.
- Sabil, K. M., N. Azmi, and H. Mukhtar. 2011. A review on carbon dioxide hydrate potential in technological applications. *Journal of Applied Sciences*. doi:10.3923/jas.2011.3534.3540.
- Saghafi, A. 2010. Potential for ECBM and CO₂ storage in mixed gas Australian coals. *International Journal of Coal Geology* 82 (3–4):240–51. doi:10.1016/j.coal.2010.01.002.
- Sakakura, T., J. C. Choi, Y. Saito, T. Masuda, T. Sako, and T. Oriyama. 1999. Metal-catalyzed dimethyl carbonate synthesis from carbon dioxide and acetals. *Journal of Organic Chemistry* 64 (12):4506–08. doi:10.1021/jo990155t.
- Sakakura, T., J. C. Choi, Y. Saito, and T. Sako. 2000. Synthesis of dimethyl carbonate from carbon dioxide: catalysis and mechanism. In *Polyhedron* 19:573–76. doi:10.1016/S0277-5387(99)00411-8.
- Salvatore, R. N., F. Chu, A. S. Nagle, E. A. Kapxhiu, R. M. Cross, and K. W. Jung. 2002. Efficient Cs₂CO₃-promoted solution and solid phase synthesis of carbonates and carbamates in the presence of TBAI. *Tetrahedron* 58 (17):3329–47. doi:10.1016/S0040-4020(02)00286-7.
- Salvatore, R. N., S. I. Shin, A. S. Nagle, and K. W. Jung. 2001. Efficient carbamate synthesis via a three-component coupling of an amine, CO₂, and alkyl halides in the presence of Cs₂CO₃ and tetrabutylammonium Iodide. *Journal of Organic Chemistry* 66 (3):1035–37. doi:10.1021/jo001140u.
- Sapal, V. B., and B. M. Bhanage. 2017. Bifunctional Ionic Liquids Derived from Biorenewable Sources as Sustainable Catalysts for Fixation of Carbon Dioxide. *ChemSusChem* 10 (6):1145–51. doi:10.1002/cssc.201601228.
- Scripps Institution of Oceanography. 2018. “The Keeling Curve.” UC San Diego. <https://scripps.ucsd.edu/programs/keelingcurve/>.
- Sebastian, J., and D. Srinivas. 2013. Influence of method of preparation of solid, double-metal cyanide complexes on their catalytic activity for synthesis of hyperbranched polymers. *Applied Catalysis A: General* 464–465:51–60. doi:10.1016/j.apcata.2013.05.024.
- Selvarajah, K., N. H. H. Phuc, B. Abdullah, F. Alenazey, and D. V. N. Vo. 2016. Syngas production from methane dry reforming over Ni/Al₂O₃ Catalyst. *Research on Chemical Intermediates* 42 (1):269–88. doi:10.1007/s11164-015-2395-5.
- Senboku, H., and A. Katayama. 2017. Electrochemical Carboxylation with Carbon Dioxide. *Current Opinion in Green and Sustainable Chemistry*. doi:10.1016/j.cogsc.2016.10.003.
- Senboku, H., K. Nagakura, T. Fukuhara, and S. Hara. 2015. Three-component coupling reaction of benzylic halides, carbon dioxide, and n,n-dimethylformamide by using paired electrolysis: sacrificial anode-free efficient electrochemical carboxylation of benzylic halides. *Tetrahedron* 71 (23):3850–56. doi:10.1016/j.tet.2015.04.020.
- Singh, A., P. S. Nigam, and J. D. Murphy. 2011. Mechanism and challenges in commercialisation of algal biofuels. *Bioresource Technology* 102 (1):26–34. doi:10.1016/j.biortech.2010.06.057.
- Styring, P., D. Jansen, H. de Coninck, H. Reith, and K. Armstrong. 2011. *Carbon Capture and Utilisation in the Green Economy*. Birmingham, UK: Centre for Low Carbon Futures.
- Sun, D.-L., J.-H. Ye, Y.-X. Fang, and Z.-S. Chao. 2016. Green Synthesis of N,N'-dialkylureas from CO₂ and amines using metal salts of oxalates as catalysts. *Industrial and Engineering Chemistry Research* 55:1. doi:10.1021/acs.iecr.5b02936.
- Sutradhar, M., A. P. C. Ribeiro, M. F. C. G. Da Silva, A. M. F. Palavra, and A. J. L. Pombeiro. 2017. Application of molybdenum complexes for the oxidation of cyclohexane in acetonitrile, ionic liquid and supercritical CO₂ media, a comparative study. *Molecular Catalysis*. doi:10.1016/j.mcat.2017.10.026.
- Sweatman, R. E., M. E. Parker, and S. L. Crookshank. 2009. “Industry experience with CO₂-enhanced oil recovery technology.” 2009 SPE International Conference on CO₂ Capture, Storage and Utilization, San Diego, California, November: 1–15. doi:10.2118/126446-MS.
- Taherimehr, M., and P. P. Pescarmona. 2014. Green polycarbonates prepared by the copolymerization of CO₂ with epoxides. *Journal of Applied Polymer Science*. doi:10.1002/app.41141.
- Tamura, M., K. Ito, M. Honda, Y. Nakagawa, H. Sugimoto, and K. Tomishige. 2016. Direct Copolymerization of CO₂ and Diols. *Scientific Reports* 6. doi:10.1038/srep24038.
- Tan, X. B., M. K. Lam, Y. Uemura, J. W. Lim, C. Y. Wong, and K. T. Lee. 2018. Cultivation of microalgae for biodiesel production: a review on upstream and downstream processing. *Chinese Journal of Chemical Engineering*. doi:10.1016/j.cjche.2017.08.010.
- Tateno, H., Y. Matsumura, K. Nakabayashi, H. Senboku, and M. Atobe. 2015. Development of a novel electrochemical carboxylation system using a microreactor. *RSC Advances* 5 (119):98721–23. doi:10.1039/C5RA19289G.
- Tommasi, I., and F. Sorrentino. 2006. Synthesis of 1,3-Dialkylimidazolium-2-carboxylates by direct carboxylation of 1,3-dialkylimidazolium chlorides with CO₂. *Tetrahedron Letters* 47 (36):6453–56. doi:10.1016/j.tetlet.2006.06.106.
- Tommasi, I., and F. Sorrentino. 2009. 1,3-Dialkylimidazolium-2-carboxylates as versatile N-heterocyclic carbene-CO₂ adducts employed in the synthesis of carboxylates and α -alkylidene cyclic carbonates. *Tetrahedron Letters* 50 (1):104–07. doi:10.1016/j.tetlet.2008.10.107.

- Trott, G., P. K. Saini, and C. K. Williams. 2016. Catalysts for CO₂/epoxide ring-opening copolymerization. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 374 (2061):20150085. doi:10.1098/rsta.2015.0085.
- Ugwu, C. U., H. Aoyagi, and H. Uchiyama. 2008. Photobioreactors for mass cultivation of algae. *Bioresource Technology*. doi:10.1016/j.biortech.2007.01.046.
- Vaessen, R. J. C., F. Ham, and G. J. Witkamp. 2006. Eutectic freeze crystallization using CO₂ clathrates. *Annals of the New York Academy of Sciences*. doi:10.1111/j.1749-6632.2000.tb06803.x.
- Vega, F., M. Cano, M. Gallego, S. Camino, J. A. Camino, and B. Navarrete. 2017. Evaluation of MEA 5 M performance at different CO₂ concentrations of flue gas tested at a CO₂ capture lab-scale plant. *Energy Procedia* 114 (114):6222–28. doi:10.1016/j.egypro.2017.03.1760.
- Veluswamy, H. P., A. Kumar, Y. Seo, J. D. Lee, and P. Linga. 2018. A review of solidified natural gas (sng) technology for gas storage via clathrate hydrates. *Applied Energy*. doi:10.1016/j.apenergy.2018.02.059.
- Vert, M., Y. Doi, K.-H. Hellwich, M. Hess, P. Hodge, P. Kubisa, M. Rinaudo, and S. François. 2009. *Compendium of Polymer Terminology and Nomenclature (IUPAC Recommendations 2008 - Purple Book)*. Pure and Applied Chemistry, UK. Vol. 84. doi: 10.1039/9781847559425.
- Vessally, E., R. Mohammadi, A. Hosseini, L. Edjlali, and M. Babazadeh. 2018. Three component coupling of amines, alkyl halides and carbon dioxide: an environmentally benign access to carbamate esters (urethanes). *Journal of CO₂ Utilization*. doi:10.1016/j.jcou.2018.01.015.
- Viebahn, P., J. Nitsch, M. Fischedick, A. Esken, D. Schüwer, N. Supersberger, U. Zuberbühler, and O. Edenhofer. 2007. Comparison of carbon capture and storage with renewable energy technologies regarding structural, economic, and ecological aspects in Germany. *International Journal of Greenhouse Gas Control* 1 (2007):121–133. doi:10.1016/S1750-5836(07)00024-2.
- von der Niklas, A., and A. Bardow. 2014. Life cycle assessment of polyols for polyurethane production using CO₂ as feedstock: insights from an industrial case study. *Green Chemistry* 16 (6):3272. doi:10.1039/c4gc00513a.
- Wang, B., L. Yanqun, W. Nan, and C. Q. Lan. 2008. CO₂ bio-mitigation using microalgae. *Applied Microbiology and Biotechnology* 79 (5):707–18. doi:10.1007/s00253-008-1518-y.
- Wang, H., Z. Xin, and L. Yuehui. 2017. Synthesis of Ureas from CO₂. *Topics in Current Chemistry* 375(2):1–26. Springer International Publishing. doi: 10.1007/s41061-017-0137-4.
- Wang, J., H. Zhang, Y. Miao, L. Qiao, X. Wang, and F. Wang. 2016a. Waterborne Polyurethanes from CO₂ based polyols with comprehensive hydrolysis/oxidation resistance. *Green Chemistry* 18(2):524–30. Royal Society of Chemistry. doi: 10.1039/C5GC01373A.
- Wang, J., Y. Wang, L. Zheng, S. Ni, Z. Fan, R. Yao, and K. Chen. 2014. Kinetic study on extraction of red pepper seed oil with supercritical CO₂. *Chinese Journal of Chemical Engineering* 22(1):44–50. Chemical Industry and Engineering Society of China (CIESC) and Chemical Industry Press (CIP). doi: 10.1016/S1004-9541(14)60003-3.
- Wang, L., W. Liu, J. Hu, Q. Liu, H. Yue, B. Liang, G. Zhang, D. Luo, H. Xie, and C. Li. 2017. Indirect mineral carbonation of titanium-bearing blast furnace slag coupled with recovery of TiO₂ and Al₂O₃. *Chinese Journal of Chemical Engineering*. doi:10.1016/j.cjche.2017.06.012.
- Wang, P., S. Liu, and Y. Deng. 2017. Important green chemistry and catalysis: non-phosgene syntheses of isocyanates – thermal cracking way. *Chinese Journal of Chemistry*. doi:10.1002/cjoc.201600745.
- Wang, W., Z. Yun, Z. Tang, and X. Gui. 2016b. Solubilities of CO₂ in some glycol ethers under high pressure by experimental determination and correlation. *Chinese Journal of Chemical Engineering* 24(3):373–78. Elsevier B.V.. doi: 10.1016/j.cjche.2015.08.007.
- Wang, X., J. Zhang, J. Chen, M. Qingxiang, S. Fan, and T. S. Zhao. 2018. Effect of preparation methods on the structure and catalytic performance of Fe-Zn/K catalysts for CO₂ hydrogenation to light olefins. *Chinese Journal of Chemical Engineering* 26(4):761–67. Elsevier B.V.. doi: 10.1016/j.cjche.2017.10.013.
- Wang, Y., Y. Qin, X. Wang, and F. Wang. 2015. Trivalent titanium salen complex: thermally robust and highly active catalyst for copolymerization of CO₂ and cyclohexene oxide. *ACS Catalysis* 5 (1):393–96. doi:10.1021/cs501719v.
- Wu, C., H. Cheng, R. Liu, Q. Wang, Y. Hao, Y. Yu, and F. Zhao. 2010. Synthesis of urea derivatives from amines and CO₂ in the absence of catalyst and solvent. *Green Chemistry* 12 (10):1811. doi:10.1039/c0gc00059k.
- Xiang, X., L. Guo, X. Wu, X. Ma, and Y. Xia. 2012. Urea formation from carbon dioxide and ammonia at atmospheric pressure. *Environmental Chemistry Letters* 10 (3):295–300. doi:10.1007/s10311-012-0366-2.
- Xiong, W., C. Qi, Y. Peng, T. Guo, M. Zhang, and H. Jiang. 2015. Base-promoted coupling of carbon dioxide, amines, and diaryliodonium salts: a phosgene- and metal-free route to o-aryl carbamates. *Chemistry: a European Journal* 21 (41):14314–14318. doi:10.1002/chem.201502689.
- Xu, J., E. Feng, and J. Song. 2014. Renaissance of aliphatic polycarbonates: new techniques and biomedical applications. *Journal of Applied Polymer Science*. doi:10.1002/app.39822.
- Yan, C., B. Lu, X. Wang, J. Zhao, and Q. Cai. 2011. Electrochemical synthesis of dimethyl carbonate from methanol, CO₂ and propylene oxide in an ionic liquid. *Journal of Chemical Technology and Biotechnology* 86 (11):1413–17. doi:10.1002/jctb.2647.

- Yang, L., L. Fu, and G. Li. 2017. Incorporation of Carbon Dioxide into Carbamate Directing Groups: Palladium-Catalyzed meta-C-H Olefination and Acetoxylation of Aniline Derivatives. *Advanced Synthesis & Catalysis* 359 (13):2235–2240. doi:10.1002/adsc.v359.13
- Yang, Z., J. Sun, W. Cheng, J. Wang, Q. Li, and S. Zhang. 2014. Biocompatible and recyclable amino acid binary catalyst for efficient chemical fixation of CO₂. *Catalysis Communications* 44:6–9. doi:10.1016/j.catcom.2013.07.025.
- Yu, K., M. Kerry, I. Curcic, J. Gabriel, and S. C. E. Tsang. 2008. Recent advances in CO₂ capture and utilization. *ChemSusChem*. doi:10.1002/cssc.200800169.
- Yuan, G., C. Qi, W. Wu, and H. Jiang. 2017. Recent advances in organic synthesis with CO₂ as C1 Synthon. *Current Opinion in Green and Sustainable Chemistry* 3:22–27. doi:10.1016/j.cogsc.2016.11.006.
- Zhang, L., and Z. Hou. 2017. Transition metal promoted carboxylation of unsaturated substrates with carbon dioxide. *Current Opinion in Green and Sustainable Chemistry*. doi:10.1016/j.cogsc.2016.11.003.
- Zhang, R., L. Guo, C. Chen, J. Chen, A. Chen, X. Zhao, X. Liu, Y. Xiu, and Z. Hou. 2015a. The role of mn doping in ceo₂ for catalytic synthesis of aliphatic carbamate from CO₂. *Catalysis Science & Technology* 5:2959–72. doi:10.1039/C5CY00166H.
- Zhang, Y., L. Zhang, Y. Wang, M. Wang, Y. Wang, and S. Ren. 2015b. Dissolution of surfactants in supercritical CO₂ with co-solvents. *Chemical Engineering Research and Design* 94:624–31. doi:10.1016/j.cherd.2014.10.002.
- Zhang, Z. 2016. Comparisons of various absorbent effects on carbon dioxide capture in membrane gas absorption (MGA) process. *Journal of Natural Gas Science and Engineering*. doi:10.1016/j.jngse.2016.03.052.
- Zhang, Z., F. Chen, M. Rezakazemi, W. Zhang, C. Lu, H. Chang, and X. Quan. 2018b. Modeling of a CO₂-piperazine-membrane absorption system. *Chemical Engineering Research and Design*. doi:10.1016/j.cherd.2017.11.024.
- Zhang, Z., J. Cai, F. Chen, L. Hao, W. Zhang, and W. Qi. 2018a. Progress in enhancement of CO₂ absorption by nanofluids: a mini review of mechanisms and current status. *Renewable Energy*. doi:10.1016/j.renene.2017.11.031.
- Zhao, S.-F., M. Horne, A. M. Bond, and J. Zhang. 2014. Electrocarboxylation of acetophenone in ionic liquids: the influence of proton availability on product distribution. *Green Chemistry : an International Journal and Green Chemistry Resource : GC* 16 (4):2242–51. doi:10.1039/C3GC42404A.