Integration of CO_2 Capture in Urban Wastewater Treatment Plants to Obtain Added-Value Products

Integración de la Captura de CO_2 en EDAR Urbanas para la Obtención de Nuevos Recursos Valorizables

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PhD Thesis

A mi abuela Concha

¿Qué es la vida?

Aquellos que no me conocen, pensarán que empezar el documento que recoge los resultados de una tesis doctoral con esa pregunta es de locos. Les anticipo que sí, que nunca me he caracterizado por tener la cabeza del todo cuerda. ¿En qué forma iba entonces a decidirme por hacer una tesis doctoral?

Aquellos que me conocen y acompañan en este camino saben que me gusta la filosofía y pensar sobre preguntas tan básicas como ésta. Una pregunta tan sencilla y tan difícil a la vez. No he conocido a nadie hasta el momento que sepa definir de una forma sencilla y satisfactoria qué es la vida. Muchos de aquellos a los que les pregunto tienden a definir la vida haciendo referencia al bien y al mal. “La vida es buena, sin duda”, dicen algunos. Por supuesto, tienen razón. La vida nos da miles de cosas que nos hacen felices. “La vida es muy jodida”, dicen otros. Tampoco les falta razón.

Pero volvamos a la pregunta inicial. ¿Qué es la vida? Para daros mi respuesta de lo que para mí significa la palabra vida, dejadme, por favor, que os cuente una historia.

Nació el de 2 de febrero de 1936. Desde ese mismo momento, su vida no fue nada fácil. Siendo tan sólo un bebé, se vio rodeada por una guerra civil y afectada por las dificultades que una situación de esa magnitud conlleva. Superó esa primera etapa de su vida, pero tuvo la desgracia de perder a su madre cuando apenas era una niña y de tener que trabajar desde muy temprana edad para poder ayudar a su familia. Pasaron los años, vivió su adolescencia y llegó a ser adulta. Parecía que la vida le daba un respiro por fin. Se casó con el amor de su vida y dio a luz a dos maravillosas niñas. Pero de nuevo la vida le daba un revés, quitándole demasiado pronto a ese hombre con quién compartía la felicidad. Tuvo la obligación de tener que dejar de cuidar de sus dos hijas, de siete y cuatro años por aquel entonces, para ponerse a trabajar infinitas horas diarias y así criar a los únicos tesoros que hasta ese momento le había dejado la vida. Cosía para ganarse el pan de cada día, que era la profesión que a lo largo de su vida mejor se le dio y de la que muchos nos sentimos orgullosos a día de hoy. Y así, entre hilos y puntadas, su vida transcurrió en paz durante muchos años. No la veía con mis propios ojos, pero no me cabe duda de que, a pesar de que esa profesión hiciera que perdiese la vista poco a poco, lo hacía con todo el amor que a ella la caracterizaba. Volvieron a pasar los años y con esfuerzo y dedicación, vio crecer a sus dos hijas, a sus dos mayores regalos. Las vio salir con sus amigas, encontrar parejas, ser felices, casarse y abandonar la casa donde ella les dio todo para comenzar sus vidas por separado. Y ella era feliz, muchísimo, no tengo dudas. Vinieron los primeros nietos. En pocos años se juntaron tres, y ella rabiaba de felicidad. Disfrutaba de ellos, los veía crecer y les daba todo el amor que tenía. Vinieron luego dos más, los pequeños de la casa, y aún más feliz era ella. Sólo pensaba en poder verlos crecer, en estar con ellos cuando la necesitaran al igual que había estado con sus hijas. Pero, entonces, la vida la golpeó de nuevo. El cáncer, la maldita enfermedad que a tantos se lleva cada año, vino para complicarle las cosas otra vez. ¿No tuvo suficiente la vida con arrebatarle a su madre, con quitarle su niñez, con llevarse a su marido? No, eso no fue suficiente. Cualquier otro se habría dado por vencido, por supuesto. Pero, ¿que hizo ella? Pues lo que llevaba haciendo toda su vida: luchar. Y venció la primera gran batalla. Le ganó el primer pulso a esa maldita enfermedad. Y fue feliz unos años más, en los que pudo ver a sus nietos crecer un poco más. Pero la vida aún tenía guardado un poco más de sufrimiento para ella. La enfermedad volvió una vez más y, aunque ella volvió a luchar con uñas y dientes dando todo lo que tenía, no puedo vencerla. Murió rodeada de todos los que la vieron luchar. Se fue dejando entre aquellos que la querían con locura un hueco que nunca se podría volver a llenar.

La protagonista de esta historia, bien podría ser el personaje principal de alguna película dirigida por algún director de cine famoso o de cualquier libro de algún destacado escritor. Pero no. La protagonista de esta historia es mi abuela Concha; tan real como la vida misma.

Llegados a este punto y tras la historia que os he contado, pensaréis que soy de los que me inclino a definir la vida como algo malo. Sin embargo, la vida, para mí, quedó definida por mi abuela, por tal y como ella decidió encararla. Ella no lo sabía, pero con su actitud ante la vida me estaba dando la respuesta que durante muchos años busqué. Si alguien alguna vez me pregunta que es para mí la vida, le diría que la vida es esfuerzo y superación, nunca rendirse ante nada y nunca darse por vencido en la búsqueda de la felicidad.

Mucha gente me dice que trabajo mucho, que echo demasiadas horas, me preguntan que de donde saco la fuerza para seguir, que donde está mi motivación, que cual es mi secreto. “Para un poco, Fran”, “Baja el ritmo, tío”, me dicen, con infinito cariño, aquellos que me conocen y quieren. Mi abuela sólo quería seguir viviendo. Ella sólo quería un poco más de tiempo para ser feliz, para disfrutar de los que la rodeaban, para ver crecer a sus nietos, para ver hacer la comunión a su tercera nieta, para ver envejecer a sus hijas. Ella nunca se rindió. Si hoy estoy escribiendo estas palabras y defendiendo ésta tesis doctoral es porque ella nunca dejó de luchar. Por supuesto que tengo días en los que quiero dejarlo todo, sería de necios no reconocerlo. Pero entonces, justo cuando ya me faltan las fuerzas para seguir, recuerdo que ella nunca se rindió. Si algún día me rindo en el camino, le estaría fallando a todo lo que ella me dio.

Ella, y sólo ella, es mi motivación, mi secreto más grande guardado. Es por todo esto que siempre ocupará las dedicatorias de todos los logros que consiga en mi vida, ya que en gran parte son también suyos. Es lo único que puedo hacer para agradecerle lo mucho que nos dio a todos los que hoy en día estamos aquí, en esta vida, gracias a ella.

Te quería cuando estabas, te quiero ahora que no estás, y te querré toda mi vida. Te quiero y te echo de menos, abuela.

Nunca te olvidaremos.

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CHAPTER I: Background, goals and scope

The main forthcoming challenges that our society faces during the next decade are natural resources consumption, climate change and energy security [1,2]. The first challenge is a direct consequence of our high life standard's and elevated growth of resources consumption. Climate change is mainly due to the increase of Greenhouse Gases (GHG) emissions caused by our industrial sector. Thirdly, the forthcoming scarce of traditional fossil fuels, which have ensured our energy availability during the past decades, entails the need of finding alternatives energy sources. Currently, the European Union (EU) is planning new strategies to address the aforementioned issues through the new programme Horizon Europe (HE) [3]. The first strategic plan of HE gives some orientations for breaking-down the dependence on non-renewable resources and pursues the transition towards a circular/bio-based economy. The achievement of these goals demands progress on technical solutions for transforming our present manufacturing processes into climate-neutral options [3,4]. Among the different alternatives, the first strategic HE plan contemplates the use of biomass and waste to produce biofuels, renewable chemicals and materials. Undoubtedly, biomass – waste utilization will promote the creation of bio-based supply chains for the establishment of circular/bio-economy policies [5,6].

One of the potential uses of biomass – organic waste is its anaerobic digestion to produce biogas [7], which is mainly composed by CH_4 (60%) and CO_2 (40%) [8,9]. Biogas is a very versatile resource with multiple potential outcomes for green energy and clean chemicals production [10]. Typically, there are three alternatives to exploit biogas namely, its utilization in a combined heat and power (CHP) unit to produce electricity and heat [11]; its conversion in a solid oxide fuel cell (SOFC) for direct electricity generation with a high energy efficiency [12,13]; or its upgrading to produce biomethane [14]. The use of biogas for the production of electricity in a CHP or SOFC enhances the energy security as well as it reduces the dependence of fossil fuels [15]. Nevertheless, the CO_2

contained in the biogas mixture would be released to the atmosphere, affecting negatively to the climate change. The third path consists on upgrading biogas to biomethane, which is also considered a synthetic natural gas [16]. This option avoids the consumption of natural resources while simultaneously producing an added value product from organic waste. However, the CO_2 separated from biogas needs an ending-use to transform biogas upgrading process in a 100% environmentally friendly option [17]. Carbon capture and utilization technologies (CCU) have been widely studied in this regard [18,19]. Nevertheless, there is a substantial knowledge gap and lot of room to develop CO_2-derived products in a biogas upgrading configuration. The future directions of the scientific community are devoting great efforts to pursue alternatives to supply the future demand of chemicals and fuels.

Wastewater treatment plants (WWTPs) are a clear example of industry which can promote the circular economy concept pursued by the EU. Indeed, biogas is commonly produced in WWTPs through waste anaerobic digestion. The proper use of biogas to produce biomethane and an added-value product from the CO_2 splitted could boost the circular/bio-based economy within the facilities of WWTPs. In this line, the aim of this PhD thesis is to explore potential paths to synergize biogas upgrading and CCU in a WWTP. In this line, the Department of Chemical and Environmental Engineering of the Higher Technical School of Engineering of the University of Seville has demonstrated extensive experience in both the field of industrial processes optimization and waste treatment – recycling. Indeed, our research group has participated in numerous international – national projects related to carbon capture and storage (CCS), being the core of our research group during the last decades. Some examples of these research projects are: 1) COMPARAE: “Desarrollo de un proceso regenerativo de captura de CO_2 mediante absorción química en condiciones de oxicombustión parcial”; 2) O2GEN: “Optimisation of Oxygen-based CFBC Technology with CO_2 capture”; 3) HIBRICAP: “Caracterización y optimización de la tecnología de absorción química regenerativa aplicada a la captura de CO_2 en procesos de combustión con aire”; 4) RECO2VAL: “Demostración integrada de procesos de reducción de CO_2 industrial mediante carbonatación de producto”.

In this PhD project we step towards the utilization of CO_2 to produce added-value compounds, taking renewables sources of CO_2 emissions as biogas and hence favoring the development of negative emission alternatives. The research topic of this PhD thesis arises from the participation of the PAIDI TEP-135 group from the aforementioned department in NURECCO2 project: “Integración de la captura de CO_2 en edar urbanas para la obtención de nuevos recursos valorizables", supported by EMASESA and Corporación Tecnológica de Andalucía (CTA). Thus, as explained before, the main goal of this project is to synergize biogas upgrading and carbon capture and utilization in a WWTP, seeking the implementation of circular economy processes within this industrial area. In this research project we study the technical viability and the economic performance of a novel process which includes a solution for the main present problems given in WWTP: 1) the utilization of waste to produce added-value chemicals/fuels; 2) and the concentration of nutrients from anaerobically digested sludge centrate, with high content of nitrogen and phosphorus, whose emissions are a potential problem for the environment. This work contributes to facilitate a rational management – utilization of waste and collaborates in the achievement of a sustainable economy goals in terms of natural resources consumption. In general, this responsible management of waste will mean improvements in health and the environment. These actions will promote new business opportunities and social improvements, helping our society in the evolution towards a more sustainable future and ensuring the well-being of new generations.

CHAPTER II: General introduction and objectives

2.1. European Union Bet: Horizon Europe Programme and European Green Deal

Horizon Europe (HE) is a seven-year scientific research initiative which is aimed to replace the current Horizon 2020 program. The European Commission developed and approved a plan for Europe to level up the European Union (EU) science through a spending increase of 50% during the years 2021-2027. In April 2019 the European Parliament and Council reached a political agreement on the key elements for the proposal of the new HE project. According to this agreement, HE will be structured on three pillars (Figure 2.1), supported by activities aimed at strengthening innovation and research. These pillars are:

- Pillar I “Excellent Science”, which will strengthen the EU's scientific leadership through the European Research Council (ERC), Marie Skłodowska-Curie Actions and research infrastructures.
- Pillar II “Global Challenges and European Industrial Competitiveness”, aimed to address society challenges and support industrial technologies to reinforce EU – global political priorities and accelerate industrial transformation.
- Pillar III “Innovative Europe”, focuses on stimulating, fueling and deploying disruptive and market-creating innovations, as well as enhancing European ecosystems conducive to innovation, in particular through the new European Innovation Council.

Figure 2.1. Pillars of Horizon Europe. Adapted from [3].

With a proposed budget of €100 billion for the period 2021-2027, HE represents the largest multinational investment in collaborative research and innovation in Europe and is open to participants from around the world. The EU makes an investment of this magnitude because research and innovation are essential to find new solutions to the current challenges we face. These challenges are of such magnitude that they cannot be tackled down by a single country but for collaborations among the EU members. The new research and innovation actions are expected to create new opportunities, help to tackle climate change, support sustainable economic growth and the competitiveness of companies and industries, and improve welfare and public services for all Europeans.

Climate change and the transition towards a sustainable development will affect many aspects of today's European society and economy, especially in carbon-intensive sectors and regions. While the transition will lead to far-reaching changes in European industries, Europe also has a good starting point for transforming challenges into new opportunities and for spreading solutions around the world. Europe is focused, perhaps more than any other part of the world, on fostering competitiveness in a sustainable way, and European companies already represent five of the ten largest clean technology companies in the world. In this sense, the main objectives of HE through its second pillar, is to generate knowledge, strengthen the impact of research and innovation in the development, support and implementation of EU policies and support access to innovative solutions with its adoption in European industry. All in all, this pillar seeks to tackle global challenges such as climate change and sustainable development.

Becoming the world's first climate-neutral continent is the greatest challenge of Europe. To preserve our environment, our biodiversity and make Europe the world's first climate-neutral continent by 2050, it is necessary to change the way we produce, trade and consume, as well as driving unprecedented technological, economic and social transformations. Through the European Green Deal, the EU will spearhead global efforts for circular economies and clean green technologies, and will work to decarbonize energy-intensive industries. The Green Deal will also ensure that the ongoing sustainable transition is socially fair and leaves no EU citizen or region behind, while protecting citizens' health from environmental degradation and pollution and addressing air and water quality. What is good for our planet must also be good for our people, our regions and our economy. Europe has a good starting point for these ambitions. In the area of climate change, the EU is at the forefront of implementing the Paris Agreement, and the European Commission has adopted a vision to achieve a climate-neutral economy by 2050. The EU also aims to lead the global community in drafting and applying a new approach to protect the planet's biological diversity and borders. Finally, efforts to achieve climate neutrality also offer opportunities for new jobs and growth in European commerce and industry, where many European companies, old and future, have a competitive advantage. Investments in research and innovation related to digital, industry and space will help transform the EU into a circular and climate-neutral economy, and will focus on impacts especially in the following areas:

- Climate-neutral, circular and clean EU industries. This fact can be achieved by: setting up plants in various regions with zero emissions and waste; developing and demonstrating low-carbon breakthrough processes, especially in energy-intensive industries; new technologies efforts to produce sustainable products.
- Achieve greater autonomy in critical raw materials, through increasing the resource efficiency or replacing traditional sources, recycling or improving primary production.

Investments in climate, energy and mobility research and innovation will contribute to transforming the EU into a climate-neutral and resilient society, and will focus on impacts especially in the following fields [3]:

- Climate science and solutions for a climate-neutral and resilient society.
- New competitive cross-sector solutions for decarbonization, such as batteries, hydrogen and other types of storage (chemical, mechanical, electrical and thermal), as well as sustainable buildings and infrastructure that enable low-carbon solutions and other cutting-edge technologies.
- A cost-efficient net greenhouse gas energy system with a focus on renewables sources.
- Low carbon and competitive transport solutions for road, rail, aviation and maritime transport.

Investments in research and innovation in food, bio-economy, natural resources, agriculture and the environment will advance knowledge, build capacities, and develop and demonstrate innovative solutions to accelerate the transition to sustainability. The following effects will be sought:

- Improving knowledge and innovation will lay the foundation for climate neutrality by reducing GHG emissions and enhancing carbon sink and storage, as well as improving the management of water resources and production systems.

- A better comprehension of frontiers to obtain innovative solutions for the use of natural resources, as well as for the prevention and elimination of pollution, guaranteeing healthy soils, clean water and air for all.
- A better understanding of behavioral, socio-economic and demographic changes which leads to innovative approaches that drive the sustainability and balanced development of rural – urban areas.

2.2. Circular economy: the concept and its limitations

Circular economy concept has been created during the last decades as a political tool to redefine growth, focusing on positive society-wide benefits though the re-use of waste. Indeed, governments are prone to this idea and many countries such as Japan, Canada, China, as well as all the countries belonging to the EU as aforementioned, have started to launch policies to increase the presence of circular economy. The reasons are clearly economical since in agreement with the last data of European Union, 600 billion euros could be created in the manufacture sector annually [20]. Furthermore, circular economy concept embrace both economic growth and sustainable development. A circular economy is restorative and regenerative by design, and it is proposed to always keep products, components and materials at their highest levels of use. Moreover, circular economy is a positive continuous development cycle that preserves and increases the natural capital, optimizes resources performance and minimizes the risks of the humankind system, managing finite stocks and renewable flows. It works effectively at any scale [21]. The principles on which circular economy concept holds are listed below [22,23]:

- Principle 1. Preserve and increase natural capital, controlling finite stocks and balancing the flows of renewable resources. When resources are needed, the circular system will select wisely and choose technologies and processes.

Renewable resources or the techniques with the best performance should be used whenever possible. A circular economy also increases natural capital by encouraging nutrient flows in the system and creating the conditions for soil regeneration.

- Principle 2. Optimize the performance of resources, always re-circulating products and by-products, components and materials at their highest level of utilization. The aforementioned means design to re-work, renovate and recycle to keep the materials and components circulating in the overall economy. Circular systems use tighter internal loops whenever possible (i.e. maintenance better than recycling), preserving built-in energy as well as other values, seeking to extend the lifespan of the product.
- Principle 3. Promote the effectiveness of the overall system, making patents and planning to eliminate negative externalities. This includes reducing the damage caused to systems and areas that affect people, such as food, mobility, homes, education, health or entertainment, and managing externalities such as air pollution, water, land, and noise, emissions of toxic substances and climate change.

In accordance with the concept and principles that have been defined, we can point out the following key characteristics of a circular economy:

- Reduction of inputs and less use of natural resources: Minimized and optimized exploitation of raw materials, providing more value with less materials. Reduction of dependence on imports of natural resources. Efficient use of all natural resources. Minimization of total water and energy consumption.
- Employing more renewable and recyclable resources: Replace non-renewable resources with renewable resources with sustainable levels of supply. Higher proportion of recyclable and recycled materials that can replace virgin materials.

Extract raw materials in a sustainable way, only when no more options are available.

- Emission reduction: Reduction of emissions throughout the entire material cycle. Less pollution through clean material cycles.
- Reduce material and waste losses: Minimize waste accumulation. Limit, and try to minimize, the amount of waste incinerated and discharged. Minimize losses caused by to dissipation of resources.
- Maintain the value of products, components and materials in the economy: Extend the life of the products, maintaining the value of the products in use. Reuse components. Preserve the value of materials in the economy, through high quality recycling.

The transition to a circular economy requires fundamental changes in many different areas of the current socio-economic system. Below some of the most important technical, economic or social instrumental factors that guide and accelerate the transition process are described [24].

- *Products-services systems*: A products-services system consists of a mixture of tangible products and intangible services, designed and combined so that, together, they are able to meet the final needs of the consumer. This concept is based on two pillars: (i) the functionality or satisfaction that the user wants to achieve as a starting point for the development of the business is taken; (ii) to elaborate the business system that provides such functionality with a mentality of "undeveloped land", instead of taking as existing and immovable the existing structures and routines and the position of the company itself [25]. There are different types of product-service systems: a) product-oriented services, which simply add services (i.e. maintenance) to the existing product system; b) use-oriented services (i.e. leasing, shared use or group use); c) results-oriented services, which provide concrete results (i.e. the creation of a pleasant office environment).

- *Materials and products second life*. The second life of materials and products works when a company can efficiently recover and recondition its products after use. Afterwards, the company should put the same products on the market to obtain a second or third income.
- *Product transformation*. Not all products can be completely reconditioned for its re-utilization, but most products have certain components or materials that have a high added-value. Materials often have an embedded energy component that makes them even more valuable than their origin sources. With the right design and reworking capabilities, they can be put together to form new products.
- *Recycling 2.0*. Innovation in recycling technology (Recycling 2.0) is rapidly evolving and makes possible the production of high quality materials with fantastic results in terms of sustainability.
- *Collaborative Consumption*. Collaborative consumption (or collaborative economy) is defined as an interaction between two or more people, that satisfies a real or potential need. The four key factors that drove collaborative consumption were the following: 1) a renewed belief in the importance of the community; 2) a torrent of peer-to-peer social networks with real-time technologies; 3) pressure for unresolved environmental problems; 4) a global economic recession. There are three systems of collaborative consumption worldwide recognized: 1) redistribution markets, when a used item is taken from a place where it is not necessary to another place or to another person where it is; 2) collaborative lifestyle: exchange of resources such as money, skills and time; 3) product service: pay for the benefit of the product.

2.3. Wastewater treatment plants (WWTPs) as an example model of circular economy implementation

Wastewater treatment is an important and basic process to recover water while preserving its properties and restoring to a desirable quality. One of the purposes of this process is to reduce the environmental impact of contaminated water. To this end, wastewater treatment usually consists on a combination of chemical, biological and physical processes. The required quality of the recovered water may be related to its final use, which can be aquatic life, drinking water or irrigation, among others. Obviously a higher quality requires higher stages/operations which inevitably entails greater costs.

Within the new circular economy strategy adopted by the EU, WWTPs faces important challenges from a sustainable development perspective. The overreaching goal of wastewater treatment is the sustainable development of new processes which allows to keep the balance between water use, protection of public health and environment. Thus, the objectives for the forthcoming years relays on meeting the needs of society today at the same time that ensuring the resources quality for future generations. From a water quality perspective, sustainable development may be described as a respectfully current use which does not compromise the future uses. To fulfil the sustainable development explained, the main environmental – operational problems of WWTPs may be addressed. To this end, this point describes the main wastewater treatment methods and operations, focusing on the current environmental problems which need research attention in the forthcoming years.

2.3.1. General scheme of WWTPs

WWTPs are based on several unit operations which seek a final water product quality defined [26]. A scheme of typical processes presented in an urban WWTP is shown in Figure 2.2, although the final characteristics rather depends on the wastewater composition, the required effluent quality, costs and resources availability [27]. In brief, wastewater treatment processes are typically classified as follow: pretreatment, primary treatment, secondary treatment, and tertiary – advanced wastewater treatment. Pretreatment methods seek to make compatible the wastewater with the treatment process available in the WWTP. These processes typically include the following operations: screening/coarse sieve, where the coarse solid waste bigger than 1-2 mm are removed; grit removal, which removes the coarse solid between 250 µm and 1-2 mm; and oil and grease separation. The waste separated in these operations are pressing, washing, draining or skimming in agreement with the requirements and sent to the waste management facilities. Following pretreatment methods, primary treatment involves physicochemical separation consisting on: equalization – neutralization, which adapt the pH in those cases when is needed (i.e. industrial wastewater comes to the WWTP); and primary sedimentation. The main waste product from this primary sedimentation is subjected to sieving (to remove particles between 5-250 µm) and thickening operations to obtain the final primary sludge, which will be later mixed with the sludge produced in the secondary treatments. Another waste which results from the primary sedimentation is the floating waste. The first stage in the secondary treatments implies a biochemical reaction which seeks to activate the remaining sludge and remove the organic matter. Afterwards, the waste obtained is subjected to a flotation stage to further concentrated the sludge obtained. This last one is known as secondary sludge and it is mixed with the primary sludge [28]. The concentrated sludge mixed is sent to an anaerobic digestion stage where two main waste – products are obtained: the first one is a gaseous product known as biogas, a mix of CH_4 (approximately 60%) and CO_2 (approximately 40%); the second waste product is known as digestate and further treatment is needed to get it stabilized. These treatments are first a chemical treatment, normally through the addition of a polyelectrolyte which precipitates the remaining organic matter; and a centrifugation stage, where the final waste is separated from the liquid fraction. This liquid fraction, known as anaerobically digested sludge centrate, has a high content of nutrients (nitrogen and phosphorus), and it needs to be further treated to avoid eutrophication. The main processes used to remove or decrease the concentration of these contaminants are ion exchange, nitrification, denitrification, membrane processes, air stripping, adsorption, and chemical oxidation [29]. The current challenge in this point is the concentration of nutrients before these operations to reduce process volumes [28].

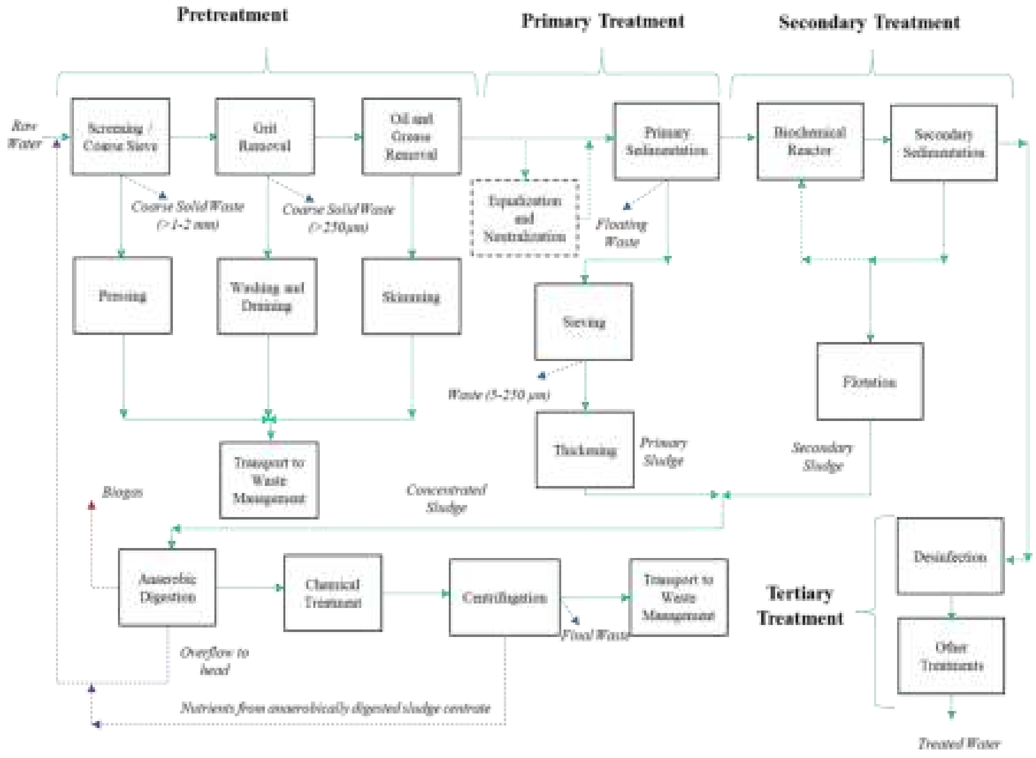


Figure 2.2. WWTPs process scheme

2.3.2. Environmental challenges of WWTPs

Even though billions of euros have been invested across Europe for improving wastewater treatments, many challenges still remain. Figure 2.3 shows the current challenges, potential solutions and opportunities [30]. Among the challenges collected in Figure 2.3, preference is giving to improve resources and energy efficiency, contaminants of emerging concerns and financing. The main reason is the previously said bet of the EU to achieve a sustainable – circular economy Europe. Indeed, the solutions proposed in Figure 2.3 could be summarized in finding new technologies and processes to decrease the pollution levels – evolve towards greener society, enabling the implementation of a circular economy. To achieve this goal, the main environmental problems of WWTPs must be tackled down searching sustainable – profitable paths. Among the main environmental problems facing by WWTPs, we can point out the following challenges: reducing CO_2 emissions or even evolves towards negative emission WWTPs; and decrease the amount of waste generated in WWTPs, in particular those that can cause serious environmental problems such as eutrophication. The first challenge said can be achieved by implementing carbon capture storage and utilization technologies in WWTP. The main source of CO_2 emissions in WWTP biogas. The use of biogas for the production of electricity in a CHP or SOFC enhances the energy security as well as it reduces the dependence of fossil fuels [15]. Nevertheless, the CO_2 contained in the biogas mixture is released to the atmosphere. If biogas is upgraded to biomethane, which is also considered a synthetic natural gas, CO_2 emissions are avoided [16]. This option avoids the consumption of natural resources while simultaneously producing an added value product from organic waste. However, the CO_2 separated from biogas needs an ending-use to transform biogas upgrading process in a 100% environmentally friendly option [17]. The main focus of the second challenge is to reduce or concentrated the excess nutrients (nitrogen and phosphorus). Some technologies have been proposed, being alternatives far from being profitable. The key to solve this problem may be to produce an added-value product from the nutrients. Tackling down these two challenges is a big step in the path towards a bioeconomy.

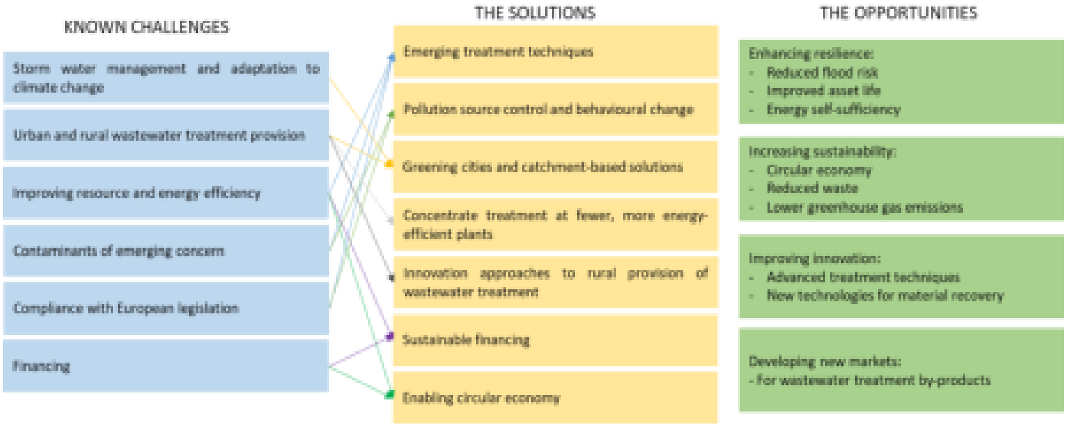


Figure 2.3. Current challenges in wastewater treatment. Adapted from [31].

2.4. Biomethane from biogas as promising renewable energy

During the last decades, the insecurity of energy policies derived from the lack of fossil fuels in the coming centuries, as well as the global concern for human-induced climate change, have led to part of the researching attention and resources guide towards the development and increasingly growing use of renewable energy [32]. Within the different kind of renewable energy, the use of biogas as an energy source is widely extended at an industrial level due to the flexibility offered by the process from which it comes (anaerobic digestion) [33]. Biogas can be defined as the product of the anaerobic digestion biomass, consisting mainly of CH_4 and CO_2 [34].

Typical raw materials to produce biogas are manure and wastewater, wastes from agricultural production, the organic fraction of household wastes and industries, as well as energy crops [35]. The main difference in the composition between biogas and natural gas falls on the CO_2 content. The typical composition of biogas versus natural gas can be seen in Table 2.1. Depending on the biogas origin, there are also some differences in its composition. This can be seen in Table 2.2. As can be seen, CO_2 is the contaminant with a higher percentage in biogas composition. This CO_2 content needs to be removed before biogas utilization. To meet this needs, many biogas upgrading technologies are available in a commercial scale. During the last years, the number of biogas plants has increased as can be seen in Figure 2.4. As shown, biogas production plants have increased from 10508 in 2010 to 18202 in 2018, which represents an increase of 73%.

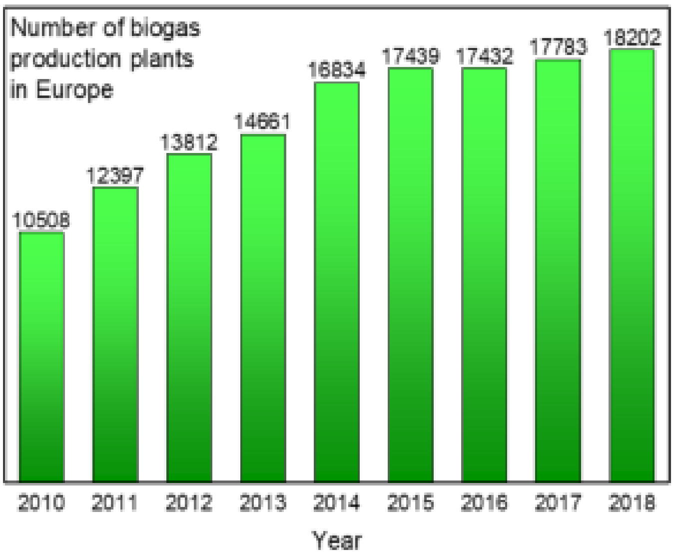


Figure 2.4. Biogas production plants evolution in Europe (2010-2018). Adapted from [36].

Table 2.1. Typical biogas composition

Composition	Biogas	Natural gas	References
Methane (% vol)	60-70	81-89	[32,37]
Other hydro carbons (% vol)	-	3,5-9,4	[32,38]
Carbon dioxide (% vol)	30-40	0,67-1	[32,38]
Nitrogen (% vol)	0-0,2	0,28-14	[37]
Hydrogen sulfide (ppm)	0-4.000	-	[32,37]
Ammonia (ppm)	0-100	-	[37,38]

Table 2.2. Typical biogas composition from different sources [39,40].

Composition (% vol)	Agricultural waste	Landfills	Industrial waste
Methane	50-80	50-80	50-70
Carbon dioxide	30-50	20-50	30-50
Nitrogen	0-1	0-3	0-1
Hydrogen sulfide	0,70	0,10	0,8
Ammonia	Traces	Traces	Traces
Hydrogen	0-2	0-5	0-2
Oxigen	0-1	0-1	0-1
Carbon monoxide	0-1	0-1	0-1
Siloxanes	Traces	Traces	Traces
Water	Saturation	Saturation	Saturation

Biogas is supplied to a huge rank of uses or markets, such as for example electricity, heat and transport fuels [41]. The combustion of biogas to produce heat is the most common and simplest way to use the energy contained in this gas. The only one of its elements to separate, if it contains it, is water, whose separation is usually done by draining the pipe system. From an environmental point of view, the separation of hydrogen sulfide (H_2S) would be a benefit, since it is not emitted into the atmosphere as a pollutant. Besides H_2S can react with H_2O to produce sulfuric acid (H_2SO_4), which may cause corrosion problems in the system [42].

The biogas produced by the co-fermentation of manure with energy crops or crop residues may contain H_2S levels between 100 and 3.000 ppm. The employ of biogas in Combined Heat and Power (CHP) systems needs H_2S levels below 250 ppm, to avoid corrosion which may involve higher maintenance costs [43]. The use of biogas for its supply to the natural gas network has the advantage that the infrastructure already exists, causing the investment costs in structure to be reduced and the enhance the overall efficiency of the process. However, this advantage is compromised by the high costs of another investments and operation, as well as by the regulatory barriers imposed by governments and companies: permits, quality standards, gas testing and monitoring [44]. The requirements to use biogas in different applications can be seen in Table 2.3.

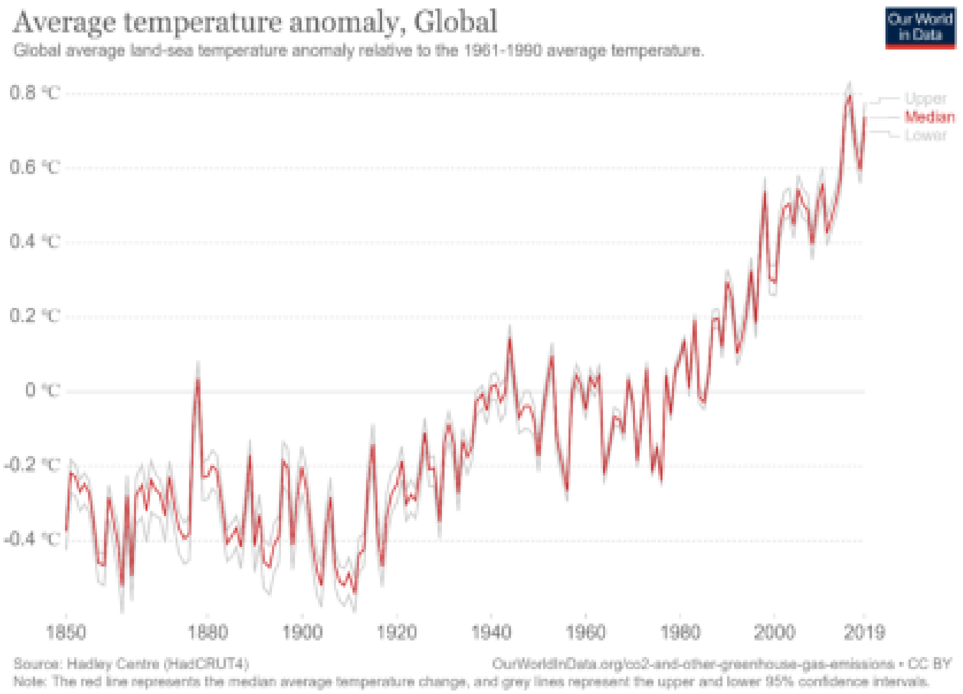
Biomethane, which is obtained after subjecting the biogas to an upgrading can be used to fuel it in vehicles in the form of Compressed Natural Gas (CNG) or Liquefied Natural Gas (LNG). Light vehicles (ideal for working with biogas) can be designed to work with gasoline and with CNG (in separate tanks), while heavy vehicles are designed to work with only one type of fuel. When using natural gas instead of diesel, reductions in emissions of 60-85% for NOx, between 10-70% for CO and 60-80% for particles, are achieved [45,46]. Others uses as fuel are the employment in stoves or boilers, for engines and gas turbines for producing electricity or fuel for fuel cells [46].

Table 2.3. Requirements and recommendations to remove impurities when using biogas in different applications [37,47].

Application	**Hydrogen sulfide**	**Carbon dioxide**	**Water**	**Siloxanes**
Boiler	< 1000 ppm	Not allowed	Not allowed	Not allowed
Cooker	Allowed	Not allowed	Not allowed	Not allowed
Stationary engine	< 250 ppm	Not allowed	Not allowed	Allowed
Vehicle fuel	Allowed	Recommended	Allowed	Not allowed
Natural gas grid	Not allowed	Eventually	Eventually	Eventually

2.5. Carbon dioxide importance among Greenhouse gases

GHG are a pressing problem for our society, as it has been demonstrated its direct influence on climate change [48,49]. Indeed, in agreement with Figure 2.5, the planet temperature has increased from 1900 to this date about 0.8ºC. Scientist and experts of this field beliefs indicate that GHG emissions are to be blame for this temperature raised [50,51].


Average temperature anomaly, Global

Global average land-sea temperature anomaly relative to the 1961-1990 average temperature.

Source: Hadley Centre (HadCRUT4) OurWorldInData.org/co2-and-other-greenhouse-gas-emissions • CC BY

Note: The red line represents the median average temperature change, and grey lines represent the upper and lower 95% confidence intervals.

Figure 2.5. Average temperature increase from 1900 to 2019 [52].

The main GHGs in the Earth's atmosphere are water vapor (WV), CO_2, CH_4 and nitrogen oxides (N_2O) [53]. WV is a direct consequence of evaporation. The amount of WV in the atmosphere depends on the temperature of the ocean surface. Most of it originates as a result of natural evaporation, in which the action of man does not play a trivial role [54]. CO_2 is the primarily responsible for the GHG effect. The major percentage of its concentration in the atmosphere is due to the fossil fuels utilization for industrial processes and transport purposes [55]. CH_4 origin is found in fermentation processes which are produced by specialized anaerobic bacteria, typically located in swampy areas, crops such as rice, and in emissions from the intestinal tract of cattle. It is also produced by the escapes of natural deposits and industrial pipes [56]. N_2O is a GHG mainly produced through the massive use of nitrogen fertilizers in intensive agriculture. It is also produced by other sources such as thermal power plants, automobile and aircraft engine exhaust pipes, biomass burning and nitric acid manufacturing [57]. Figure 2.6 reveals the percentage distribution of the global GHG emissions causing by each gas.

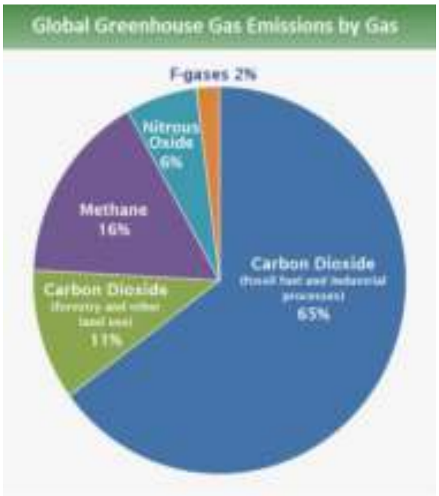


Figure 2.6. Global GHG emissions by gas. Adapted from [58].

As Figure 2.6 shows, CO_2 is the main responsible for GHG emissions. Indeed, CO_2 concentration has been accumulating in the atmosphere dangerously during the last decades, achieving values of 410 ppm in the last year (2019) [59]. The initial movement which provokes the increase of CO_2 emissions was the industrial revolution. Since that moment the global carbon cycle was disrupted, leading to a planetary warming impact. Both global warming and climate change may have potentials disasters in the form of impacts, such as ecological, physical or health [60]. Some extreme weather events such as floods, unexpected storms and heatwaves may be also natural consequences of the above-mentioned changes. As can be seen in Figure 2.7, CO_2 emissions have increased approximately 2 parts per million per year.

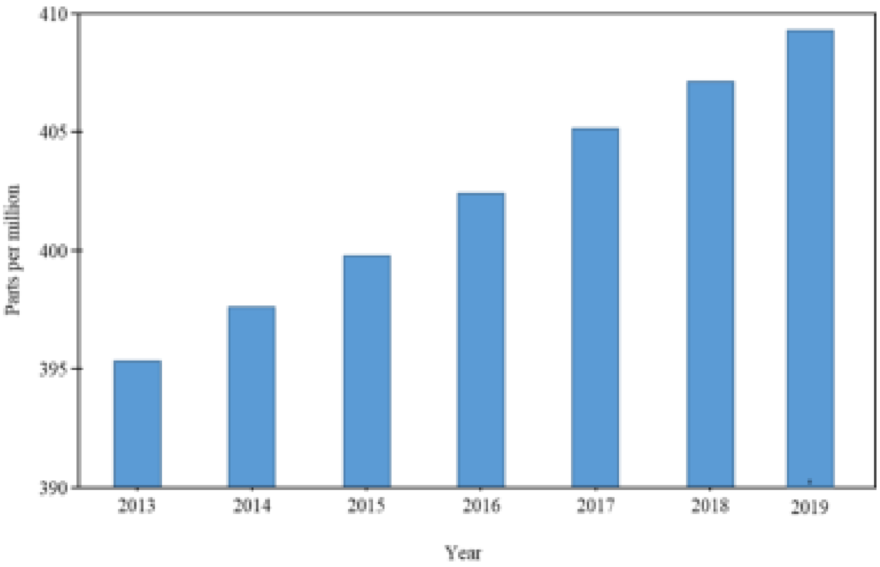
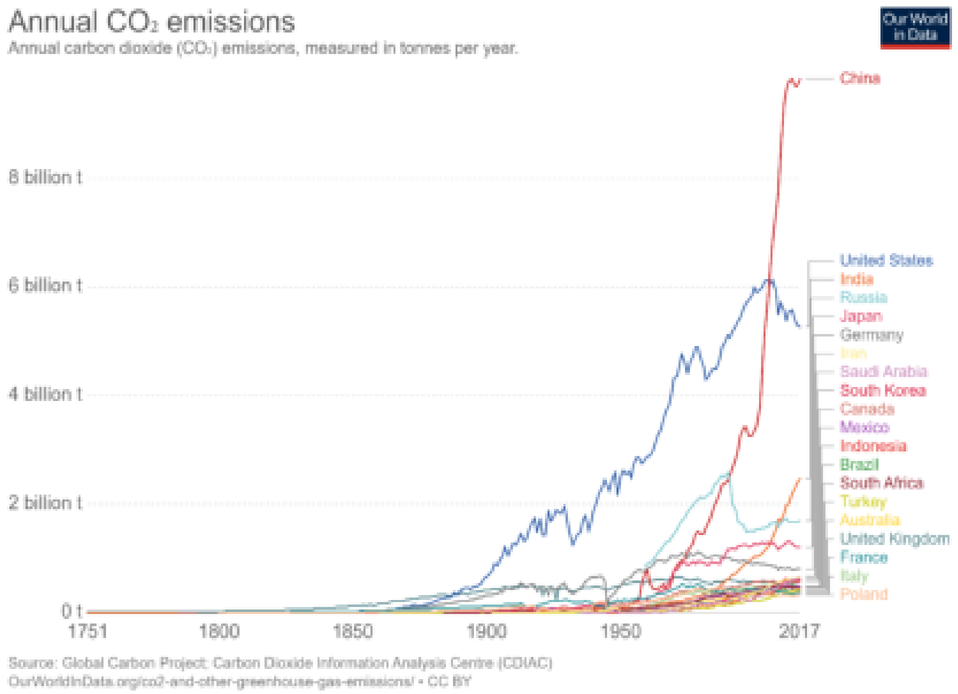


Figure 2.7. Monthly record of the concentration of CO_2 in the atmosphere. Adapted from [59].

CO_2 emissions are clearly unbalanced among the different countries. For instance, higher emissions are found in some countries which are currently in a development process, such as China or India. Also United States is one of the heading countries in CO_2 emissions. According to the data presented in Figure 2.8, European countries such as Italy or Germany did not overcome 1 billion of CO_2 emissions tons until 2017. Even if some countries are considered the principal CO_2 emitters, the solution for cutting CO_2 emissions falls on every industrialized country and therefore a worldwide effort is needed [52].


Annual CO_2 emissions

Annual carbon dioxide (CO_2) emissions, measured in tonnes per year.

Source: Global Carbon Project; Carbon Dioxide Information Analysis Centre (CDIAC)
OurWorldInData.org/co2-and-other-greenhouse-gas-emissions/ • CC BY

Figure 2.8. Annual CO_2 emissions per country [52].

The logical path to solve this problem would be the reduction of these emissions and therefore to evolve towards decarbonized systems. Currently, the direct reduction of the aforementioned emissions is complicated in the short term due to the established technologies in the different industries, which are based mainly on the use of fossil fuels [61–63]. Even with the help of green energy sources coming from renewable energy, CO_2 would be still release to the atmosphere [64]. As a consequence, the concept of Carbon Capture and Storage (CCS) emerges as an attractive idea for the reduction of emissions [65].

2.5.1. CCS technologies. Where are we now?

The global warming brake goes through ambitious goals for decarbonized systems of the planet's economy [66,67]. In fact, there are still no technologies that allow economically an acceptable decarbonization [68]. This idea of decarbonized-energy systems cannot be achieved only through improving energy efficiency or transforming into a mix of fully renewable [69]. There is a need of complementing both measures with CCS technologies which should be applied to both fossil fuels and biomass CO_2 emissions [70]. Three stages are required for CCS: (1) CO_2 separation from the rest of the flue gases; (2) CO_2 transport to the storage location; and (3) CO_2 long-term isolation from the atmosphere through storage [71,72]. The most direct application for this route to reduce CO_2 emissions can be carried out at power plants, since they emit the 42% of total global anthropogenic CO_2 emissions [73]. Flue gas generated in the combustion of fossil fuels contains between 4-20% of CO_2, being the rest mainly N_2 [74,75]. If the flue gas were to be stored directly, transportation costs would be prohibitive, due to the difficulty of moving such a high flow rate and the technical difficulties of compressing a diluted CO_2 stream [76]. Moreover, the life-time spam of CO_2 deposits would be reduced. Therefore, the use of technologies that allow the separation of CO_2 from the rest of combustion gases is necessary, this being the most expensive stage of the global process. There are three possible ways of capturing CO_2 in energy production systems [77–79]:

1) Pre-combustion capture: in this stage, carbon CO_2 is removed prior to combustion. Figure 2.9 shows an alternative of process-scheme for pre-combustion CO_2 capture. The process starts with a gasification or reforming stage of the fossil fuel, which produces a rich CO-H_2 stream (commonly known as syngas) [80]. Afterwards the syngas is converted to CO_2 and H_2 through Water Gas Shift reaction. Finally, CO_2 is split from the flue gas stream and pure H_2 is obtained, which can be burnt to obtain heat or electricity. The biggest advantage

of this process is that it generates H_2 as a product, which can be used in different ways [81]. For instance, H_2 can be combusted in gas turbines for the production of electric energy, or it can be use in transport by means of fuel cells. Pre-combustion processes have lower energy penalties, since the CO_2-H_2 separation is carried out at medium pressures (20-40 bar), and high CO_2 concentrations (~ 40%) [82]. Thus, the overall energy penalty is lower than in the case of post-combustion separation. However, it should be noted that for the gasification process O_2 is used, which must be separated from the air by cryogenic methods. Some authors estimated an energy penalty of 4-11% in natural gas reforming and 7-13% in coal gasification [83].

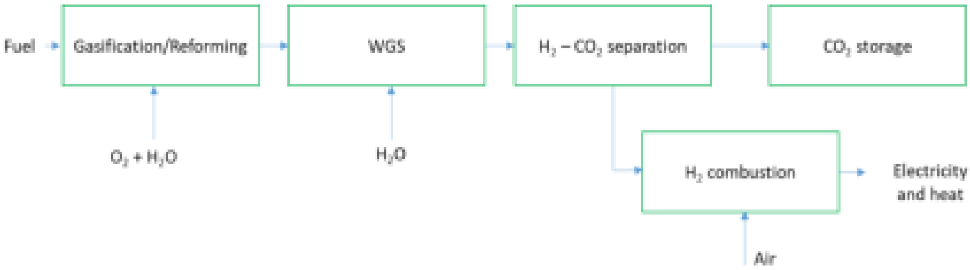


Figure 2.9. Alternative of process-scheme for pre-combustion CO_2 capture

2) Post-combustion capture: herein CO_2 is separated from the combustion gases produced in the combustion of the primary fuel, as shown in Figure 2.10. This separation can be done by different methods: physical or chemical absorption, membranes, cryogenic methods, adsorption, etc [73]. Among these capture processes, the most developed in terms of commercial availability is chemical absorption with amines [84]. Even though this method has proved to be promising in terms of captures efficiencies, they have a high energy penalty due to the necessary regeneration of the absorbent for reusing [85]. Otherwise the process would be unaffordable. In addition, the CO_2 separation must be carried out in a

diluted stream (CO_2 concentration between 5-20%) and at atmospheric pressure, which increases both investment and operational cost [86]. The energy penalty estimated by some authors is 8-16% for coal plants and 5-10% in combined cycle natural gas plants.

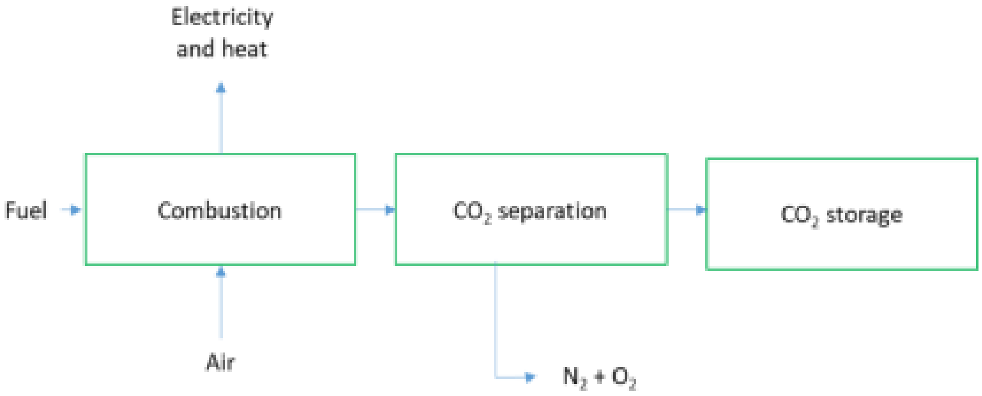


Figure 2.10. Process-scheme for post-combustion CO_2 capture

3) Oxy-combustion: this combustion system use oxygen instead of air for fuel combustion in order to produce a combustion gas composed solely of WV and CO_2. This results in a rich CO_2 stream which is easily separable from WV. An outline of this process can be seen in Figure 2.11. In addition, when combustion is carried out with O_2, a very high temperature increase in the combustion chamber would occur. To avoid this, CO_2 must be recirculated to lower the combustion temperature [87]. The disadvantage of this technology is the use of pure O_2 whose production has a significant energy penalty due to the O_2 separation from air process. Energy penalty has been estimated at 6-9% for coal plants and 5-12% for natural gas plants in oxy-combustion [88].

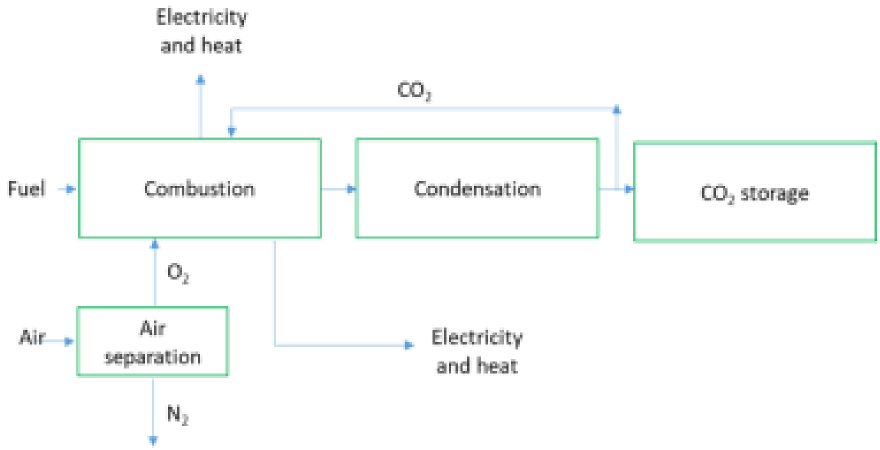


Figure 2.11. Process-scheme for oxy-combustion CO_2 capture

Regarding the economic viability, the costs of CCS technologies could be acceptable depending on fuel price and the cost of CO_2 emissions [89]. The price of fuel is essential to know what the future cost per ton of CO_2 avoided will be [90]. For example, for an improved supercritical pulverized coal plant with CCS systems, this cost varies between 20-90€ per ton of CO_2 avoided [91]. In the case of a natural gas plant with combined cycle and implemented CCS systems, costs vary between 60-100€ per ton of CO_2 avoided. Concerning oxy-combustion technologies the cost of CO2 avoided is slightly similar [92]. Nevertheless, electricity cost seems to be to some extend lower for power generation plant optimized with CCS (63 €/MWh compared to 67 €/MWh of post-combustion). However, this technology needs to gain maturity in terms of technological advances to reduce operational and investment cost. For these reasons, novel CO_2 capture processes are currently being investigated to reduce the energy penalty and CO_2 capture costs.

Before definitely storing the sequestered CO_2, it must go through a series of stages for compression and subsequent transport to the injection place. This transport can be done by pipeline, where CO_2 must be compressed at pressures between 100 and 200 bar (liquid CO_2), or by boat, where the CO_2 must be liquefied at -30ºC and between 15-20 bar pressure [93]. Finally, the last step is the storage of the captured CO_2. There are several ways to storage, but all must meet common criteria. These criteria are [94]:

- Safety in terms of storage stability.
- Low costs, including transportation.
- Minimize environmental impact and environmental risks.
- Comply with current legislation.

Two options are commonly considered for CO_2 storage: geological storage and ocean storage [95,96]. The overall CO_2 storage capacity depends on the location chosen. As can be seen in Table 2.4, the largest storage capacity is the ocean, followed by saline aquifers and spent oil and gas wells. The main problem that ocean storage face is the high environmental impact generated due to the pH variation [97]. Wells main drawbacks are the insufficient capacity for the current emissions [98].

Table 2.4. CO_2 storage capacity.

Alternative	**CO_2 storage capacity range (Gt CO_2)**
Ocean	18000-7000000
Saline aquifers	1700-3700
Spent oil and gas wells	675-900

Currently the most viable storage option is CO_2 storage in deep-sea saturated saline aquifers [99]. There are currently a large number of projects underway for the application of this technology in the world [100]. Among them, the Sleipner platform has been the first commercial scale project dedicated to storage in a deep-sea CO_2 aquifer (800m deep). The Sleipner platform is located 250 km north of the Norwegian coast in the North Sea. Natural gas is extracted from this well with a high concentration of CO_2 (around 9%). Since 1996 it is being injected into a salt formation of the platform itself of the order of 1 Mt of CO_2 per year, and in which it is expected to introduce about 20 Mt of CO_2 during its useful life [101].

As can be seen, not only economic targets are a very serious drawback for CO2 capture but also transport and storage issues remain uncertainty. Researchers nowadays focus their efforts on reducing the capture cost through proposing new applications for CO_2, both its direct utilization or its employment as raw material for other chemicals. These technologies are known as Carbon Capture and Utilization (CCU). Through the employ of these technologies, CO_2 would not need to be storage since it would be reuse for industrial purposes.

2.5.2. CCU technologies: a partial solution for CCS problems.

The use of carbon dioxide as valuable compound seeks not only to reduce the volume of emissions into the atmosphere, but to obtain a benefit through the use of CO_2 in different types of industrial processes where it can replace conventional raw materials [19]. These methods will not be enough to achieve the desired objective, but they could be key to complement the use of renewable carbon-free technologies [102]. In fact, in our daily life it is very likely that one way or another we will encounter this compound, or even eat or drink it [103]. The areas of CO_2 current applications can be seen in Figure 2.12. CO_2 is already used in applications that range from water treatment (as a pH modifier for wastewater treatment, as a source of minerals in demineralized water or for the treatment of recreational water), clothing cleaning, product extraction (including the extraction of caffeine or chocolate fat), the accelerated growth of plants in greenhouses, the extinction of fires, and the treatment of food products (both in the carbonation of beverages such as Coca-Cola or beer, as in the preservation of food in a modified atmosphere) [18,79,102].

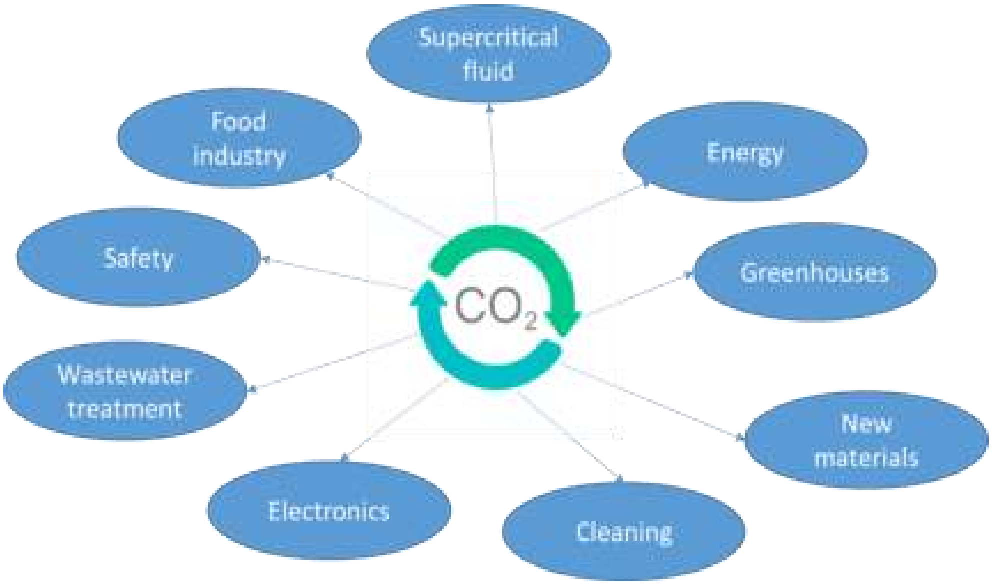


Figure 2.12. Areas of CO_2 current applications

In the field of electronics, CO_2 is generally used in the treatment of liquid effluents, as a solvent in solutions for cleaning chips or during cooling of electronic components in climate tests. In medicinal uses, three major applications are worth highlighting: 1) it is used in the manipulation of artificial organs, since it produces an atmosphere similar to physiological conditions, 2) mixed with air or oxygen, it is employed as a stimulant to improve the aeration of the respiratory system and 3) CO_2 is used in surgical dilation to perform abdominal laparoscopy. As regards its applications in the field of chemical synthesis, it is used to manufacture other compounds. These chemical processes include, among others, urea (which is then used to obtain fertilizers), acetylsalicylic acid, cyclic carbonates and polycarbonates, of numerous applications in the market [104,105].

The use of CO_2 can be technological, biological or chemical, and all of them seek to improve or replace traditional processes with the incentive of double contributing to curbing climate change. CO_2 utilization would reduce its emissions to the atmosphere and could lead to a decrease in the extraction of fossil fuels, as well as economic savings for companies that consider their use [104].

The direct or technological use of CO_2 includes applications such as the extraction of compounds with supercritical CO_2, dry cleaning and water treatment, as well as multiple uses in the food industry, among others. In the case of the food industry, CO_2 replaces toxic elements used for food disinfection; in the extraction of compounds, organic solvents and water treatment, CO_2 replaces more dangerous acidic species [106]. Table 2.5 shows other possible technological applications of carbon dioxide and the compounds they would replace.

Table 2.5. Examples of direct or technological applications of CO_2 [104]

Application	**Substituted product**	**Application**	**Substituted product**
Dry cleaning	Chlorides compounds	Fire extinguisher	Flame retardants
Wastewater treatment	Sulfuric acid	Electronic parts cleaning	Fluorinated compounds
Air conditioning	Fluorinated compounds	Caffeine extraction	Hexane
Antibacterial	Pharmaceutical complexes	Nanomaterials production	Organic solvents

From the side of biological use, it is worth mentioning the direct fixation of CO_2 in fast growing biomass. This can contribute to reduce CO_2 accumulation in the atmosphere much more rapidly than it would naturally occur. This procedure can be used both for the manufacture of renewable fuels and for the production of energy. For instance, growth biomass can be converted into gaseous or liquid fuels, as well as it can be directly burned. A remarkable example of this fast-growing biomass is photosynthetic microorganisms or microalgae. Finally, chemical use consists of the conversion of CO_2 into other valuable chemicals products, such as methanol, acetic acid, synthesis gas, carbonates and polymers [107–109].

The main problem for the application of these technologies and processes lies in the great thermodynamic stability of CO_2, which make the overall process to have a high energy consumption [110]. The use of CO_2, whether technological, biological or chemical, must meet certain requirements to cause an effective reduction of emissions into the atmosphere. First, it must reduce global CO_2 emissions, which is not easy to quantify. In addition, it must have a lower energy and material consumption than the process to be replaced. This consumption should be minimized by controlling process parameters, such as performance and selectivity, temperature, pressure and post-reaction operations. The new process must be safer and work in more environmentally friendly conditions. Finally, it must be economically viable. There are several sources of CO_2 and its price will depend on the quality required in terms of the purity necessary for the process. Thus, the processes with higher purity CO_2 requirements will be comprehensible more expensive than those where this parameter is not important. Therefore, to fulfill with affordability conditions, applications which no high CO_2 purity needed are preferred [111].

As stated in the beginning of this section, CCU technologies are not enough to mitigate climate change since both its direct use or products manufactured from CO_2 have a limited capacity which is much lesser than CO_2 emissions. Thus, the key to achieve a carbon-free energy economy needs to accomplish the task of complementing CCU technologies with renewable energy. In this sense, systems which combines renewable energy production with CCU technologies are under evaluation. Among renewable energy, experts in this area assure than biogas coming from anaerobic digestion is a potential candidate for CCU applications for the following points:

- Biogas can be converted to biomethane after CO_2 removal (upgrading).
- Biomethane can be used as vehicle fuel, as natural gas substitute and used for combined heat and electricity generation.
- Waste valorization through biomass production favors waste management.
- CO_2 captured and converted into valuable products will be in a production rate which could fits into the market.
- Circular economy policy will be increased by this combination.

2.6. Objectives and preliminary strategy

As stablished in Chapter I, the overall objective of this PhD Thesis is to explore potential paths to synergize biogas upgrading and CCU in a WWTP, designing a novel process which could give an added-value product and hence boosting the implementation of circular economy processes within this industrial area. However, first a deep analysis of biogas upgrading and CCU technologies is needed to evaluate the optimal combination to be implemented in a WWTP. Moreover, potential synergies of biogas upgrading – CCU technologies with other traditional processes of WWTP must be considered. To this end, the following preliminary strategy is pursued:

- Analysis of current research and commercial biogas upgrading technologies, in which the most recent advances in biogas purifying are reviewed (Chapter III)
- State of the art of CCU technologies, performing on an exhaustive literature review and recent advances carried out in the field (Chapter IV)
- Once both technologies have been reviewed, the main characteristics of both of them which may have an influence on WWTP must be weighted and evaluated. This point will allow the final selection of biogas upgrading and CCU technology, as well as the establishment of a novel process (Chapter V)
- Afterwards, the main stages of the process selected must be defined and experimentally tested. Once at this point, a new strategy will be defined for the rest of the PhD Thesis here developed.

CHAPTER III: Recent advances in biogas purifying technologies

3.1. Objectives

The main objective of this chapter is to provide a range of technologies which are able to remove CO_2 from biogas, aiming to decide the best alternative later for the overall goal of this work. To this end, this chapter presents a comprehensive list of biogas upgrading technologies focused on CO_2 removal, both from a research and commercial perspective. Additionally, an extensive cost – life cycle analysis – performance comparison among the technologies studied is discussed.

3.2. Introduction

The main objective of biogas upgrading is to remove the CO_2 contained in the biogas. The removal of CO_2 is the central core of biogas purification, and the main techniques for separating this component will be the basis of this chapter. Although it is also important to remove H_2S, NH_3, siloxanes and H_2O, among others, due to corrosion problems when using biogas in boilers or combined heat and power (CHP) combustion, these compounds have not a high percentage in biogas composition and can be easily removed [37]. In practice, to remove CO_2 from biogas, several methods are successfully used at industrial scale to meet this objective: physical and chemical absorption, adsorption, gas separation through membranes and cryogenic methods [112]. Pressure Swing Adsorption (PSA), High Pressure Water Scrubbing (HPWS), Organic Physical Scrubbing (OPS), Amine Scrubbing (AS), Inorganic Solvent Scrubbing (ISS), Membranes Separation (MS) and Cryogenic Separation (CS) are the technologies which present greater availability and industrial development [113]. For the separation of other components, such as H_2S, a pre-cleaning step is required previously to the operations mentioned above [114]. CO_2 separated from biogas could be also used as an alternative raw material to produce chemicals or fuels, making the process even more attractive industrially and economically [18,115–117]. Below the main technologies for biogas upgrading will be described in deep.

3.3. Pressure Swing Adsorption

Adsorption systems consist of the transfer of a desired compound in a gaseous stream to the surface of an adsorbent material [34]. With PSA systems, some undesirable gases such as CO_2, O_2, and N_2 can be separated by adsorption on solids with a very high specific surface as zeolites or activated carbon mainly, at different pressure [118]. The adsorption material also adsorbs H_2S from the biogas, but unlike the adsorption of CO_2, it is irreversible. For this reason and in order not to deactivate the adsorption material, the H_2S is removed in a previous independent stage [37]. A typical PSA plant configuration is represented in Figure 3.1.

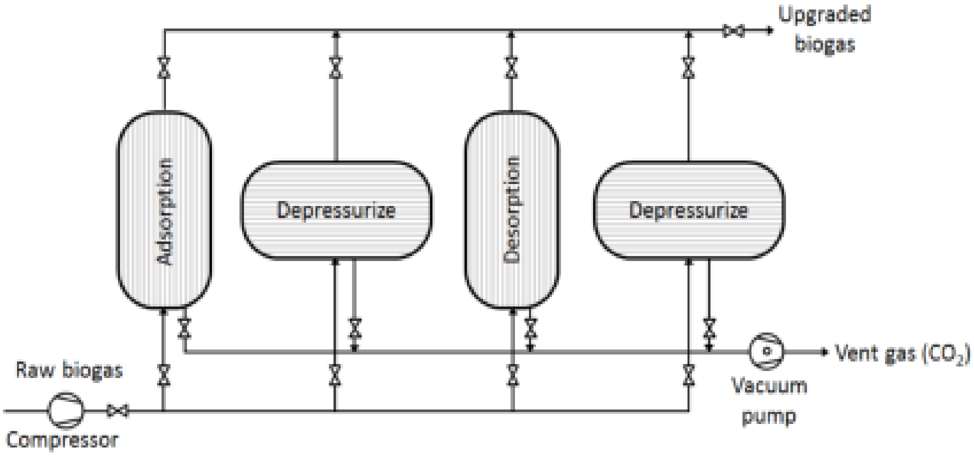


Figure 3.1. PSA system. Adapted from [119].

Some PSA systems presents a maximum CH_4 purity of 91% [120], while others ensure purities between 95-99% if an efficient previous stage is included [119,121]. CH_4 loses are usually about 2-4% [46,122]. However, the core of the system relays in the choice of the most suitable adsorbent material, both for the selectivity to be higher to CO_2 than

CH_4 and to be able to removal other contaminants simultaneously [34]. Adsorbents such as cationic zeolites, silicates, aluminas or activated carbon are widely used commercially [123]. In the last years, some researchers have focused their investigations in getting a new material through synthesis with better capacities results. For example magnesium based metal organic framework (MOF) proved to have better CH_4 and CO_2 adsorption capacities than for example zeolite 13X under same operational conditions [122]. For biogas upgrading, the desirable properties that the adsorbent may have are the following [121,124]: contact surface (equilibrium-base adsorbents); pore diameter of the adsorbent suitable for the particle diameter of CO_2, but not for that of CH_4 ; and the captured compound must be easily regenerated, with a low energy consumption.

3.4. Absorption

Biogas purification by absorption consists on a liquid scrubbing which, through some physical or chemical principles, allow to capture CO_2. Subsequently, the liquid is regenerated for re-using and hence to keep the overall system affordable [32]. The main physical absorption alternatives are High Pressure Water Scrubbing (HPWS) and Organic Physical Scrubbing (OPS), while outstanding chemical absorption options are Amine Scrubbing (AS) and Inorganic Solvent Scrubbing (ISS) [39].

3.4.1. High Pressure Water Scrubbing

HPWS is a technique capable of simultaneously absorbing CO_2 and H_2S, giving as a product a gas enriched in CH_4. The key to the process is that both CO_2 and H_2S are more soluble compared to CH_4, N_2 or O_2. To use this upgrading technique, it is therefore necessary to know the solubility of the major components of the gas in water [125]. This technique is usually carried out in packed bed columns, optimizing the operating conditions to achieve high levels of CO_2 abatement, which normally leads to a less energy expenditure [126]. In Figure 3.2 a scheme of the HPWS system with regeneration is presented.

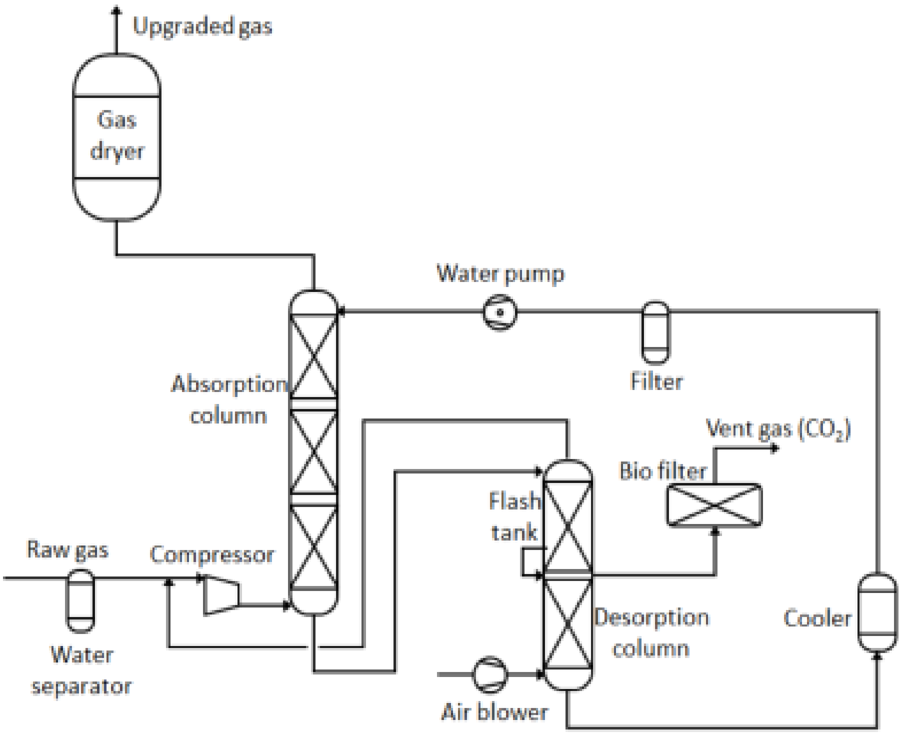


Figure 3.2. HDPS process. Adapted from [125].

By means of this technique a biomethane with a purity of 95-97% can be obtained [127], with a minimum supervision of the operation and a single passage through the column, which is increased in cases of recirculation. Also, some studies have achieved a 99.1% of reduction in siloxanes and 99.9% in halogenated compounds by increasing the working pressure to 20-25 bars [128]. The advantages of this technique are that it is a simple technology, widely used in industry and relatively inexpensive. In addition, HPWS presents few losses of CH_4 (less than 2% losses) due to the large difference between the solubility of CO_2 and CH_4 [46,129]. The main disadvantage of HPWS is that it is less efficient than other processes in terms of energy [130]. When using HPWS, few resources are consumed. The most important resource needed is the water to be replaced to prevent the accumulation of unwanted compounds from biogas, as well as to avoid the decrease in pH caused by the oxidation of H_2S [37]. The volume of water required varies according to the different sizes and operating conditions, but an average consumption of 0.5-5 m^3 / day can be established.

3.4.2. Organic Physical Scrubbing

Absorption with organic solvents is quite similar to HPWS, with the difference that CO_2 is absorbed in an organic solvent, such as, for example, polyethylene glycol or selexol [40,131]. CO_2 is much more soluble in polyethylene glycol than in water, so for the same gas flow, less liquid flow is needed. Therefore, smaller equipment is required, which has a positive effect on investment costs. Moreover similar CH_4 purity is obtained by both methods [132]. The polyethylene glycol solution is normally regenerated by means of heating or depressurization. In addition, H_2S, H_2O and O_2 can also be removed from biogas along with CO_2 if they have not been previously removed in the biogas cleaning process. Commercial examples of organic solvents are Selexol and Genosorb [32,129].

Selexol has a low freezing point and is not corrosive. The solubility of CO_2 and NH_3 is higher in Selexol than in water, being able to absorb three times more CO_2. The drawback of this type of organic solvents is that they are more difficult to regenerate than water [129,133]. The main difficulties are caused by the higher pressure – temperature needed. The solubility of H_2S in Selexol is greater than the solubility of CO_2. To regenerate the Selexol of H_2S and water, an increase in temperature is required, which is also of different value for both. Thus, these compounds must be eliminated in different stages before sending the Selexol back to the absorption [129]. Figure 2.3 shows a scheme of an absorption system with Selexol used in a plant in Sweden [133].

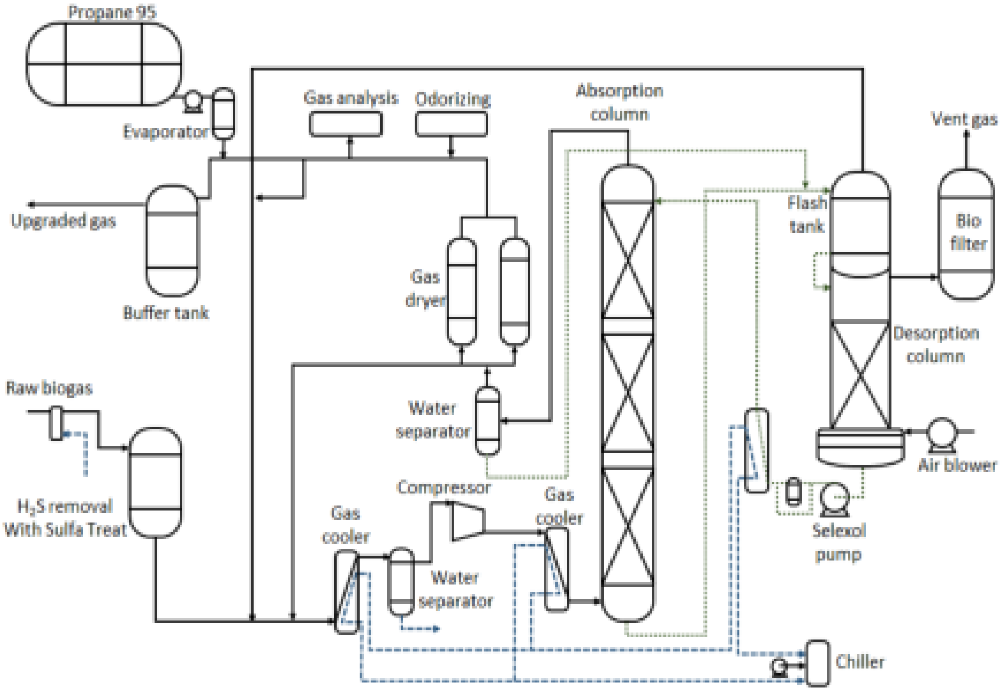


Figure 3.3. Selexol process. Adapted from [133].

The energy consumption to valorize the biogas with organic solvents is similar to water scrubbing, being also the compressor, the pump and the cooler the equipment with higher consumes. Similarly, the energy consumption depends on the size of the unit, but not on the CH_4 concentration in the biogas. This consumption is 0.2-0.25 kWh / Nm^3 of biogas [130].

3.4.3. Chemical Scrubbing

Chemical absorption involves reactions between the absorbed substance and the absorbing component. Within organic compounds, amines are typically the most commonly used for the removal of gases such as CO_2 or H_2S either in the form of Diethanolamine (DEA), Monoethanolamine (MEA) or Methyldiethanolamine (MDEA). As inorganic components, they generally consist of an aqueous solution of an alkaline salt such as sodium, potassium, ammonium or calcium hydroxide [34,134].

In the case of chemical absorption with amines the chemical reaction is very selective, so that the CH_4 losses are below 0.1% whereas 99% of CH_4 purity could be obtained [32,129]. Typical working parameters operation are 120ºC and 1-2 bar of pressure [135,136]. However, due to the evaporation that must be subjected to the process, a part of the amine solution is lost, which must be replaced [37]. The regeneration of the solution to separate the CO_2 from the amines to which they are attached is done by heating with steam where the CO_2 returns to the gas phase. This regeneration is a process that involves a very high energy consumption [32,34,137]. Some authors have achieved very important reductions in energy terms of almost 30%, achieving a 90% of CO_2 capture efficiency [135]. Loading capacity of the most common amines lies around 0.5-1.0 mole of CO_2 per mole of amine [37,138]. Figure 2.4 shows the typical operating scheme of regenerative chemical absorption.

As advantages of this technique can be named the high selectivity of the amines by CO_2 and the great reduction of volume that this process implies with respect to others. For example, chemical absorption can dissolve 1 to 2 orders of magnitude more CO_2 per unit volume than if absorption with water were used. On the other hand, if there is any residual heat that can be used for the absorption stage, the overall energy consumption is lower than in other cases such as absorption with Selexol or water [129,133].

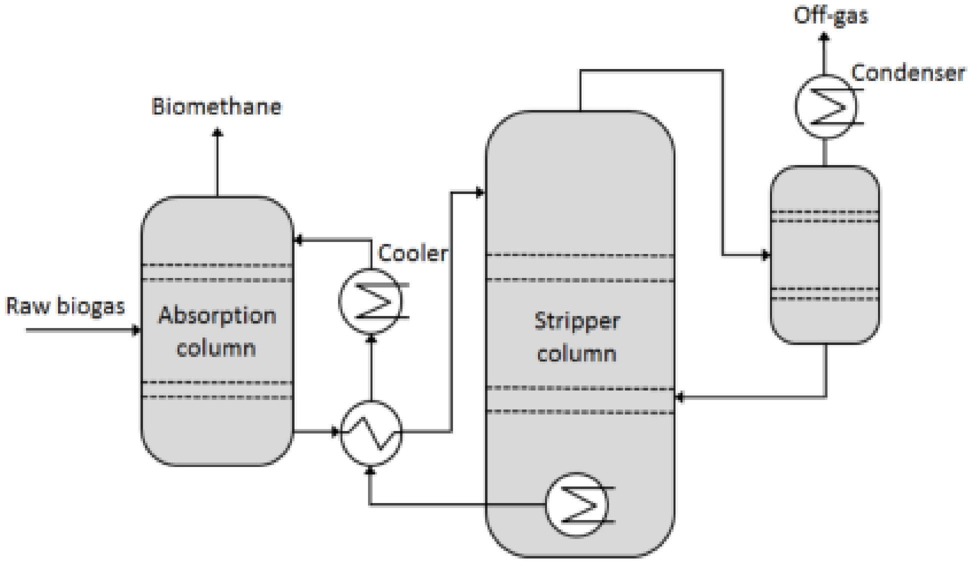


Figure 3.4. Process flow diagram of an amine scrubber process. Adapted from [130].

In terms of consumption, the use of utilities as water, electricity and some chemical compounds are required. The electricity consumption depends slightly on the capacity to which the units are working: with the lowest specific consumption at the maximum load, of 0.12 kWh/Nm^{3}h, and the highest consumption at the lowest load, of 0.14 kWh/Nm^{3}h. In addition, the desorption column heat to regenerate the amines, is approximately 0.55 kWh/Nm^{3}h of biogas [133].

In the case of chemical absorption with inorganic components, the use of compounds with alkaline character is used to convert CO_2 into carbonated salts. With the aim of definitely storing CO_2, precipitation reactions are commonly used which can also regenerate the spent solvent [139]. One of the most used solvents is NaOH, mainly due to its strong alkaline character that allows it to be fully ionized in water and have been deeply studied by lot of researchers [140–143]. The cheaper price compare with other solvents, the availability, the high capture capacity and the possibility of forming a non-polluting byproduct [144], make NaOH a serious candidate for CO_2 capture in biogas upgrading. NaOH is typically used in concentrations ranging from 5% to 12% [140,141], absorbing CO_2 and forming a sodium carbonate solution as indicated in Eq. (1).

$$2NaOH\ (aq) + \ CO_2(g) \rightarrow \ Na_2CO_3(aq) + H_2O\ (l) \tag{1}$$

Yoo et al., (2013) [140] achieved CO_2 capture efficiencies of around 60% with a 5% concentration of sodium hydroxide, while Tippayawrong & Thanompongchart (2010) achieved a 90% of removal efficiency with 15% sodium hydroxide. Another good characteristic of using NaOH as a solvent is the easy regeneration via carbonation of CO_2, using calcium as a precipitating agent (Eq. (2)). This technique has been used by several researchers, who have used both calcium hydroxide and residues with high calcium content to permanently solidify CO_2 [140,145–147].

$$Na_2CO_3\ (aq) + \ Ca(OH)_2(s) \rightarrow \ 2NaOH(aq) + CaCO_3\ (s) \tag{2}$$

Another highly used solvent for capturing CO_2 is KOH, for the same reasons as sodium hydroxide. The most important disadvantage with respect to sodium hydroxide is that potassium hydroxide is more expensive, but this cost could be reduced if it is possible to sell the potassium carbonate from the absorption reaction (Eq. (3)), or by regenerating the KOH in a similar way to NaOH (Eq. (4)) [146].

$$2KOH\ (aq) + \ CO_2(g) \rightarrow \ K_2CO_3(aq) + H_2O\ (l) \tag{3}$$

$$K_2CO_3\ (aq) + \ Ca(OH)_2(s) \rightarrow \ 2KOH(aq) + CaCO_3\ (s) \tag{4}$$

The results obtained in terms of removal efficiency are similar to those obtained through the use of sodium hydroxide, being around 70-80% [148,149]. Both NaOH and KOH could remove also the others impurities that are contained in the biogas, but a previous removal is recommended to make easier the regeneration of sodium hydroxide [118,150].

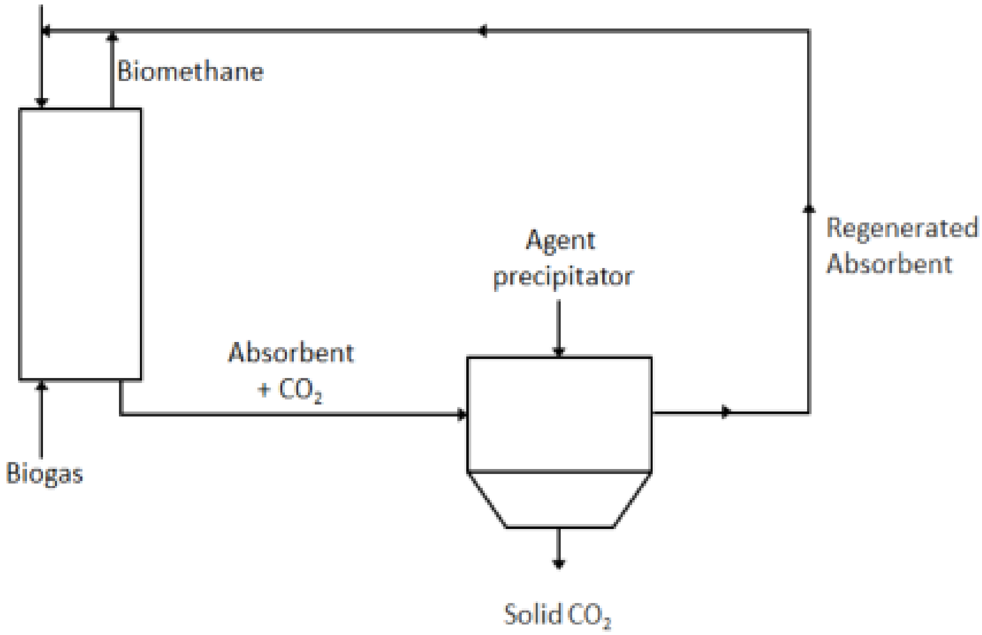


Figure 3.5. Caustic absorption process with regeneration and storage. Adapted from [151].

Calcium hydroxide is a really cheap and environmentally friend solvent, but operational problems like incrustations could appear due to the low solubility of it in case the absorption process in a classical packed column. This carry to some researchers to capture CO_2 in supercritical reactors to overcome those problems [152]. When using calcium oxide or others minerals containing it, the process is called mineral carbonation and follow the Eq. (5) [153]:

$$CaO\ (s) + CO_2(g) \rightarrow CaCO_3(s) \tag{5}$$

3.5. Membrane separation

Membranes for biogas recovery are made of materials permeable to CO_2, H_2O or NH_3. A process scheme can be observed in Figure 3.6. Part of the H_2S and O_2 pass through the membranes, while the N_2 and CH_4 pass in a very low proportion, what makes separation possible [32]. This permeability is based on differences in concentration, pressure, temperature and electric charges of different compounds that create a driving force [34,154].

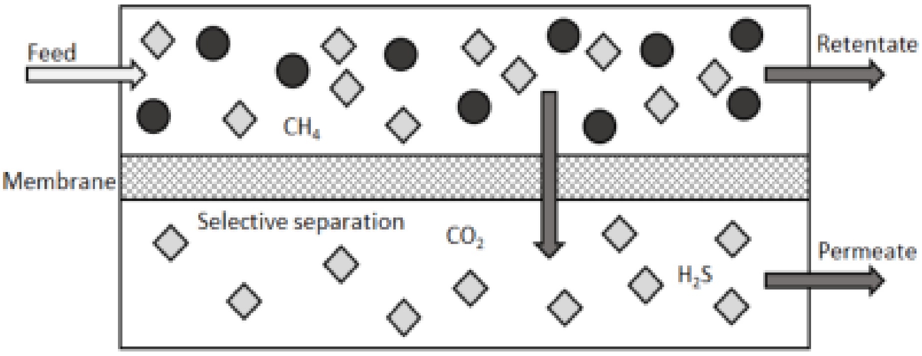


Figure 3.6. Biogas separation process by membranes. Adapted from [34].

For separation with membranes there are wet and dry techniques [155]. Dry techniques are based on the fact that certain substances pass more easily through membranes than others. The rate of passage of each substance depends on the difference in partial pressure of each substance on either side of the membrane. The partial pressure is dependent on the permeability, which is a function of the chemical solubility of the substance in the membrane. To achieve a good separation of CO_2 the membrane must be selective for this compound and the difference in permeability between CO_2 and CH_4 must be high [37,133]. Membranes for this type of operation are hollow fiber module type in order to achieve the greatest possible surface area. These hollow fibers can be made of different polymers, which have a permeability of 20 to 60 times higher for CO_2 and H_2S than for CH_4 [156]. To prevent corrosion, H_2S is removed before passing the biogas through the membrane [157]. It may also be necessary to separate the H_2O drops, since these reduce the efficiency of the membranes [40]. Separation is achieved at high pressure, usually between 25 and 40 bar. CH_4 remains on the side of the high pressure, while CO_2 passes through the membrane. This decreases the compression needed by the gas when it is distributed to the natural gas network or vehicle fuel [158].

The energy consumption for a specific application depends on several parameters such as the CH_4 losses, the CH_4 purity of the biomethane produced, the membrane area and the pressure applied to the membrane. Finally, the area of the membrane determines the pressure that will be applied to valorize a certain volume of biogas. If the membrane is larger, a lower pressure may be used because the gas flow is smaller [46,159]. The membranes most used commercially are composed of polymers that come from organic materials such as polycarbonate or cellulose acetate [160]. Some researchers have achieved the enrichment of CH_4 in biogas from the concentrations of 55-85% up to 91-95% [161]. Others have achieved a 99.5% of CH_4 recovery from a 80% in the raw biogas [162]. A previous removal of H_2S from biogas is necessary to not affect negatively to membrane performance. As well, drops or aerosol that biogas could contain should be eliminated from raw biogas. This last removal is done usually by a previous membrane filter [32,159]. A diagram process can be seen in Figure 3.7.

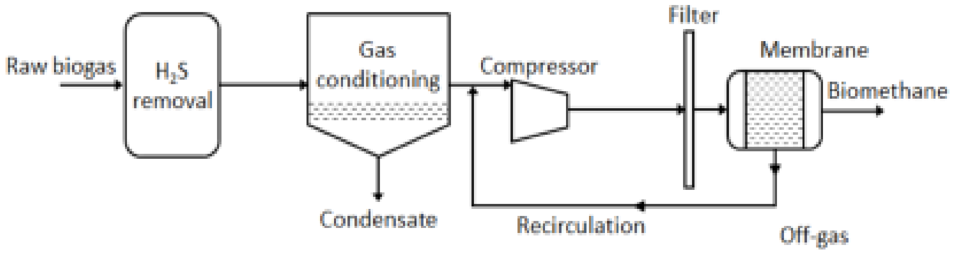


Figure 3.7. Diagram of membrane separation process. Adapted from [32].

3.6. Cryogenic separation

Cryogenic processes are based on the different boiling points of the different gases for the separation of CO_2 and CH_4. The biogas is compressed and cooled to a temperature where the CO_2 condenses and can be separated as a liquid, while the gas phase is concentrated in CH_4. The separation is achieved because the CO_2 condenses at a higher temperature than the CH_4 (-78.2ºC vs -161.5ºC) [37], and typical operational parameters of this separation technique are 80 bar of pressure and -170ºC of temperature [163,164]. To prevent freezing, H_2O is removed before entering the cryogenic process [32]. An example diagram of cryogenic separation process can be seen in Figure 3.8. The sublimation point of pure CO_2 is 194.6 K. However, since CO_2 is in a mixture in the biogas, lower temperatures and / or higher pressures are needed to get the CO_2 sublime or condense in the biogas [133].

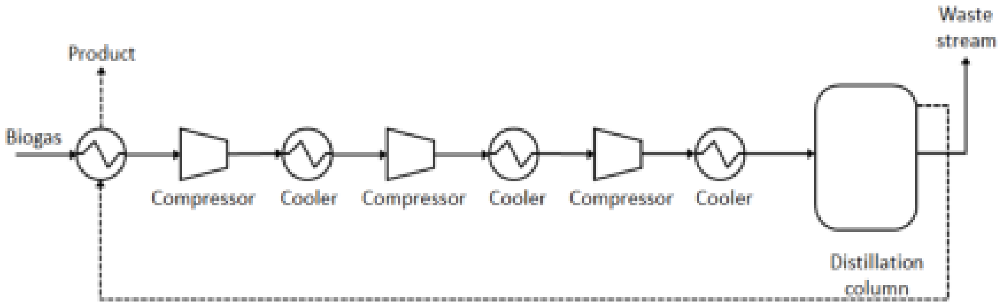


Figure 3.8. Cryogenic separation process diagram [133].

Johansson (2008) [165] indicates that electricity consumption is around 0.8 kWh / Nm^3 of biogas for a flow range of 50-2400 Nm^3 / h for the process marketed by the company gas treatment services. As in others techniques explained before, it is highly recommended to remove the others impurities such as H_2S or H_2O drops to not clogging the equipment [46].

3.7. Techniques comparison

In Table 3.1, a comparison of the advantages and disadvantages of the different techniques described in previous sections is presented, as well as a comparison of the characteristics of the biogas obtained through the use of each of the mentioned techniques. In general, the highest purity of biomethane is obtained using chemical absorption techniques with amines, while the lowest CH_4 losses are gotten by cryogenic separation techniques. The highest levels of impurities present in the final product are given in water scrubbing techniques and membrane separation. However, the quality of the final biomethane required depends on the final use pursued [42,130,166–170]. Regarding the costs of the different biogas upgrading technologies, it is first necessary to distinguish between Capital Cost (CC) and Operating and Maintenance Cost (OMC)

[46]. The first of those ones depend on the size of the plant on an inversely proportional way. OMC are mainly composed of the consumption of electricity and the raw material used (H_2O or chemical compounds, for example). This cost is usually higher in cryogenic plants, due to the high energy expenditure to achieve the operating conditions [169,171]; and chemical absorption plants, due to the regeneration of the solvent [130,169,171–173]. Generally, these costs are related to the capacity of the plant. A range of costs given by other studies can be seen in Table 3.2. Concerning the environmental impacts of each alternative, Table 3.3 collects a life cycle assessment comparison classified by impact category. As shown there are not remarkable differences between the upgrading technologies.

Table 3.1. Advantages and disadvantages of general techniques for biogas upgrading.

Technique	Advantages	Disadvantages	References
PSA systems	Low energy consumption Chemicals not needed Compactness Very common in low scale industries.	Medium-high CH_4 composition is obtained (>96%) compared with very high purities (>99%) Less efficiency than others techniques (2-4% methane losses) Pre-treatment to remove water and H_2S is required Strict control of the process High electricity consumption (0.25 kWh / Nm^3)	[32,122]
Water scrubbing	Easy to use and cheap Low electricity consumption (<0.25 kWh / Nm^3) Able to remove NH_3 and H_2S Flexible in capacity The most applied in industries	Medium-high CH_4 composition is obtained (>97%) compared with very high purities (>99%) CH_4 losses about 2% Not very flexible regarding biogas composition Dried stage after scrubbing is needed	[114,126,174]
Organic Physical Scrubbing	It presents a greater solubility of CO_2 than water Low losses of CH_4 It also eliminates ammonia, H_2S and other impurities, but a pretreatment is recommended	Medium-high CH_4 composition is obtained (>96%) compared with very high purities (>99%) High cost of investment and operation (electricity consumption 0.24-0.33 kWh / Nm^3) Difficulty of operation Warm up is required for a complete regeneration	[37,130]
Chemical Absorption Scrubbing	The highest purity of biomethane (>99%) and low losses are obtained (<0.1%) There is no pressurization of biogas High CO_2 elimination	High investment costs High heat demand for regeneration Corrosion and salt precipitation. Possible formation of foams Pre-treatment is needed to remove H_2S	[147,150]
Membrane Separation	Simple construction and operation Requires little maintenance Modular configuration No heat and no chemical products are required High reliability Small gas flows can be treated without great costs increases	Low selectivity of the membrane Several stages are required to achieve a high purity of CH_4 Medium / high losses of CH_4 (<10%) Not suitable for a biogas with pollutants not determined, such as landfill gas or wastewater biogas High cost of membranes Not widespread in industry	[163,175]

Cryogenic Separation	A high purity biomethane is achieved (aprox. 98%) Low methane losses (<1%) Pure CO_2 is obtained as a byproduct No chemicals required	High cost of capital and operation Pretreatment is necessary to eliminate contaminants Very recent large-scale implementation Efficiency and technology is not very demonstrated	[112,165]

Table 3.2. Cost of general techniques for biogas upgrading.

Technique	CC (€/kWh)	OMC (€/kWh)	References
PSA Systems	255-831	0.92-6.50	[46,122]
Water Scrubbing	357-731	0.47-0.94	[130,169]
Organic Physical Scrubbing	510-969	0.92-1.05	[46,163]
Chemical Absorption Scrubbing	264-438	1.15-1.92	[46,150]
Membrane Separation	305-367	0.79-5.50	[130,162]
Cryogenic Separation	394-960	4.80-7.10	[37,46]

Table 3.3. Life cycle assessment comparison for biogas upgrading alternatives [176].

Impact Category	PSA Systems	Physical Scrubbing	Chemical Absorption Scrubbing	Membrane Separation	Cryogenic Separation
Global Warming (kg CO2 eq)	1.11	1.11	1.27	1.09	1.16
Stratospheric Ozone Depletion (kg CFC11 eq)	3.55×10^{-6}	3.53×10^{-6}	3.54×10^{-6}	3.51×10^{-6}	3.60×10^{-6}
Terrestrial Acidification (kg SO2 eq)	1.61×10^{-2}	1.61×10^{-2}	1.64×10^{-2}	1.60×10^{-2}	1.62×10^{-2}
Freswater Eutrophication (kg SO2 eq)	8.21×10^{-4}	8.20×10^{-4}	8.01×10^{-4}	8.01×10^{-4}	8.77×10^{-4}
Human Toxicity (kg 1,4-DCB)	1.94	1.93	1.93	1.91	1.99
Mineral Resource Scarcity (kg Cu eq)	2.82×10^{-3}	2.84×10^{-3}	2.76×10^{-3}	2.76×10^{-3}	3.00×10^{-3}
Fossil Resource Scarcity (kg oil eq)	9.87×10^{-2}	9.91×10^{-2}	1.51×10^{-1}	9.50×10^{-2}	1.11×10^{-1}
Water Consumption (m^3)	1.63×10^{-2}	2.04×10^{-2}	1.52×10^{-2}	1.52×10^{-2}	1.97×10^{-2}

3.8. Conclusions and futures perspectives

This study confirms that a range of biogas upgrading technologies are available both on a commercial and research scale. Several industries can apply this kind of techniques as a method to generate their own energy for consumption – cutting cost option. Some examples of this industries are water treatment plants, agriculture companies or any other which produces residues considered as biomass. Mainly these techniques are focused on the removal of CO_2 as major contaminant with the potential for meaningful cuts in CO_2 emissions globally. Among the different alternatives presented chemical scrubbing stood out to achieve high biomethane purities. Cryogenic technologies proved to be effective when not highs CH_4 losses are allowed. Regarding the different costs, water scrubbing presents the minimal OMC while the lowest CC refers to membrane separation plants. As it is gathered in this paper, technological advances in this field are being a slow but constant process. The number of studies on biogas upgrading technologies continues to increase achieving promising results, hence it is of vital importance to continue investing in researching to bridge the differences between the pilot scale and the industrial scale of innovative options.

Future work should be aimed at the economic improvement of the processes mentioned above since the yields already obtained have proved to be satisfactory. Since membrane based biogas upgrading technologies may be the most affordable among this technologies, further efforts on reducing CH_4 losses are needed. This could help to this type of technique to achieve a commercial scale presence more active.

CHAPTER IV: Carbon capture and utilization technologies: A literature review and recent advances

4.1. Objectives

The main objective of this chapter is to provide a range of technologies to use the CO_2 previously capture from biogas. Therefore, this chapter presents a comprehensive list of carbon capture and utilization (CCU) technologies and applications, ranging from lab-scale R&D activities reported in academic papers to commercially established uses of CO_2. A literature review and recent advances of each technology are deeply explained. Furthermore, most relevant life cycle assessment and economic studies carried out by experts in this field are included in order to evaluate the best environmental – sustainable – profitable option for a potential application in the process of this work.

4.2. Introduction

CO_2, as a source of carbon, has the potential to be used as a solvent, as 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. CCU seeks not only to reduce the volume of emissions to the atmosphere, but also to obtain a benefit through the use of CO_2 in different types of industrial processes, replacing conventional raw materials [104,177]. 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 [178]. The studied technologies have been grouped in four categories as shown in Figure 4.1: CO_2 as solvent, Chemicals from CO_2, Fuels from CO_2, and Enhanced Oil Recovery (EOR) & Enhanced Coal Bed Methane (ECBM).

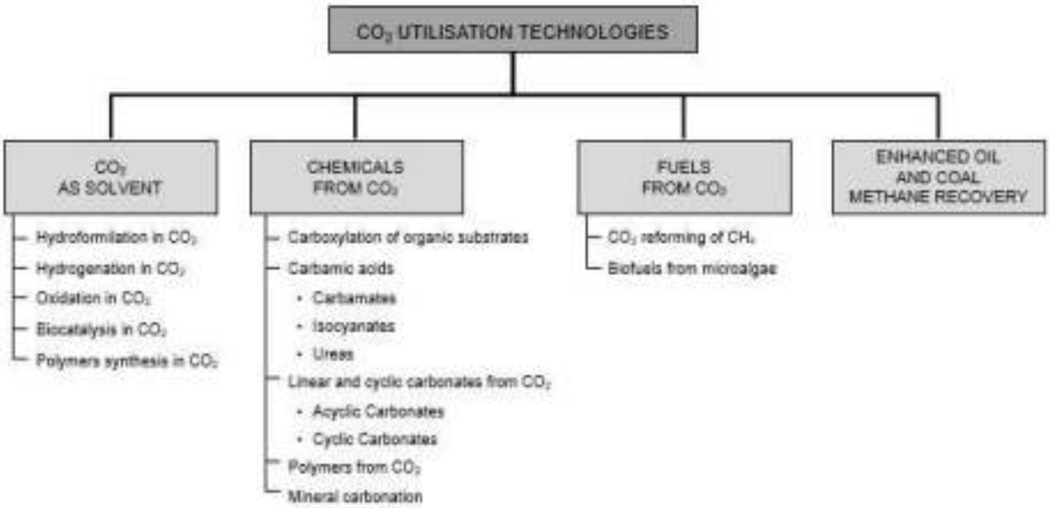


Figure 4.1. CCU technologies included in this study.

4.3. Carbon Capture and Utilization Technologies

The use of CO_2 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. Its use would reduce CO_2 emissions into the atmosphere and could lead to a reduction in the extraction of CO_2 from fossil fuels, as well as an economic saving for companies that consider their utilization [104,179–182]. On the one hand, the direct or technological use of CO_2 includes applications such as the extraction of compounds with supercritical CO_2 ($scCO_2$), dry cleaning, water treatment and food industry uses, among others. In the case of the food industry, CO_2 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 [104]. On the other hand, for the biological use, it is worth mentioning the direct fixation of CO_2 in fast growing biomass. This can help to reduce the accumulation of CO_2 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 [104,179]. Finally, the chemical use consists on the conversion of CO_2 into other products, such as methanol, acetic acid, carbonates and polymers, among others [104,182].

4.4. CO_2 as a Solvent

The use of solvents in the chemical industry involves large costs, both environmental and economic. The use and separation of solvents entails 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 [104,183–186]. Under these conditions, CO_2 appears as a possible candidate, which seems to meet all the criteria, except that related to global warming. Even so, this CO_2 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 CO_2 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 [179,183,187,188].

CO_2 can be used as a solvent in both liquid (lCO_2) and $scCO_2$ states. A pure gaseous component is considered in a supercritical state when its temperature and pressure exceeds its critical values, for CO_2 these are 304.1 K and 7.4 MPa respectively [188]. Its easily accessible critical point, high diffusivity, low viscosity and surface tension make

CO_2 even more attractive as a solvent [104,183–186,188,189]. Properties of the solvents can be expressed through different parameters such as dipole moment, dielectric constant, refractive index or solubility degree. $ScCO_2$ has characteristic properties of non-polar solvents, such as n-hexane. Table 4.1 shows some properties of lCO_2 and $scCO_2$.

Table 4.1. lCO_2 and $scCO_2$ physical properties [183,190]

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}	$1.060 \times 10^{-4\,C}$	0.846 ^{C}	0.090 (Var)	1.10-1.50
lCO_2	1.000 ^{B}	$1.200 \times 10^{-4\,E}$	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) [191] . 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) [183,192]. 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 [104,193]. 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 [194]. 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) up to between 10 to 20 (batch reactor) 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, 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 [104]. The reactions where the use of $scCO_2$ has been most developed are hydroformylation, hydrogenation, oxidation, biocatalysis and polymers synthesis [104].

4.4.1. 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 [195]. 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 [104,183,195].

4.4.2. 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 4.2.

Table 4.2. Hydrogenation reactions in $scCO_2$. Modified from [196].

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

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 hours. However, at the conditions of 55 bar of expanded CO_2, the reaction achieves a 97% conversion after only one hour [183,196–200].

4.4.3. Oxidation in CO_2

Another reaction that has been the target of several investigations, is the selective oxidation of organic substrates in dense CO_2. One of the key aspects that CO_2 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 [104,183].

Some of the most recent studies [201,202] 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 $scCO_2$ has concluded that cyclohexanol has the highest selectivity in $scCO_2$ (98%) [201]. However, using Fe (II) scorpionate complexes, the highest selectivity of the cyclohexanone was given for a mixed solvent medium of $scCO_2$ and an ionic liquid (bmim-PF6), reaching values up to 96%, while the maximum obtained in pure solvents was 77% [203]. The partial oxidation of alcohols to obtain carbonyls or carboxylic compounds are of high industrial interest. Thus, $scCO_2$ 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% [104,204,205].

4.4.4. Biocatalysis in CO_2

Another field in which $scCO_2$ can be used as a solvent is biocatalysis. The capability of being adjusted in its properties and its previously mentioned characteristics make the $scCO_2$ especially suitable for use in organic synthesis. The attractive idea of combining natural catalysts such as enzymes with a natural solvent such as CO_2 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, $scCO_2$ 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 $scCO_2$ has tried to be avoided due to the interactions between the solvent and the catalyst, which lead to the generation of carbamates [183,206,207].

4.4.5. Polymers Synthesis in CO_2

$ScCO_2$ 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 $scCO_2$ as a solvent in polymerization reactions has a drawback, since high molecular weight compounds, especially polymers, are generally poorly soluble in $scCO_2$ under relatively soft conditions ($T<373$ K, $P<35$ MPa) [188,208–210]. Polytetrafluoroethylene (PTFE) was synthesized in a heterogeneous CO_2 medium, using a water-soluble persulphate 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 [211,212].

4.5. 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.

4.5.1. 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 [213–215]. 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 (-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 [216]. 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 [217]. Subsequently, this sparked research into variations of this reaction such as some works have presented [218]. They carried out several studies proposing different promotors 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 $ZrO\text{-}SO_4^{2-}$ 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 4.3 represents an extract of the results produced in two studies for HBA obtaining.

Table 4.3. Extract of results obtained for the two studies on the direct synthesis of HBA [218,219].

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 [219]				
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 CO2 in the presence of aluminum bromide [218]				
ZnCl2	5.20	5.20	0.00	100.0
ZnBr2	12.90	12.90	0.00	100.0
AlCl3	2.70	2.70	0.00	100.0
AlBr3	55.90	55.90	0.00	100.0

As can be seen in Table 4.3, 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 suggested, since the greatest increase in HBA formation occurs at this amount [219]. 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 [214,220]. 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 [220–223]. 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 [221].

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 [214,224–227].

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 [214,228].

4.5.2. 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 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 ($RR'NCO_2$). 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 [229].

4.5.2.1. Carbamates

The carbamate esters (urethanes) are fundamental structural elements for the development and obtaining of therapeutic agents, such as drugs or agrochemicals [230]. 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 CO_2 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 Cs_2CO_3 as a base, tetrabutylammonium iodide as an additive and Dimethylformamide (DMF) as a solvent, under a CO_2 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% [231–233].

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 CO_2. Various radio-labelled carbamates were obtained by the treatment of $[^{11}C]$ CO_2 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 CO_2 halides in very soft conditions, at atmospheric pressure of CO_2 and at room temperature, using K_2CO_3 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 CO_2. 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 CO_2 at atmospheric pressure, using Cs_2CO_3 as a base in Dimethyl sulfoxide (DMSO). The reaction provided the carbamates corresponding to 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-ethylbenzonitrile bromides and CO_2 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 [234,235]. 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 CO_2 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 CO_2 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.

4.5.2.2. 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 [229,236,237]. 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 CO_2, 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 CO_2, amines and alcohols [236].

The synthesis of carbamates by reacting CO_2, amines and alcohols were tested in [238]'s work. Initially, they used tin-based catalysts at pressures of 30 MPa of CO_2 and 200°C. After 24 hours 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 [238,239]. Honda et al. (2011) used commercial CeO_2 as a heterogeneous catalyst to synthesize methyl benzyl carbamate in one step from CO_2, benzylamine and methanol. Under a pressure and temperature of CO_2 of 5 MPa and 150°C, after twelve hours 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 hours. More recently, a catalyst of cerium and manganese ($MnOx$-CeO_2) was prepared, which showed high activity in the synthesis of aliphatic carbamates from CO_2, 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 [240]. Although there have been several studies conducted in recent years regarding the use of CO_2 for the synthesis of isocyanates which are also summarized in Table 3.4, most are still in pilot scale [236].

Table 4.4. Summary of studies on the synthesis of carbamates to obtain isocyanates from CO_2 [236,241–243].

Catalyst	**Operating conditions**	**Yield (%)**
Bu_2SnO	200 ºC, 24 h, 30 MPa CO_2	14
Bu_2SnO	$Me_2C(OEt)_2$, 200 ºC, 24 h, 30 MPa CO_2	84
$Ni(OAc)_2$-bipiridina	200 ºC, 24 h, 30 MPa CO_2	67
Cs_2CO_3	200 ºC, 24 h, 2.5 MPa CO_2	44
CeO_2	150 ºC, 12 h, 5 MPa CO_2	91
$MnO_x(0.03)$-CeO_2	150 ºC, 12 h, 5 MPa CO_2	82

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 CO_2; 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.

4.5.2.3. Ureas

In this section the manufacturing of urea from CO_2 will be looked into. The synthesis of urea is currently the main consumer of CO_2 in organic synthesis. Urea, ($CO(NH_2)_2$), is the most widely produced nitrogen fertilizer and is commonly marketed. It is produced at industrial level via the reaction of ammonia with CO_2, a two-stage process where ammonia and CO_2 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 and 250°C with pressures of 5-25 MPa [244,245].

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 CO_2 by NH_3 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 NH_3/CO_2 and the frequency of discharge. Recently, the use of metal salts of oxalates as catalysts for the synthesis of N, N'-dialkylureas from CO_2 and amines was described [246]. 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 $Y_2(C_2O_4)_3$ being the catalyst that provided higher yields. Under the optimal conditions, which were found to be 20 atm of CO_2, 10 atm of NH_3 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'-dialkyloxamide, Nalkynylcyanate and N-N'-dialkyl carbodiimide. A recent method for the production of ureas in which primary amines and CO_2 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 CO_2), the aliphatic primary amines react gently with CO_2 to give ureas of different types, with a selectivity of 100% and yields that in some cases reached up to 97% after 24 hours of operation [247]. 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 CO_2, amines or carbamates so to be able to take them as soon as possible on a large scale.

4.5.3. Linear and Cyclic Carbonates from CO_2

Among the various chemical conversion processes that involve the transformation and consumption of CO_2, 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 ($COCl_2$) and carbon monoxide (CO) [248,249].

4.5.3.1. Acyclic Carbonates

In recent decades, the synthesis of CO_2 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 [250,251]. More than 90000 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 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 [252,253]. Most acyclic carbonates are synthesized from alcohols and CO_2 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 [254,255].

Some of the studies carried out on homogeneous catalytic systems for the formation of DMC from methanol and CO_2 investigated the use of titanium, zirconium and nionium compounds, as well as complexes of tin and other organometallic compounds, whose efficiency was quite low [256]. Furthermore, using ortho-esters as a dehydrating agent and $[Bu_2Sn(OMe)_2]$ 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 CO_2 and 180°C, resulting in a problem concerning ortho-esters including difficult recycling [257]. 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 tin catalyst [258]. Organic desiccants were also used, which made zeolites, considered inefficient at high temperatures, achieved yields of up to 45% in DMC from methanol [243]. 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 CO_2 with CeO_2 as a catalyst, since at 0.5 MPa of CO_2 and 150°C, the yield of DMC after 48 hours 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 hours of operation under a pressure of 1 MPa and at 150°C [259].

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 hours of reaction at 5 MPa of CO_2 and 120°C were surprisingly high. In addition, the use of 2-cyanopyridine as a desiccant had the advantage that its dehydration by Na_2O and SiO_2 was feasible, although its efficiency could be improved [260,261]. Due to the excellent results in performance and selectivity registered when combining CeO_2 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 4.2.

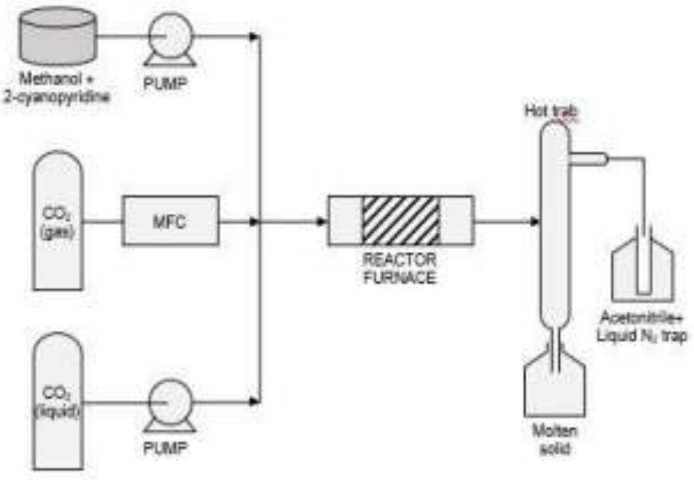


Figure 4.2. Flowchart of the continuous process for the production of DMC. Adapted from [262].

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 CO_2, while the CO_2 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 4.5.

Table 4.5. Results of the analysis of the effects of temperature and pressure in the continuous production process of DMC from CO_2 and methanol, with 300 mg of catalyst [262].

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 CO_2, and that the optimum operating temperature was 120°C, as presented in Table 4.5. 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 [262]. 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 CO_2 and diols [263,264]. 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 CO_2, 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 hours of operation, working between 90-100°C [265]. 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 CO_2) 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 [248]. Another method reported for the manufacture of DMC is the electrochemical synthesis from methanol, CO_2 and propylene oxide in an ionic liquid (bmimBr). Under optimum conditions; temperature of 30 °C, atmospheric pressure of CO_2, with a molar ratio of methanol / propylene oxide of 11.5:1 and after 48 hours of reaction, 97% conversion of methanol as well as the yield of the DMC of 75.5% was obtained [241].

4.5.3.2. Cyclic Carbonates

The production of cyclic carbonates from CO_2 synthesis is a well-established field. One of the most investigated reactions in this field is the addition of CO_2 to epoxides which has also been used on an industrial scale for the manufacture of cyclic carbonates and polycarbonates (PC) [249]. For the reaction of epoxides with CO_2, 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 CO_2 with epoxides. Relatively adverse conditions, more than 6 MPa of CO_2 at 130 ºC for 48 hours, were necessary to obtain satisfactory results from the use of amino acids [266]. Even so, when combining alkaline metal salts with aminoacids, excellent results were reported, reaching a propylene oxide conversion of 99% after one hour of operation at a temperature of 120 ºC and 2 MPa of CO_2 [267].

Chang et al. (2018) recently proposed the use of wool powder (WP) as a catalyst for the coupling of epoxides with CO_2. By having hydroxyl, carboxyl and sulfonic acid groups, which turn out to be activators of epoxides while amino groups are the activator of the CO_2 molecule, it seems to be a good candidate to catalyze this type of reactions. Using CO_2 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 hours of operation at 120 °C and 1.5 MPa of CO_2, and without the use of any solvent, the results obtained are shown in Table 4.6.

Table 4.6. Results of PC synthesis from different catalysts. Modified from [268].

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

When WP was exclusively used, PC performance was only 12%, while as can be seen in presented Table 4.6, 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 hours, reaching its maximum in 94%, practically constant even when the operating time increased [268].

The direct carbonylation of glycerol and CO_2 to obtain glycerol carbonate (GC) is a very interesting and challenging route, since it would involve converting two materials considered as waste into into a valuable products for the chemical industry [269]. One of the most recent studies about the synthesis of GC, deals with the carbonylation of glycerol with CO_2 on cerium oxide catalysts, using as a desiccant agent of 2-cyanopyridine. Under optimized operating conditions of 150 °C, 4 MPa of CO_2, 10 mmol of glycerol, 30 mmol of 2-cyano-ridin and 10 mmol of CeO_2 producing GC with the yield of approximately 79% after 5 h of reaction [270]. Using the same system of CeO_2 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 ºC and 5 MPa of CO_2 while using 20% molar of catalyst [264].

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 CO_2 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 have made it possible to use more ecological and sustainable catalytic methods in pharmaceutical production and bulk chemistry.

4.5.4. Polymers from CO_2: Polycarbonates and Polyurethanes

The use of CO_2 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 CO_2 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 CO_2 are biodegradable [271,272]. Polycarbonates obtained from CO_2 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 [273].

The most widely studied CO_2-based copolymers are propylene polycarbonate (PPC) and cyclohexene polycarbonate (PCHC), synthesized from propylene oxide (PO) and cyclohexene oxide (CHO), respectively [274]. 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 CO_2 is treated, due to its high stability [275]. 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 [276]. 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) [272]. 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 26000 h^{-1} with low catalyst loads (ratio [catalyst] / [PO] = 1: 25000) [277]. Lee et al. (2005) were pioneers in the use of a series of complexes of bis(anilido-aldimine) 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 CO_2 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 $Zn_3(CoCN_6)_2$. In some cases, they are used industrially as epoxide homopolymerization catalysts, although for their use in CO_2 copolymerization much stronger conditions are required than for homogeneous catalysts. They need high CO_2 pressures and generally produce polyether carbonates instead of polycarbonates [272,278]. 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 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 [279].

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) [279], 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%) [280]. In addition, the PU synthesized from these polyols presents an improved resistance to oxidation and hydrolysis with respect to that based on polyether polyol [281]. 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 [272]. To reduce this problem, the use of organic dicarboxylic acids as initiators has begun to be carried out. Using sebacic acid as 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% [282]. The CO_2-triol was synthesized in a similar way using 1,3,5-benzene tricarboxylic acid (TMA) as initiator, providing an MN between 1400-3800 g/mol and a content of CU somewhat lower than for the CO_2-diol (20-54%) [283]. 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 [272]. 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 catalyst after

6 hours of operation at 2 MPa of CO_2 and 75°C [284]. 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% [285,286].

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.

4.5.5. 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 [179,287].

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 [288], while approximately 39 million Gt of carbon are present in the carbonated rocks of the earth's crust, such as marble, limestone or chalk [150,289]. 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 [289,290]. 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 4.7 [287,290].

Table 4.7. Industrial waste suitable for mineral carbonation [291,292].

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

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 [290]. When dealing with this project of using CO_2 to obtain useful chemical products, only ex situ carbonation will be developed (Figure 3.3) [293].

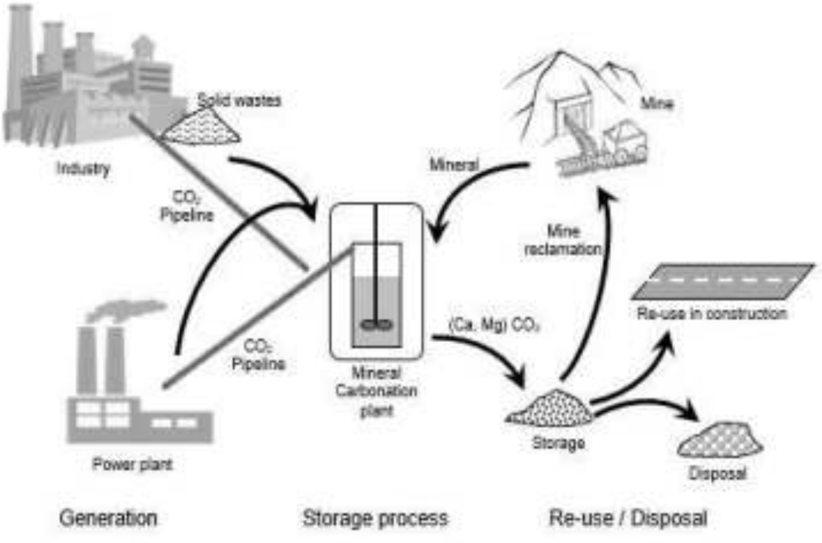


Figure 4.3. Ex situ mineral carbonation process. Adapted from [293].

As can be observed in Figure 4.3, 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 [294]. 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 [290,293,295]. 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 [145,146,149,290,296]. 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 [297]. 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 of 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 of CO_2 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 CO_2 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 CO_2 emissions on a large scale.

Aqueous mineral carbonation of Ca-Mg hydroxides or chlorides to obtain $CaCO_3$-$MgCO_3$ is a promising alternative which should be taken into consideration. In this process, first CO2 need to be capture by a basic compound which typically is NaOH or KOH. Both solvents are difficult to regenerate by means of traditional thermal methods as can be done with MEA or other amines. Then, to keep the process economically affordable, the hydroxide compound is regenerated through chemical reaction with the above-mentioned Ca-Mg hydroxide-chloride. Even though, no many studies have been presented to this moment since again the carbonate quantity to be launched into the market would be massive. For this reason, there is a need of focusing on small-medium CO_2 producers such as for example biogas producers. Some studies have focused on mineralizing aqueous CO_2 previously captured through residues such as Air Pollution Control (APC) wastes. An example of this process can be seen in Figure 3.4. In this case, the final carbonate agent can be employed in many sectors such as civil engineering, construction, concrete bricks or building materials.

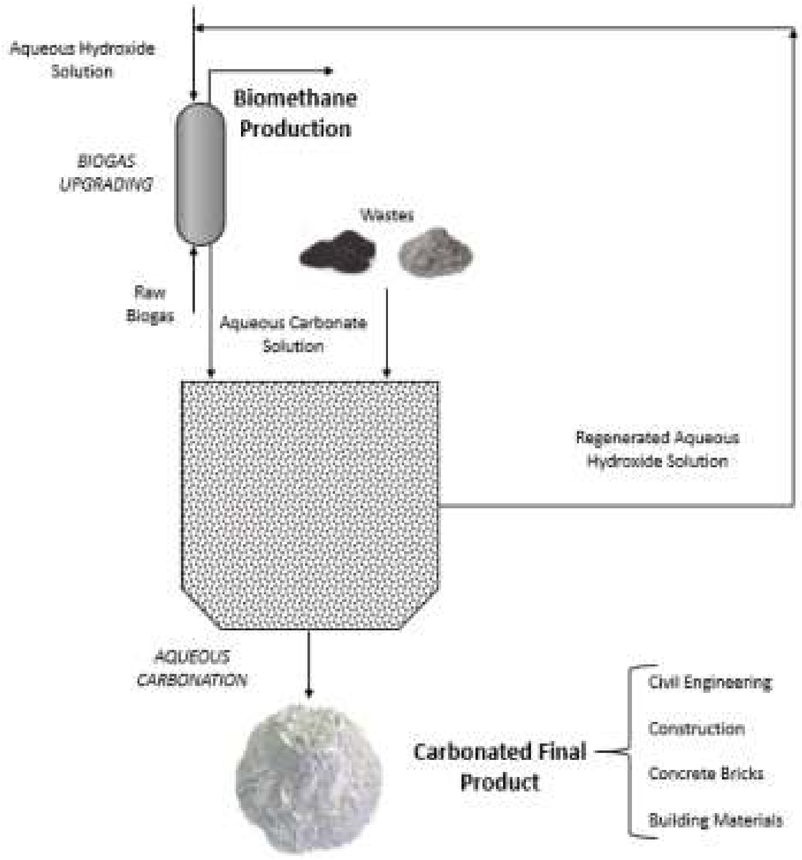


Figure 4.4. Regeneration stage through aqueous carbonation with waste as precipitating agent in a biogas upgrading plant. Adapted from [298].

4.6. Fuels from CO_2

Converting CO_2 into fuels generally requires a reforming reaction, typically, hydrocarbon and carbon reforming reactions and hydrogen reforming reactions (hydrogenation) [299,300]. The main processes to obtain fuels from CO_2 are syngas from reforming of CH_4, gas hydrates and biofuels from microalgae.

4.6.1. CO_2 Reforming of CH_4

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 [301]. Approximately 75% of the hydrogen produced is obtained by this process, due to its higher performance compared to the other two alternatives [302].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) [301,303].

$$\mathrm{CH_4 + H_2O \rightarrow CO + 3 \cdot H_2} \qquad \Delta H_{298K} = +228\ \mathrm{kJ/mol} \qquad (1)$$

$$\mathrm{CH_4 + \frac{1}{2} \cdot O_2 \rightarrow CO + 2 \cdot H_2} \qquad \Delta H_{298K} = -22{,}6\ \mathrm{kJ/mol} \qquad (2)$$

$$\mathrm{CH_4 + CO_2 \rightarrow 2 \cdot CO + 2 \cdot H_2} \qquad \Delta H_{298K} = +247\ \mathrm{kJ/mol} \qquad (3)$$

Thus, among 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 [304]. 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 [305,306].

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 [301,305,306]. Several authors concluded that the main and desired reaction of the dry reformate is favored thermodynamically at temperatures above 730 °C, although to achieve a 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 ºC are required [301,304,305,307]. 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 ºC, which is favored by a CO_2/CH_4 ratio greater than unity, due to the presence of H_2 [306]. 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 = 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 a H_2/CO ratio of the unit in the synthesis gas produced, temperatures higher than 850 ºC were necessary, thus giving the greatest conversion of reagents and the best performance [308]. 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 CH_4 and CO_2, respectively [309].

Despite its great environmental potential, DRM is not considered an industrially mature process. 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 CO_2. 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.

4.6.2. Gas Hydrates from CO_2

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), CH_4 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 m^3 of CH_4 hydrate below the ocean, which is more than all of the current fuel sources combined [310,311]. Many researchers in the past decades have studied the recovery of CH_4 hydrate from the ocean floor at various conditions [310–313], and more recently the idea of the replacement of CH_4 in the hydrate with high pressure CO_2 emerges as a long term storage of this gas and a way to keep the ocean floor stabilized after recovering CH_4 gas [314]. Also, the direct use of CO_2 hydrate in oil production pipelines has been reported by some authors, as well as CO_2 hydrate-technology which is growing in relative to transportation processes [315–318].

The advantages of CO_2 hydrate as a way of capturing are numerous. Firstly, the main chemical compound needed for CO_2 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 [313,319]. 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 [320,321]. Studies have been conducted where the feasibility of employing eutectic freeze crystallization with CO_2 hydrates for the separation of highly soluble salts from aqueous solutions has been shown [315,322,323]. Also CO_2 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. CO_2 hydrate based process can also be a good alternative to freeze-crystallisation processes to concentrate water-rich streams which require relatively low temperatures [315]. Another usage of CO_2 hydrate is to increase CO_2 concentration in culturing algae, where its addition to algal culture systems can increase algal biomass effectively [324].

4.6.3. Biofuels from Microalgae

Microalgae cultivation can be carried out in submerged areas, infertile lands and seawater [325,326]. The cultivation of algal biomass, apart from providing biofuel feedstock, has a favorable environmental impact by reducing the concentration of greenhouse gases because it consumes large amounts of CO_2 [327,328]. 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 CO_2, nitrogen and phosphorus [325,329,330].

There are three different sources of CO_2 for microalgae: atmospheric CO_2, industries emissions of CO_2 and CO_2 from soluble carbonates [108]. Moreover, there are two kind of possible ways to carry out microalgae cultivation: in open raceway ponds or photo-bioreactors (flat-plate, annular or tubular) [299,331]. 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 [331]. 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 [179]. Microalgae cultivation does not compete to food markets that makes them especially interesting for futures researches. These research should be lead towards a reduction of the cultivated area needed and a reduction of general costs [332]. Figure 4.5 presents a block diagram of the process needed to convert microalgae to biofuels. In this process, after converting a carbon sources in a flue gas, a microalgae cultivation stage is employed to obtain a wastewater biomass that will be dry before its transformation into biofuels.

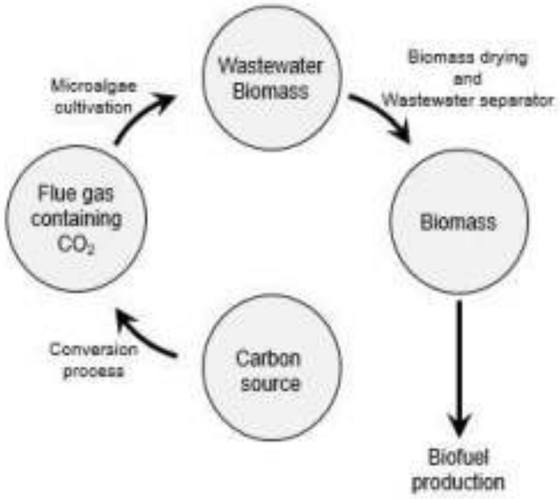


Figure 4.5. Biofuels from microalgae process. Modified from [332].

4.7. 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 CO_2 being the most common [333]. The use of CO_2 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 CO_2 is an efficient agent displacing oil and natural gas [334].

EOR with CO_2 injection is the second most improved hydrocarbon recovery technique after water injection according to the International Energy Agency [335]. Its application is preferable in oil fields with a depth greater than 800 meters that have at least between 20% and 30% of the original oil, in which there have been previously applied secondary recovery methods [336]. The injection of CO_2 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 CO_2 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) [337,338]. Lately, EOR studies assessed the impact of various methods for allocating CO_2 system emissions and the benefits of sequestration under a number of different scenarios [336,339]. Also, some studies developed some methodologies for the identification and screening of oil reservoirs that are suitable for CO_2 flooding [340,341]. Moreover, Li et al. (2016) modified these applications for estimating CO_2 sequestration capacity at depletion as well as under enhanced oil recovery [342].

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 [343–347]. EOR has been practiced for long periods of time in countries such as the United States or Canada. However, ECBM is under test phase [348]. The information collected in this section argues that CO_2-EOR deserves to be a major part of a worldwide carbon management strategy. According to IEA, growth in production from CO_2-EOR is now limited by the price of CO_2 [335].

4.8. Life cycle assessment and economic studies for carbon capture and utilization techniques

Subsequently, a comparison of the environmental impact of CCU technologies studied based on LCA found in the literature, summarized in Table 4.8, 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 CO_2 capture [179,349].

Table 4.8. LCA studies available for CCU options.

Reference	CCU option	Process	Scope	Co_2 capture method	Functional unit (kg of co_2 per item indicated)
[350]	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
[254]	Acyclic 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
[351]	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
[352]	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
[281]	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
[353]	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	Post-combustion capture via MEA	Production of 1 kg of synthesis gas

			of synthesis gas produced by each method is very different.		
[354]	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
[339]	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
[355]	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

Summarizing the alternatives included in Table 4.8, the studies performed reflect that the most environmental respectful CCU technology may be EOR (Global Warming Potential in the range of 0.45-0.55 t CO_2 eq/t CO_2 removed), followed by mineral carbonation (Global Warming Potential in the range of 0.5-1 t CO_2 eq/ t CO_2 removed). The production of polymers is still far from being environmentally competitive, as the Global Warming Potential showed is one hundred times greater than mineral carbonation and EOR [179]. Chemical and fuel production Global Warming Potential depends on the fuel – chemical produced and hence the impact of this category can be considered as medium. Concerning economic studies on CCU technologies, different values have been found in the literature. These differences are mainly caused by the different plant sizes considered (effect of economy of scale) and the location, as well as other assumptions taken in each study. Therefore, finding reliable or standardized data is difficult. In agreement with a recent report launched by Repsol, EOR and mineral carbonation are the technologies more economically suitable, followed by the production of construction materials and fuels [356]. Table 4.9 collects the economic data mentioned.

Table 4.9. Economic data for CCU options [356].

CCU option / Product	**Key Insights**	**Economic estimation**
EOR	Mature technology with nearly 50 years of experience. Part of the CO_2 is permanently trapped (40-71% CO2 injected)	9-15
Mineral carbonation	Mafic rocks are abundant and widely distributed. Validated at pilot scale and ongoing industrial scale.	22

	Rocks composition (rich in magnesium, iron and calcium) could facilitate chemical reactions with CO_2, potentially leading to mineral trapping.	
Construction materials	Alternative to carbonate wastes and salts – hydroxides. High energy intensity pretreatment processes. Low added value products restrict commercial roll-out.	180
Fuels	Thermochemical pathways require cheap green hydrogen sources. Biological pathways normally have low yields.	350
Methanol	Carbon Recycling International have deployed a small commercial scale plant (4000 ton/year). Lack of incentives for green chemicals restricts methanol to fuel use.	350
Polymers	Relative impact on CO_2 reduction depending on market volume. Thermoplastics, Polyurethane foams and Polycarbonates can be produced using CO_2 as feedstock.	1600

4.9. Conclusions and Future Prospect

This study confirms that a range of CCU technologies are available for use in several applications. From direct utilization of CO_2 as a solvent or for chemicals production, to obtain fuels or improve EOR techniques, with the potential for meaningful cuts in CO_2 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 CO_2, 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 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 CO_2 into the atmosphere. The economic studies performed over CCU alternatives cover a wide range because many factors impact on the final economic results. Among the options for mineral carbonation, mineral aqueous carbonation is a promising alternative for medium and small CO_2 producers which could help to balance the cost of gas cleaning or biogas upgrading. 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 CO_2 consuming microalgae for the generation of ethanol and the use of electrochemical reactions that are showing initial results of great interest. Moreover, more studies should focus on aqueous mineral carbonation for small CO_2 producers as a help for both GHG mitigation and value-added chemicals production. The key in this technology is to find suitable waste to employ as precipitating agent in the solvent regeneration stage. Overall, the main objective of every technology will be to improve the processes already studied, increasing the activity of the catalysts and the performance of the final products.

CHAPTER VII: Absorption stage. CO_2 capture from biogas.

7.1. Objectives

The goals of this chapter are basically the next ones:

- First, a screening of different solvents which could performance CO_2 absorption in biogas streams is addressed. The selection of the mentioned solvents is also carried out based in some criteria which will be explained below.
- Evaluation of the different solvents selected through an experimental plan which will be define in the proper section.
- Assessment of the optimal conditions in which a maximum exploitation of the solvents is gotten.

7.2. Materials and methods

7.2.1. Solvent screening and selection

For the proper characterization of the different commercially available solvents, part of the review presented in Chapter II have been used. First of all, the main characteristics that the solvent must have need to be settled, in order to be suitable in the application process described in Chapter IV. According to the objectives and expected results of the project, these characteristics are pointed out below:

- The solvent should be used in high concentrations, so that the liquid to gas ratio (L/G) in the absorption tower is minimal. This favors the energy costs derived from the supply of the liquid solution and leads to a smaller volume of equipment.
- The solvent may possess a high selectivity for CO_2. Thus, a lower tower height will be necessary to remove the contaminant.
- The solvent may cause little loss of CH_4, so that maximum benefit can be obtained by the selling of biomethane.

- The compound produced after absorbing CO_2 must have a high osmotic potential, which allows to achieve a concentration factor as high as possible of nutrients from anaerobically digested sludge centrate in the next stage of the process.
- The solubility of both the solvent and the compound formed after CO_2 absorption stage must be high in order to avoid fouling phenomena either in the absorption tower or in the membranes forward osmosis stage.
- The solvent should be regenerated by means of chemical reaction, producing a solid sub-product containing the CO_2 captured. Thus, remarkable energy savings can be obtained avoiding the thermal regeneration of the solvent, which, as it has been seen in Chapter II, is the key point in CO_2 chemical absorption nowadays. The solid product may be interesting from a commercial point of view in order to improve the overall economic performance of the process.

Based on the characteristics previously explained and in the state of the art presented in Chapter II, the main solvents for biogas upgrading can be divided into two different groups:

- Alkaline groups: in this group is a subdivision between high solubility compounds (NaOH, KOH and NH_3) and low solubility compounds ($Mg(OH)_2$, $Ca(OH)_2$) is typically found. High solubility compounds such as NaOH and KOH are very prone to capture CO_2 in biogas streams. Furthermore, fouling phenomena is avoided and CH_4 losses are almost null. Additionally, the product compounds formed after the CO_2 absorption stage have a high osmotic potential, which can favor the subsequent stage of concentration of nutrients from anaerobically digested sludge centrate. Moreover, some authors have proved that it is possible to regenerate the solvent in another subsequent stage, giving a value added compound as by-product [146,359,360]. On the other hand, low solubility compounds are Mg-Ca hydroxides. These basic groups have a very low solubility in water, of around 0.185g/100 cm^3, which would cause encrustation in the filling material of the tower and in the membrane stage [361,362]. Therefore, these kind of compounds are not suitable directly for absorption application.

- Amine groups: such as for example monoethanolamine, diethanolamine, diglycolamine and methyldiethanolamine. The use of amines in CO_2 absorption applications is widely studied and extended at research and commercial level. Without a doubt, amines are the chemical compounds that allow to work with better L/G, they have the highest CO_2 selectivity so far and produce few CH_4 losses. As was also explained in Chapter II, the capture efficiencies are the quite promising compared to other possible solvents. For the present application, the compound formed after the chemical absorption stage would have a high osmotic potential that would be used again to favor the subsequent stage of nutrients concentration from anaerobically digested sludge centrate. However, amines present a problem that does not make their use advisable in this project. The regeneration stage of amine solvents has been typically carried out by thermal regeneration methods which are highly intensive in terms of energy consumption. This means, in addition, that the CO_2 that would be obtained after regeneration would not be a CO_2 that formed part of a valorizable compound, but a pure CO_2 in the gas phase that would have to be stored in tanks or emitted into the atmosphere. Chemical reaction regeneration via is still possible but NaOH and KOH are cheaper chemicals than MEA. Moreover, NaOH and KOH could be obtained from saline waste, which would do the process even more interesting from an environmental point of view [363–365].

Considering all the points explained, it was decided to undertake the characterization of NaOH and KOH as solvents for CO_2 because they were the ones that marked a possible best performance, both for their high solubility and their low cost [366]. Subsequently, and to give more generality and flexibility to the study in order to cover possible candidates that may be interesting for both forward osmosis and recovery of commercial by-products, it was also decided to include the characterization of NH_3 and MEA in the analysis. The first of these emerges as a potential candidate to be used to obtain a valuable by-product containing N as an element of interest for using as fertilizer. The second one has been chosen because it is the reference solvent worldwide recognized. MEA is widely used in the industry and very well studied in the literature, which would provide a basis for comparison with NaOH and KOH. The physical characteristics of the absorbents have also been considered for the subsequent design of the test plan. Table 7.1 shows the values of these physical parameters.

Table 7.1. Main characteristics of tested solvents

Solvent	Concentration (M)	pH	Density(kg/L)	Viscosity (cP)
NaOH	2.5-3.75	12-14	1.056-1.111	1-1.2
KOH	2.5-3.75	12-14	1.112-1.845	1.15-1.4
NH_3	2.5-3.75	12-14	0.681-0.759	1.02-1.10
MEA	2.5-3.75	12-14	1.010-1.415	1.09-1.15

7.2.2. Experimental plan

In order to undertake the necessary experimental tests to verify the greater or lesser adequacy of the different solvents tested for the capture of CO_2 in biogas streams, it has been necessary to adapt the experimental plant available. In these experiments, CH_4 was replaced for N_2 as inert compound in order to avoid dangerous scenarios in the laboratory facilities. The proper corrections were done to ensure that this change does not affect to the result obtained. The process conditions of the installation and the simulated biogas are shown in Table 7.2.

Table 7.2. Process and working conditions of absorption stage

Parameter		Value (units)
Height		1000 (mm)
Diameter		32 (mm)
Gas flow		5.18 (l/min) 7.36 (g/min) 0.44 (kg/h)
Gas composition	CO_2	40 (%)
	N_2	60 (%)

Under these operating conditions a series of preliminary characterization tests were performed, from which the basic operating parameters for the upcoming tests were set. Specifically, the minimum duration of each test was evaluated to ensure the stability of the flue gas outlet concentration at each time that the feed conditions change. The operational time was set at 45 minutes (15 charging, 20 stabilizations and 10 sampling). As operating conditions, a base system temperature of 20ºC was set, which ensures that the solvent load does not exceed 30ºC at the exit of the tower. Thus, the safety temperature of the forward osmosis membranes which comes in the next stage is ensured. The operating pressure was set at 1 atm.

For the characterization of the dynamics of the absorption tower, different types of fill were tested with variable gas flow rates, finally identifying the Raschig 6 mm as the most suitable for the working conditions. For the proper performance of the tower with this filling and to achieve maximum flexibility in the L/G ratios for the tests, it was decided to set the gas flow at 5.18 L/min. This allows the L/G ratio to be varied over a wide range from a minimum of 6 to a maximum of 16. It must be borne in mind that, since they are high basic solutions, the characteristic pH is high. This can represent a serious inconvenience in the later stage of membranes, most of which have a limited pH of around 11-12. Above this value the manufacturer does not guarantee that they can operate correctly. Therefore, not all absorbent concentrations that have been tested can be integrated into the final process.

The first solvent tested was NaOH, as it is the most referenced absorbent in CO_2 capture in biogas upgrading applications [145,146,359,362]. Secondly, KOH was characterized as it is another alkaline compound that, together with NaOH, is widely used for biogas upgrading. The third solvent tested has been NH_3 because the final product (ammonium carbamate or ammonium carbonate) is quite interesting from a commercial point of view. Finally, MEA has been tested as a benchmark reference solvent. Table 5.3 shows the ranges that have been varied in the matrix of tests performed for each solvent solution.

Table 7.3. Matrix of experiments carried out

Solvent	Concentration range (M)	L/G
NaOH	1.25-3.75	8-16
KOH	1.25-3.75	8-16
NH_3	2.5	8-16
MEA	2.5	8-16

7.2.3. Materials

All the solvent employed in this work were provided by PanReac-AppliChem (pure-grade or pharma-grade, 99% purity). Those ones were NaOH, KOH, NH_3, MEA. In the case of NaOH and KOH, liquid solutions were prepared by dissolving the pure solid in pure water. NH_3 and MEA were supplied in liquid state and they were adjusted to the concentration needed. Examples of the solvents employed can be seen in Figure 7.1. For the gas phase, CO_2 and N_2 cylinders were supplied by Linde™ to provide the synthetic flue gas under different compositions (Figure 7.2.).

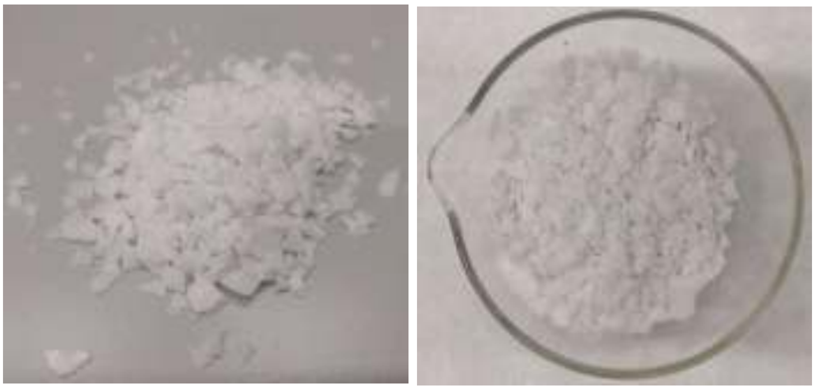


Figure 7.1. NaOH (left side) and KOH (right side).

Figure 7.2. Gas cylinders (N_2 on the left side and CO_2 on the right side).

7.2.4. Experimental setup description

The whole experimental setup scheme of the absorption stage is presented in Figures 7.3 and 7.4. The configuration showed in Figure 7.3 was used for NaOH, KOH and MEA. Nevertheless, to avoid potential problems due to the toxicity presented by NH_3, the configuration showed in Figure 7.4 was employed under an extractor hood.

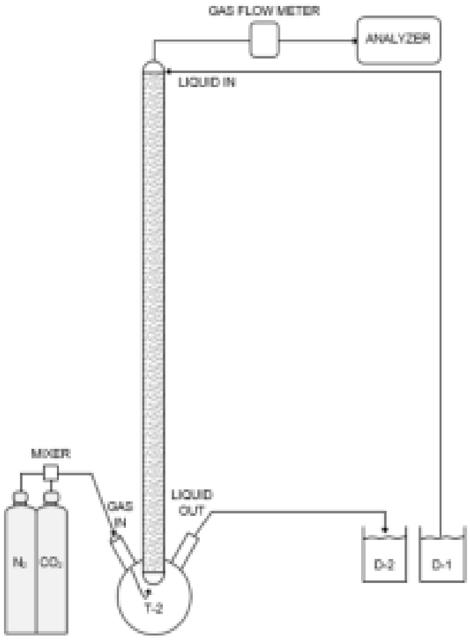


Figure 7.3. Experimental setup scheme of the absorption stage for solvents NaOH, KOH and MEA

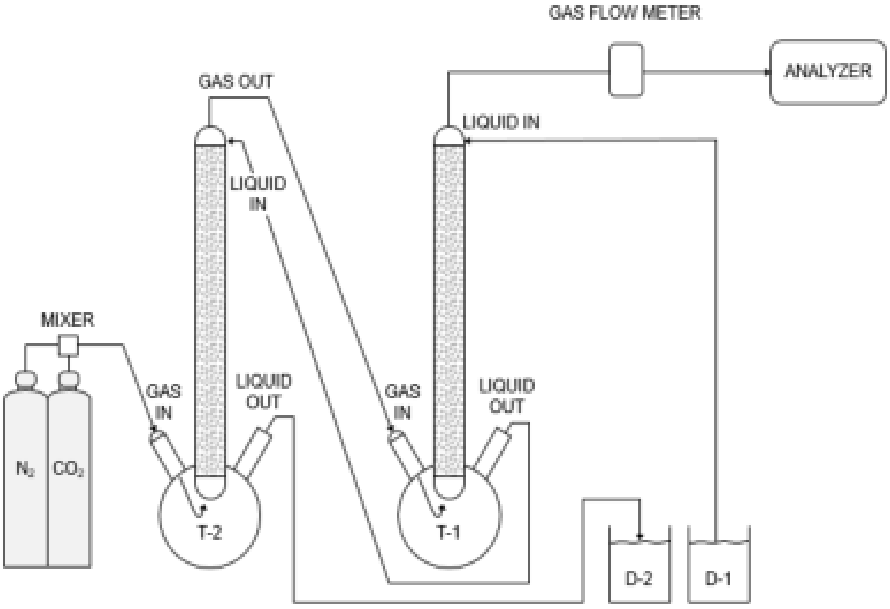


Figure 7.4. Experimental setup scheme of the absorption stage for solvent NH_3

The configurations presented in Figure 7.3 and 7.4 are composed by the following items:

- Liquid deposits (D-1; D-2). D-1 refers to the fresh solvent liquid deposit whereas D-2 storage the final liquid carbonated product (Figures 7.5 and 7.6).

Figure 7.5. Fresh liquid solvent deposit.

Figure 7.6. Final liquid carbonated product.

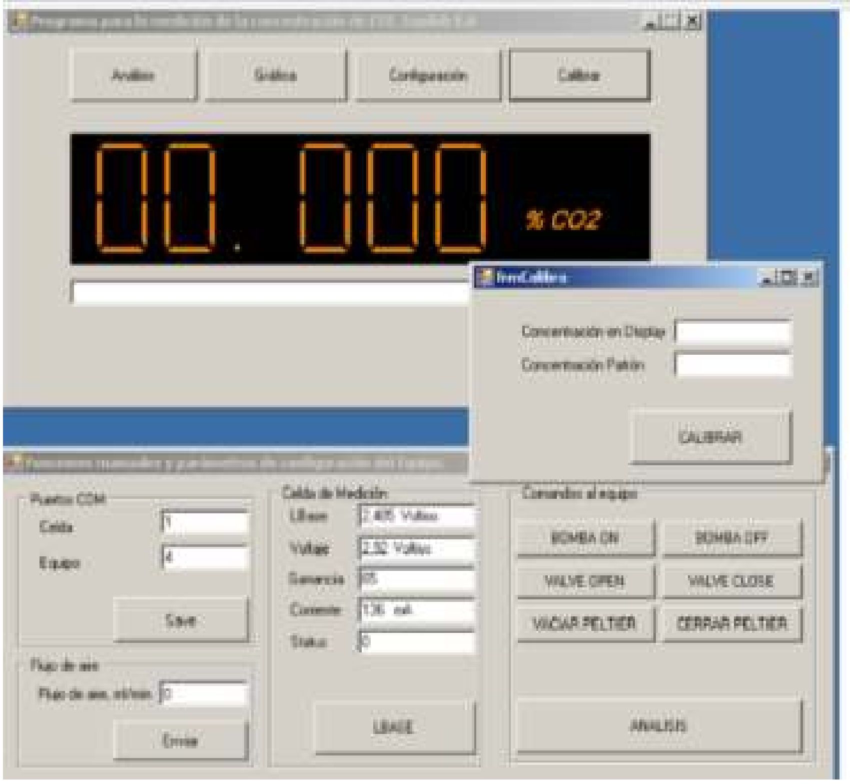
- Absorption towers (T-1; T-2). Depending on the solvent tested, it was formed by a single tower of 1 m (Figure 7.7) or two tower of 0.5 m each (Figure 7.8), as explained above.

Figure 7.7. Absorption tower used for NaOH, KOH and MEA solvents characterization.

Figure 7.8. Absorption tower used for NH_3 solvent characterization.

- CO_2 analyzer (A-1). This equipment was used to obtain the final CO_2 percentage in the gas outlet stream after the absorption stage (Figures 7.9 and 7.10).

Figure 7.9. CO_2 analyzer.



Celda: 1
Equipo: 4
Ubase: 2.405 Voltios
Voltaje: 2.52 Voltios
Ganancia: 05
Corriente: 136 mA
Status: 0
Flujo de aire, ml/min: 0

Figure 7.10. CO_2 analyzer software.

- Pumps (P-1; P-2). P-1 pumps the fresh solvent while P-2 pumps the final carbonated liquid solution (Figure 7.11)

Figure 7.11. Pumps used

- Gas mass controllers (G-1; G-2). G-1 and G2 mass controllers stablish the gas flow of CO_2 and N_2, respectively (Figures 7.12).

Figure 7.12. Gas mass controller.

- Gas bottles (B-1; B-2). B-1 and B-2 bottles storage the compressed CO_2 and N_2, respectively.

Figures 7.13. Gas bottles.

- Gas flow meter (F-1). F-1 controls the gas outlet stream from the absorption tower (Figure 7.14).

Figure 7.14. Gas flow meter.

7.2.5. Matrix of experiments

As explained before in point 7.1.2, the first solvent tested was NaOH. To cover all the possible scenarios 12 tests were carried out with this solvent (tests 1-12 according to Table 7.4). Afterwards, KOH was characterized as solvent for this application through 7 tests (tests 13-19 in Table 7.4). The third solvent tested was NH_3, corresponding with tests 20-29. Finally, MEA was tested as a benchmark reference solvent in 5 tests (tests 30-34 in Table 7.4). Different L/G and concentrations were performed in order to provide a wide range of data to analyze. Moreover, in section 7.2. more data will be presented in agreement with the different needs of each solvent characterization.

Table 7.4. Matrix of experiments

Test	Solvent	L/G ratio	Concentration (M)
1	NaOH	8	2.5
2	NaOH	10	2.5
3	NaOH	12	2.5
4	NaOH	14	2.5
5	NaOH	16	2.5
6	NaOH	10	1.25
7	NaOH	10	3.75
8	NaOH	8	3
9	NaOH	10	3
10	NaOH	12	3
11	NaOH	14	3
12	NaOH	16	3
13	KOH	8	2.5
14	KOH	10	2.5
15	KOH	12	2.5
16	KOH	14	2.5
17	KOH	16	2.5
18	KOH	10	1.25
19	KOH	10	3.75
20	NH_3	8	2.5
21	NH_3	10	2.5
22	NH_3	12	2.5
23	NH_3	14	2.5
24	NH_3	16	2.5
25	NH_3	8	2.5
26	NH_3	10	2.5
27	NH_3	12	2.5
28	NH_3	14	2.5
29	NH_3	16	2.5
30	MEA	8	2.5
31	MEA	10	2.5
32	MEA	12	2.5
33	MEA	14	2.5
34	MEA	16	2.5

7.3. Results

7.3.1. NaOH results

A total of 12 tests were performed with this solvent, whose characteristics of each of them can be seen below in Table 7.5. These test aim to characterize the influence on the capture performance of the L/G ratio for solvent concentrations between 100 and 120 g/L, as well as the influence of the solvent concentration for fixed L/G with value 10. As a summary, the results obtained for each test are shown in Table 7.6, where capture efficiency is defined by Eq. (1). G_{int} and CO_{2int} were always fixed at 5.18 l/min and 40% respectively, as previously showed in Table 7.2. The results obtained have been plotted in Figures 15-18 for sake of easiness to analyze.

$$Capture\ efficiency\ (\%) = \frac{G_{int}CO_{2int} - G_{out}CO_{2out}}{G_{int}CO_{2int}}\ x\ 100$$

Table 7.5. Characteristics of the absorption tests carried out with NaOH.

Test	L/G ratio	Concentration (g/L)	Mol NaOH/min	Solvent / CO_2 molar ratio	Concentration (M)
1	8	100	0.07	0.83	2.5
2	10	100	0.09	1.03	2.5
3	12	100	0.11	1.24	2.5
4	14	100	0.13	1.45	2.5
5	16	100	0.15	1.65	2.5
6	10	50	0.05	0.52	1.25
7	10	150	0.19	1.55	3.75
8	8	120	0.09	0.99	3
9	10	120	0.11	1.24	3
10	12	120	0.13	1.49	3
11	14	120	0.15	1.74	3
12	16	120	0.18	1.98	3

Table 7.6. NaOH results.

Test	Capture efficiency	Mol CO_2 removed mol / mol NaOH in
1	51.25	0.62
2	67.68	0.65
3	85.14	0.68
4	96.02	0.66
5	98.15	0.59
6	30.50	0.59
7	91.56	0.59
8	55.00	0.55
9	78.80	0.64
10	93.92	0.63
11	97.29	0.56
12	99.92	0.50

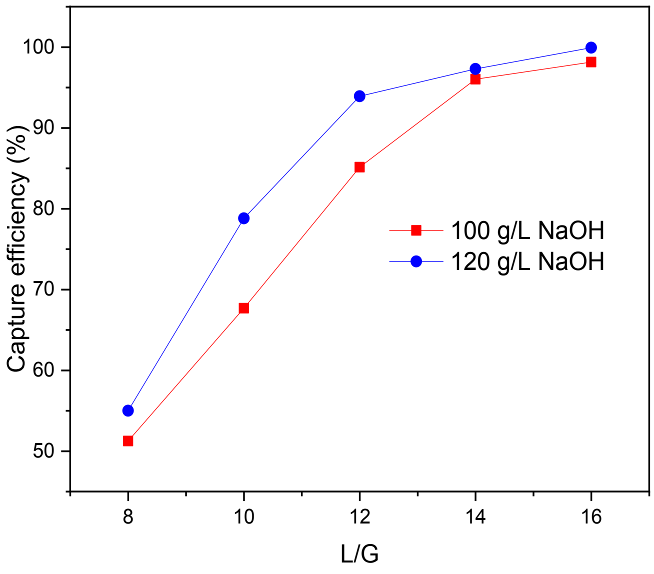


Figure 7.15. Capture efficiency at several L/G values with NaOH as solvent.

Figure 7.15 shows the absorption curves obtained for the two concentrations tested with NaOH as solvent. It can be seen that the solvent tested meets 95% of CO_2 capture efficiency from biogas streams at L/G ratio of 12 with a concentration of 120 g/L. For concentrations of 100 g/L, the L/G ratio should be 14 for the same capture efficiency. Those L/G ratios may be high in comparison with other studies but they are in agreement with the imposed CO_2 concentrations of 40%.

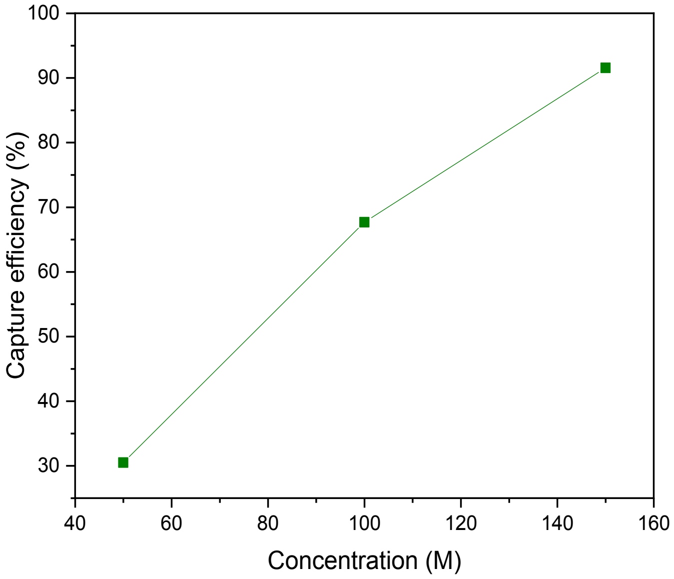


Figure 7.16. Capture efficiency at three different concentration values with NaOH as solvent.

Regarding the effect of NaOH concentration on capture efficiency for L/G = 10, it can be seen in Figure 7.16 that they are strongly influential. This will be very useful for subsequent phases of the project in which the integration of CO_2 capture techniques and their use as draw solutions and/or production of a value added by-products are proceeded.

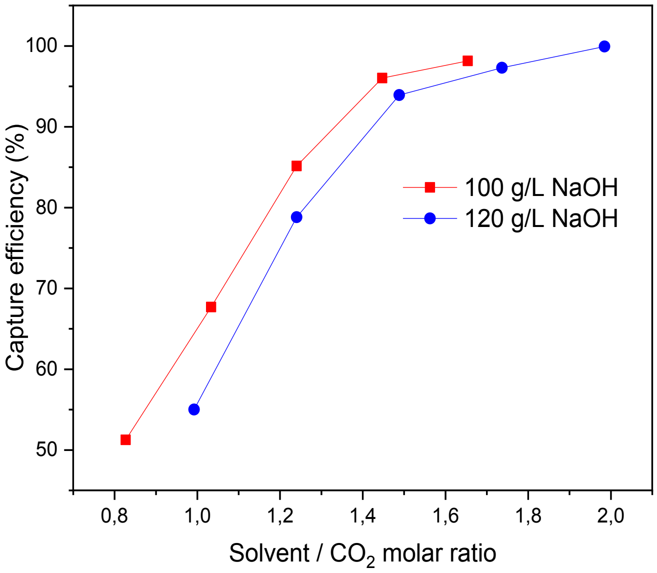


Figure 7.17. Capture efficiency vs solvent/CO_2 molar ratio with NaOH as solvent.

In order to study the utilization of the introduced solvent moles in relation to the initial moles of CO_2, Figure 7.17 represents the curves obtained for the two concentrations tested. It can be seen how by increasing the ratio, initially a much more favorable response is obtained than that obtained by increasing the molar ratio by higher values. This means that there must be a point of maximum utilization of the solvent with respect to the moles of CO_2 captured.

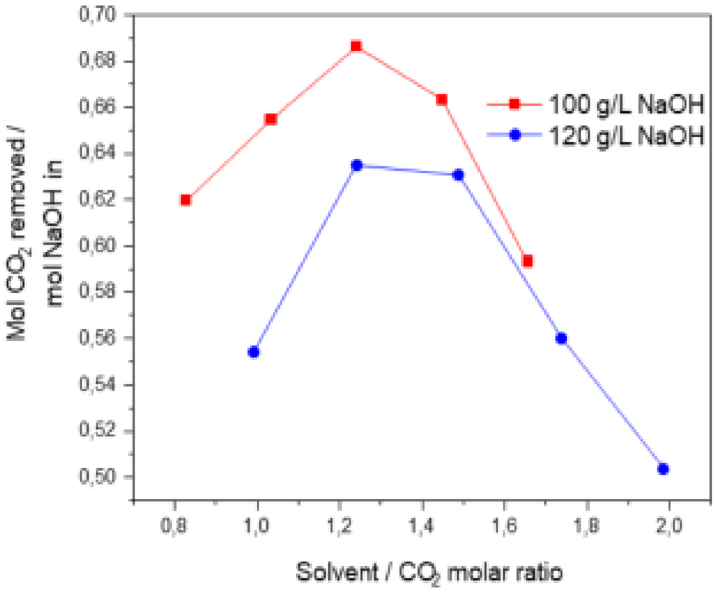


Figure 7.18. Mol CO_2 removed / mol NaOH in vs solvent/CO_2 molar ratio.

The aforementioned maximum solvent utilization is found at 1.24 solvent/CO_2 molar ratio, as plotted in Figure 7.18. This ratio is the same for both concentrations of solvent, being also not coincident with what could be concluded with the results previously obtained. Entering more amount of solvent does not mean that a better utilization of the solvent will be obtained. For example, for a concentration of 100 g/L, higher NaOH utilization values are achieved than for concentrations of 120 g/L. This means that it is more convenient to increase the L/G ratio to achieve an acceptable level of CO_2 capture efficiency than to increase the solvent concentration in the initial solution. Therefore, from this result, 2.5 M (equivalent to 100 g/L) has been taken as a reference concentration to evaluate the following solvent, although other points have also been worked to verify trends.

7.3.2. KOH results

Considering the previous results obtained with NaOH as solvent, a total of 7 tests were carried out for KOH characterization. The main characteristics of each of them are shown in Table 7.7.

Table 7.7. Characteristics of the absorption tests carried out with KOH.

Test	L/G ratio	Concentration (g/L)	Mol NaOH/min	Solvent / CO_2 molar ratio	Concentration (M)
13	8	140	0.07	0.83	2.5
14	10	140	0.09	1.03	2.5
15	12	140	0.11	1.24	2.5
16	14	140	0.13	1.45	2.5
17	16	140	0.15	1.65	2.5
18	10	70	0.05	0.52	1.25
19	10	210	0.14	1.55	3.75

The main purpose of these test was to characterize the influence on the CO_2 capture performance of the L/G ratio for a solvent concentration of 140 g/L (2.5 M), as well as the influence of the concentration for a fixed L/G value of 10. In this case, two curves of experiments were not performed for two different concentrations since, as previously verified, the optimum value of solvent utilization was achieved at 2.5 M. The results obtained for each of the tests are shown in Table 7.8. As with the previous solvent, the absorption curves obtained are plotted in Figures 7.19 to 7.22.

Table 7.8. KOH results.

Test	Capture efficiency	Mol CO_2 removed mol / mol NaOH in
13	59.46	0.72
14	78.28	0.76
15	96.86	0.78
16	100.00	0.69
17	100.00	0.60
18	45.95	0.89
19	100.00	0.64

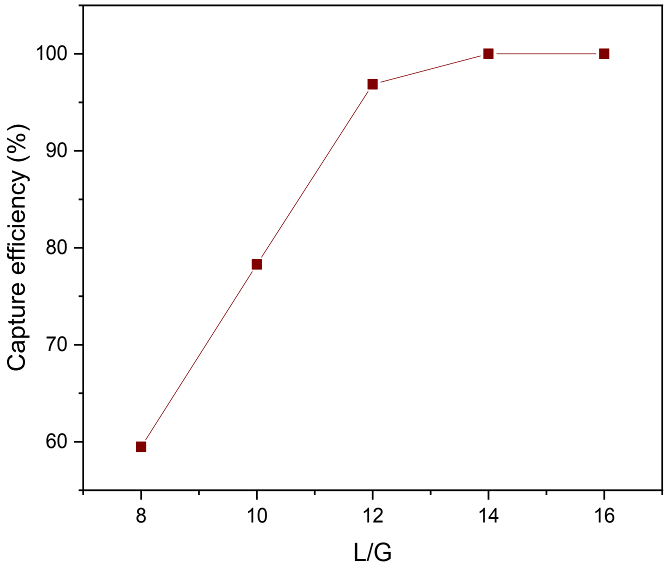


Figure 7.19. Capture efficiency at several L/G values with KOH as solvent.

Figure 7.19 presents the absorption curves obtained for the concentration of KOH tested. It can be seen that the solvent meets the CO_2 capture requirements of biogas streams from L/G ratios above 12 with a concentration of 140 g/L (2.5 M), with a capture efficiency of 96.86%. Compared to that obtained for L/G = 12 with NaOH (85.14%), for the same molar concentration (2.5 M), the use of KOH seems to provide more efficient results than the use of NaOH in terms of molar concentration. Nevertheless, higher mass flows are employed at 2.5 M concentration which can be a disadvantage from an economic point of view. This discussion will be analyzed in detail in the following points of the document.

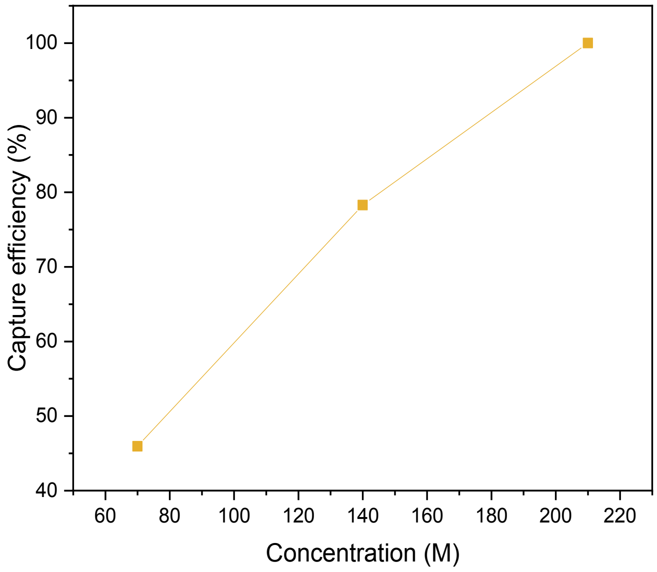


Figure 7.20. Capture efficiency at three different concentration values with KOH as solvent.

Regarding the effect exerted by the concentration of KOH on capture efficiency for a fixed L/G = 10, its strong influence can be observed in Figure 7.20 as in the previous case. This gives the process an interesting flexibility and control capacity over the capture, which will be very useful for its application in following phases of the project.

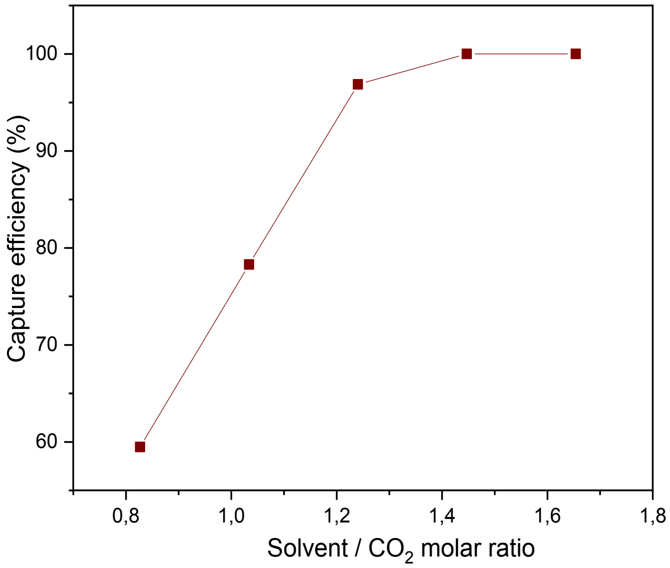


Figure 7.21. Capture efficiency vs solvent/CO_2 molar ratio with KOH as solvent.

In order to study the utilization of the solvent in relation to the CO_2 present in the gas stream as was previously done with the NaOH solvent, Figure 7.21 plots the results obtained. Exactly the same behavior as presented by NaOH can be observed, so the conclusions to be drawn are equivalent for both solvents. Furthermore, the maximum solvent utilization is achieved at a molar ratio of 1.24, as can be seen in Figure 7.22. This point also coincides with the optimal point presented by NaOH absorption curves, which identifies it as the ideal working point for these two solvents. Therefore, this point was chosen to find the optimal results in the following phases of process integration, as will be explained later.

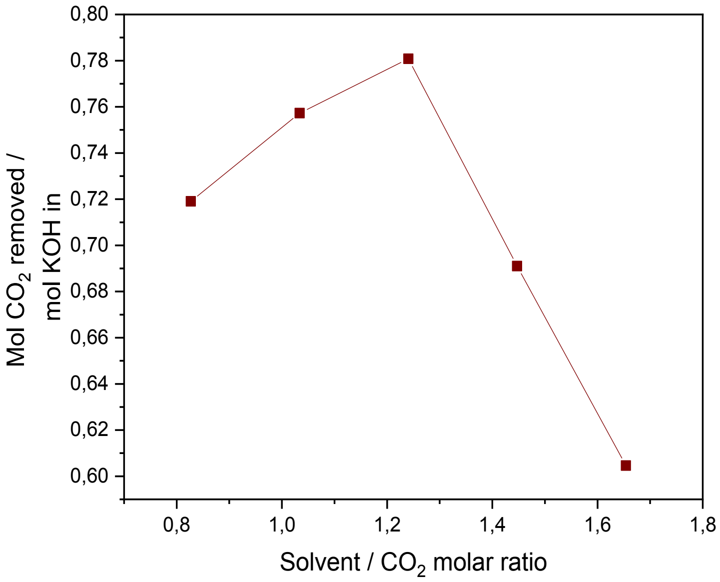


Figure 7.22. Mol CO_2 removed / mol KOH in vs solvent/CO_2 molar ratio.

7.3.3. NH_3 results

Considering the previous results, for the characterization of NH_3 as a potential solvent, a total of 10 tests were performed. The characteristics of each test are shown in Table 7.9. In this case, the objective of the tests is study if NH_3 behavior is more favorable than conventional caustic absorbents such as NaOH and KOH. Therefore, only the overall performance with the variation of the L/G ratio at a concentration of 2.5 M was studied. However, when performing tests 20 to 24, it was observed that capture efficiencies were considerably lower than those obtained with NaOH and KOH. Thus may be caused by the high volatility of NH_3 at the operation conditions described in section 7.1.4. Therefore, the test conditions were modified by lowering the temperature to values between 5 and 10 °C instead of 20 °C. This was intended to the decrease in performance that could cause the evaporation of part of the solvent. The system prepared for carrying out these tests in these temperature conditions was described in section 7.1.3 (Figure 7.4 and 7.8).

Table 7.9. Characteristics and results of the absorption tests carried out with NH_3.

Test	L/G ratio	Concentration (g/L)	Temperature (ºC)	Concentration (M)	Capture efficiency (%)
20	8	42.5	20	2.5	47.65
21	10	42.5	20	2.5	52.06
22	12	42.5	20	2.5	57.25
23	14	42.5	20	2.5	65.79
24	16	42.5	20	2.5	76.12
25	8	42.5	5-10	2.5	46.95
26	10	42.5	5-10	2.5	52.41
27	12	42.5	5-10	2.5	59.49
28	14	42.5	5-10	2.5	67.66
29	16	42.5	5-10	2.5	78.63

After performing the tests and analyzing the results, it is concluded that NH_3 cannot compete with caustic solvents previously test in terms of capture efficiencies. The results obtained for each of the tests are shown in Figure 7.23. As can be seen the influence of temperature on performance is minimal (Table 7.9 and Figure 7.23). Generally, it can be affirmed that NH_3 has absorption capacities significantly lower than those of NaOH and KOH.

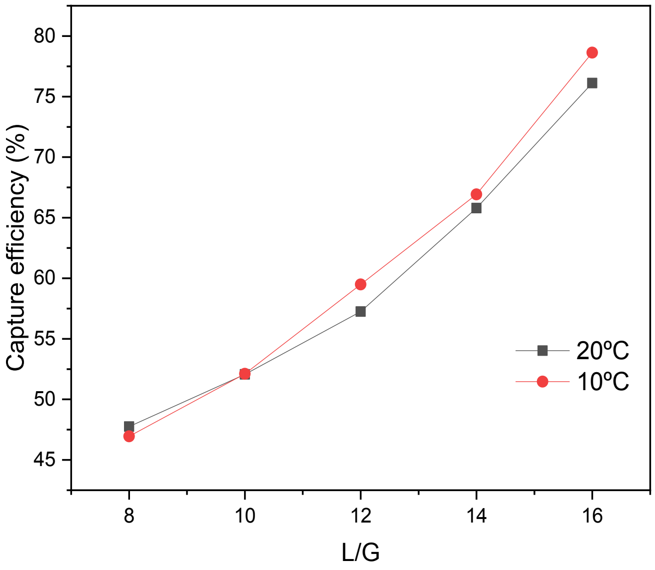


Figure 7.23. Capture efficiency at several L/G values with NH_3 as solvent.

7.3.4. MEA results

For MEA characterization as benchmark solvent for sake of comparison, a total of 5 tests have been performed, the characteristics of which are shown in Table 7.10. In this case, the objective of the tests is to verify whether the results of the caustic compounds chosen for the tests are in line with commercial widespread MEA. To set the comparison, the evolution of the overall performance was studied with the variation of the L/G ratio at a concentration of 2.5 M.

Table 7.10. Characteristics and results of the absorption tests carried out with MEA.

Test	L/G ratio	Concentration (M)	Capture efficiency (%)
30	8	2.5	48.39
31	10	2.5	66.29
32	12	2.5	83.95
33	14	2.5	94.27
34	16	2.5	96.76

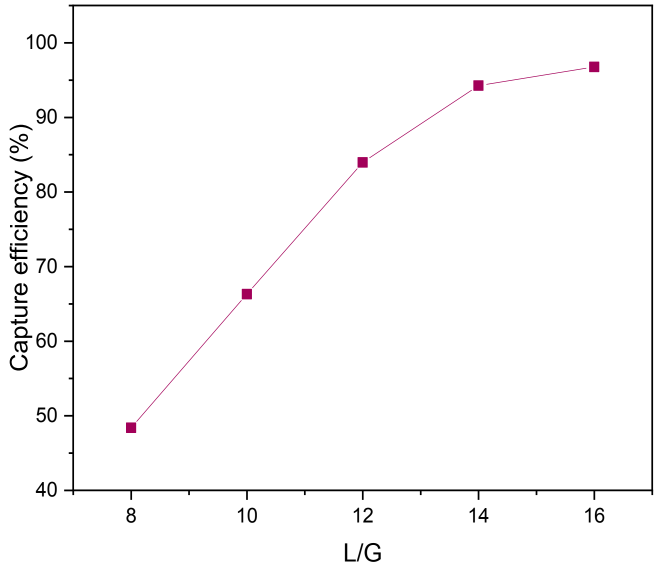


Figure 7.24. Capture efficiency at several L/G values with MEA as solvent.

Figure 7.24 presents the results obtained for MEA tests. As it will be seen in the next section 7.2.5, the results are in line with the ones obtained for NaOH. Nevertheless, high L/G ratio needs to be used in order to achieve high capture efficiencies, which are unusual when working with MEA as solvent. That could be explained for the fact that in our study MEA is employed in a lower concentration (2.5 M) than typically (5 M) [135,367,368].

7.3.5. Solvents comparison and discussion

First of all, a comparison among NaOH, KOH and MEA results is plotted in Figure 7.25, where it is possible to observe the similarities between NaOH and MEA as anticipated before. All the curves were represented for the same concentration of 2.5 M. As can be seen, even if NaOH and MEA achieve similar results, KOH presents higher capture efficiencies for the same molar concentration.

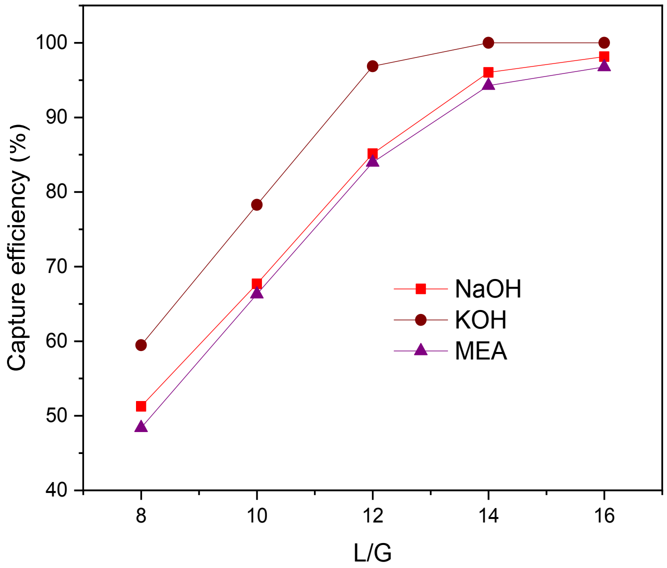


Figure 7.25. Capture efficiency comparison among NaOH, KOH and MEA.

In order to compare the two potential solvent candidates for the integration of CO_2 capture in urban WWTPs to obtain new valuable resources, Figures 7.26, 7.27 and 7.28 compare the results previously presented for both solvents. The parameters represented are their capture behavior against the L/G ratio (Figure 7.26) and solvent/CO_2 molar ratio (Figure 5.27). Furthermore, Figure 7.28 plots the each of CO_2 removed per mol NaOH inserted into the column against solvent/CO_2 molar ratio. The comparison has been made for a concentration of 2.5 M, previously characterized as optimal.

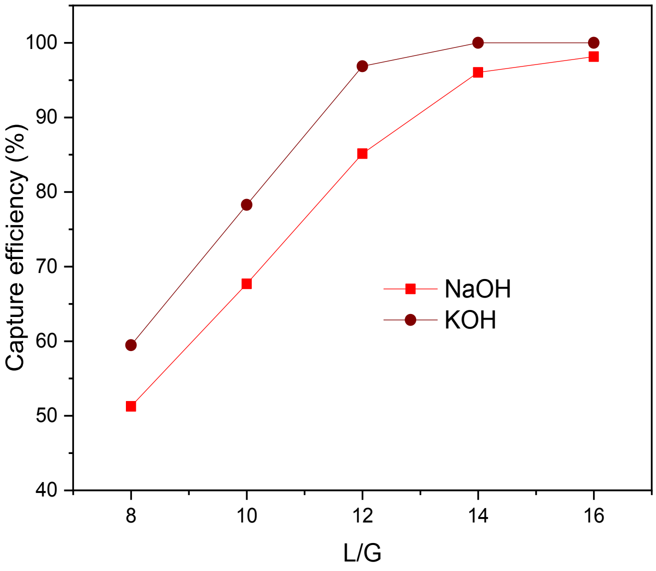


Figure 7.26. Capture efficiency comparison at several L/G values with NaOH and KOH as solvents.

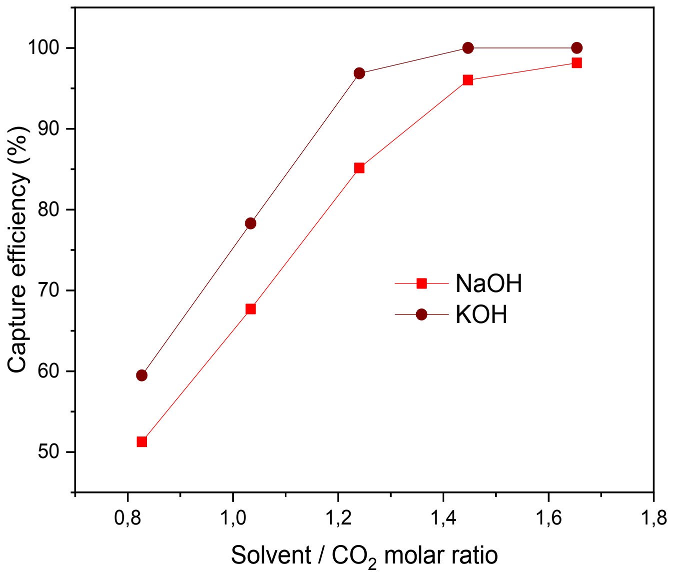


Figure 7.27. Capture efficiency vs solvent/CO_2 molar ratio comparison with NaOH and KOH as solvents.

Figure 7.27 shows the significant change that capture efficiency undergoes when increasing the molar ratio at the points of lowest value, while at the highest points this change is smoothing. This indicates the existence of an optimal use of solvent, which for comparison between the two has been represented in the following Figure 5.28. The optimum can be set at 1.24 molar ratio for both solvents. In the case of NaOH, the moles of CO_2 removed per mole of solvent inserted are almost 0.7 for this point, while with KOH as solvent a value close to 0.8 is reached. This means that there is a greater potential for solvent utilization when KOH is used. On the other hand, molecular weight of KOH is higher which suppose a higher mass flow and therefore a higher cost when using this solvent. This discussion must be considered in the integration section of the present work.

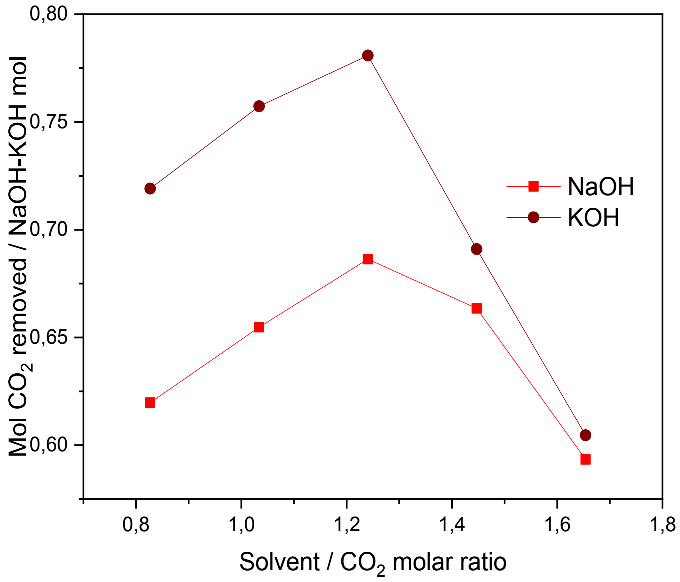


Figure 7.28. Mol CO_2 removed / mol NaOH – KOH in vs solvent/CO_2 molar ratio comparison.

7.4. Conclusions

In this chapter the capture efficiency of selected solvents was addressed. As main conclusions the following points can be extracted:

- NaOH and KOH provide similar results than commercially solvents (i.e. MEA) under the conditions herein imposed.
- NH_3 did not achieved satisfactory results in comparison with NaOH and KOH under the conditions tested.
- The optimum in terms of solvent utilization can be set at 1.24 molar ratio for both solvents.

- In the case of NaOH, the moles of CO_2 removed per mole of solvent inserted are almost 0.7 for this point, while with KOH as solvent a value close to 0.8 is reached.

All of these points will be considered in future assessments of this process, both to integrate the results obtained in each stage (Chapter X) and for a potential scaling-up of the process in future works.

CHAPTER IX: CO_2 conversion into valuable materials. Precipitation via aqueous mineral carbonation

9.1. Objective

The objectives proposed of this last stage of the process are mainly two:

- Obtaining a valuable commercial product which can definitely storage CO_2 and hence contributing with the circular economy policy.
- Regenerating the initial solvent in order to make affordable the overall economic performance of the process.

As potential value added products, carbonates were selected because the aqueous mineral carbonation process clearly fits in the proposed scheme. Carbonates solid products such as calcium carbonate ($CaCO_3$) or magnesium carbonate ($MgCO_3$) are a very attractive option from an economic point of view. Moreover, solid carbonates can be launch into the market in this application since the productions rate would be in a competitive range in comparison with the big carbonates producers.

A previous step to select a proper precipitant agent which could give as result the mentioned carbonates is needed. Therefore, the first point of this chapter will be based on studying and choosing some precipitant agents in the line of this work. Afterwards, the proposed precipitants will be evaluated trough the definition of an experimental matrix and setup.

9.2. Precipitant agent selection

In agreement with the objectives set for this stage, precipitant agents with high calcium or magnesium content were chosen. A comprehensive literature review was done in Chapters II and III and some precipitant agents were found [18,145,149,296,374]. The main characteristics of the precipitant agents looked for were high availability and low price. Moreover, the capability to highly react with aqueous CO_2 and hence to regenerate the solvent was also considered. The two chemical species that were chosen from these reviews as precipitant agents, and that meet the requirements above imposed were hydroxides and chlorides. Table 9.1 shows the chosen precipitant agents and their main advantages and disadvantages. The reactions that would take place with each of the chosen precipitation agents are the following:

$$Na_2CO_3/K_2CO_3\,(aq) + Ca(OH)_2(s) \rightarrow 2NaOH/KOH(aq) + CaCO_3\,(s)$$

$$Na_2CO_3/K_2CO_3\,(aq) + CaCl_2(s) \rightarrow 2NaCl/KCl(aq) + CaCO_3\,(s)$$

$$Na_2CO_3/K_2CO_3\,(aq) + Mg(OH)_2(s) \rightarrow 2NaOH/KOH(aq) + MgCO_3\,(s)$$

$$Na_2CO_3/K_2CO_3\,(aq) + MgCl_2(s) \rightarrow 2NaCl/KCl(aq) + MgCO_3\,(s)$$

Table 9.1. Selected precipitant agents. Advantages and disadvantages.

Agent	Advantages	Disadvantages
$Ca(OH)_2$	The solvent could be regenerated in a single step.	Possible presence of impurities in the final product.
$CaCl_2$	Obtaining a very pure product.	The solvent cannot be regenerated in a single step.
$Mg(OH)_2$	The solvent could be regenerated in a single step.	Possible presence of impurities in the final product.
$MgCl_2$	Obtaining a very pure product.	The solvent cannot be regenerated in a single step.

9.3. Materials and methods

9.3.1. Materials

$Ca(OH)_2$, $CaCl_2$, $Mg(OH)_2$, $MgCl_2$, Na_2CO_3, K_2CO_3, $CaCO_3$ and $MgCO_3$ employed in this work were provided by PanReac-AppliChem (pure-grade or pharma-grade, 99% purity). Some examples can be seen in Figure 9.1 and 9.2.

Figure 9.1. Na_2CO_3 (left side) and K_2CO_3 (right side) reagents employed in this stage.

Figure 9.2. $Ca(OH)_2$ and $CaCl_2$ reagents employed in this stage.

9.3.2. Methods

The experiments were performed in two differentiated phases: first, the reaction between the precipitant agent and the carbonated solvent to produce a solid carbonated product was carried out. Afterwards, the precipitated particles were duly extracted from the precipitation reactor for their analysis using different techniques.

9.3.2.1. Precipitation experiments

Generally, the precipitation experiments were done according to the methodology exposed below, which will be further explained later. First, both the solutions of the reactants and the instruments needed for the precipitation reaction were prepared. After this step, the reaction was carried out and once finished, the solution was filtered and separated quickly for analysis. The main result was set on the precipitation efficiency, which was defined as follow.

$$Precipitation\ efficiency\ (\%) = \frac{Carbonated\ obtained}{Maximum\ carbonate\ to\ obtain}\ x\ 100$$

Carbonated obtained was determined as the solid result of each experiment. For sake of calculations, the maximum carbonate obtainable corresponds to that stochiometrically reachable in a complete reaction. Furthermore, ICP was employed to measure the liquid product and to corroborate that the ions concentration in the liquid corresponds with the solid product obtained. The key variables studied were the reaction time, the reaction temperature, and the precipitant/reactant molar ratio (R), since these variables were proved to have an effect on the reaction rate [145,149,296,359,375–377] . More references can be found in Chapter III where an exhaustive review of this method was presented. In order to study the effect of each parameter, a standard value was set for each of them based on findings proposed in similar studies [149,359]. The standard value for the reaction temperature was set at 50°C, molar ratio at 1.2 mol Ca/Na_2CO_3, and reaction time at 30 minutes. Then each parameter was individually modified one at a time to corroborate their genuine impact in the overall process and hence establish the optimum limits. In the case of Na_2CO_3 and K_2CO_3, the aqueous solution was set at 20 g/100 ml according to the basis typical values expected after the absorption step [145,360]. However, more concentration values were tested to integrate the precipitation results with the process of study, as will be seen in Chapter VIII. On the other hand, the concentration of precipitant was stochiometrically calculated for each test, as varying the molar ratio. Table 9.2 represents the experiments carried out to analyze the effect of the variation of each parameter. As can be seen, 106 experiments were performed to obtain a proper analysis of the precipitation efficiency behavior.

Table 9.2. Matrix of experiments carried out.

Test	**Carbonated solvent**	**Precipitant agent**	**Tiem (min)**	**Temperature (ºc)**	**R**
1	Na_2CO_3	$Ca(OH)_2$	30	50	1.2
2	Na_2CO_3	$Ca(OH)_2$	5	50	1.2
3	Na_2CO_3	$Ca(OH)_2$	15	50	1.2
4	Na_2CO_3	$Ca(OH)_2$	45	50	1.2
5	Na_2CO_3	$Ca(OH)_2$	60	50	1.2
6	Na_2CO_3	$Ca(OH)_2$	90	50	1.2
7	Na_2CO_3	$Ca(OH)_2$	120	50	1.2
8	Na_2CO_3	$Ca(OH)_2$	30	30	1.2
9	Na_2CO_3	$Ca(OH)_2$	30	35	1.2
10	Na_2CO_3	$Ca(OH)_2$	30	40	1.2
11	Na_2CO_3	$Ca(OH)_2$	30	45	1.2
12	Na_2CO_3	$Ca(OH)_2$	30	50	1.2
13	Na_2CO_3	$Ca(OH)_2$	30	55	1.2
14	Na_2CO_3	$Ca(OH)_2$	30	60	1.2
15	Na_2CO_3	$Ca(OH)_2$	30	65	1.2
16	Na_2CO_3	$Ca(OH)_2$	30	70	1.2
17	Na_2CO_3	$Ca(OH)_2$	30	50	0.7
18	Na_2CO_3	$Ca(OH)_2$	30	50	0.8
19	Na_2CO_3	$Ca(OH)_2$	30	50	0.9
20	Na_2CO_3	$Ca(OH)_2$	30	50	1
21	Na_2CO_3	$Ca(OH)_2$	30	50	1.1
22	Na_2CO_3	$Ca(OH)_2$	30	50	1.2
23	Na_2CO_3	$Ca(OH)_2$	30	50	1.3
24	Na_2CO_3	$Ca(OH)_2$	30	50	1.4
25	Na_2CO_3	$Ca(OH)_2$	30	50	1.5
26	Na_2CO_3	$CaCl_2$	30	50	1.2
27	Na_2CO_3	$CaCl_2$	5	50	1.2
28	Na_2CO_3	$CaCl_2$	15	50	1.2
29	Na_2CO_3	$CaCl_2$	45	50	1.2
30	Na_2CO_3	$CaCl_2$	60	50	1.2
31	Na_2CO_3	$CaCl_2$	90	50	1.2
32	Na_2CO_3	$CaCl_2$	120	50	1.2
33	Na_2CO_3	$CaCl_2$	30	30	1.2
34	Na_2CO_3	$CaCl_2$	30	35	1.2
35	Na_2CO_3	$CaCl_2$	30	40	1.2
36	Na_2CO_3	$CaCl_2$	30	45	1.2
37	Na_2CO_3	$CaCl_2$	30	50	1.2
38	Na_2CO_3	$CaCl_2$	30	55	1.2
39	Na_2CO_3	$CaCl_2$	30	60	1.2
40	Na_2CO_3	$CaCl_2$	30	65	1.2
41	Na_2CO_3	$CaCl_2$	30	70	1.2
42	Na_2CO_3	$CaCl_2$	30	50	0.7
43	Na_2CO_3	$CaCl_2$	30	50	0.8
44	Na_2CO_3	$CaCl_2$	30	50	0.9
45	Na_2CO_3	$CaCl_2$	30	50	1
46	Na_2CO_3	$CaCl_2$	30	50	1.1
47	Na_2CO_3	$CaCl_2$	30	50	1.2
48	Na_2CO_3	$CaCl_2$	30	50	1.3

49	Na_2CO_3	$CaCl_2$	30	50	1.4
50	Na_2CO_3	$CaCl_2$	30	50	1.5
51	Na_2CO_3	$Mg(OH)_2$	30	50	1.2
52	Na_2CO_3	$Mg(OH)_2$	30	30	1.2
53	Na_2CO_3	$Mg(OH)_2$	30	70	1.2
54	Na_2CO_3	$Mg(OH)_2$	30	50	1
55	Na_2CO_3	$Mg(OH)_2$	30	50	1.5
56	Na_2CO_3	$Mg(OH)_2$	15	50	1.2
57	Na_2CO_3	$Mg(OH)_2$	60	50	1.2
58	Na_2CO_3	$MgCl_2$	30	50	1.2
59	Na_2CO_3	$MgCl_2$	120	50	1.2
60	Na_2CO_3	$MgCl_2$	60	50	1.2
61	Na_2CO_3	$MgCl_2$	45	50	1.2
62	Na_2CO_3	$MgCl_2$	15	50	1.2
63	Na_2CO_3	$MgCl_2$	30	50	1.2
64	Na_2CO_3	$MgCl_2$	30	70	1.2
65	Na_2CO_3	$MgCl_2$	30	60	1.2
66	Na_2CO_3	$MgCl_2$	30	40	1.2
67	Na_2CO_3	$MgCl_2$	30	30	1.2
68	Na_2CO_3	$MgCl_2$	30	50	1.5
69	Na_2CO_3	$MgCl_2$	30	50	1.3
70	Na_2CO_3	$MgCl_2$	30	50	1.1
71	Na_2CO_3	$MgCl_2$	30	50	1
72	K_2CO_3	$Ca(OH)_2$	30	50	1.2
73	K_2CO_3	$Ca(OH)_2$	15	50	1.2
74	K_2CO_3	$Ca(OH)_2$	60	50	1.2
75	K_2CO_3	$Ca(OH)_2$	30	30	1.2
76	K_2CO_3	$Ca(OH)_2$	30	70	1.2
77	K_2CO_3	$Ca(OH)_2$	30	50	1
78	K_2CO_3	$Ca(OH)_2$	30	50	1.5
79	K_2CO_3	$CaCl_2$	30	50	1.2
80	K_2CO_3	$CaCl_2$	15	50	1.2
81	K_2CO_3	$CaCl_2$	60	50	1.2
82	K_2CO_3	$CaCl_2$	30	30	1.2
83	K_2CO_3	$CaCl_2$	30	70	1.2
84	K_2CO_3	$CaCl_2$	30	50	1
85	K_2CO_3	$CaCl_2$	30	50	1.5
86	K_2CO_3	$Mg(OH)_2$	30	50	1.2
87	K_2CO_3	$Mg(OH)_2$	15	50	1.2
88	K_2CO_3	$Mg(OH)_2$	60	50	1.2
89	K_2CO_3	$Mg(OH)_2$	30	30	1.2
90	K_2CO_3	$Mg(OH)_2$	30	70	1.2
91	K_2CO_3	$Mg(OH)_2$	30	50	1
92	K_2CO_3	$Mg(OH)_2$	30	50	1.5
93	K_2CO_3	$MgCl_2$	30	50	1.2
94	K_2CO_3	$MgCl_2$	120	50	1.2
95	K_2CO_3	$MgCl_2$	60	50	1.2
96	K_2CO_3	$MgCl_2$	45	50	1.2
97	K_2CO_3	$MgCl_2$	15	50	1.2
98	K_2CO_3	$MgCl_2$	30	50	1.2
99	K_2CO_3	$MgCl_2$	30	70	1.2
100	K_2CO_3	$MgCl_2$	30	60	1.2
101	K_2CO_3	$MgCl_2$	30	40	1.2
102	K_2CO_3	$MgCl_2$	30	30	1.2
103	K_2CO_3	$MgCl_2$	30	50	1.5
104	K_2CO_3	$MgCl_2$	30	50	1.3
105	K_2CO_3	$MgCl_2$	30	50	1.1
106	K_2CO_3	$MgCl_2$	30	50	1

First, it was decided to start all the pairs in which Na_2CO_3 was listed and then be able to compare them with K_2CO_3, which in agreement with Chapter V were the most suitable solvents for this application. The first of the precipitating agents tested was $Ca(OH)_2$ since some references are available to compare if our results are in the line of previous studies. With this the bases were established to obtain the most important and representative points of the precipitation study. The characterization of this precipitant agent was exhaustive, carrying out a total of 25 tests as previously indicated in Table 9.2. Subsequently and to corroborate the difference with respect to $Ca(OH)_2$ as a precipitant agent, 25 more tests were performed to characterize $CaCl_2$ as a precipitant agent. Later, to study the difference in precipitation performance between Ca and Mg, $Mg(OH)_2$ was tested in a total of 7 tests. As the last precipitating agent of the sodium carbonate pairs, $MgCl_2$ was tested in greater proportion than $Mg(OH)_2$ (14 tests), since as will be seen later the results of purity of the final product are better when inorganic salts are used rather than hydroxides. Finally, in the first phase of precipitation tests, 35 additional tests were carried out for all K_2CO_3 pairs. These served to study and compare the precipitating efficiency of the final product in media where sodium and / or potassium ions predominate.

As showcased in Table 9.2, the reaction time, temperature and molar ratio were tested from 5 to 120 minutes, from 30°C to 70°C, and from 0.7 to 1.5 mol precipitant/carbonated solvent, respectively. Lab scale batch precipitation experiments were conducted in a 600 mL beaker whose temperature is controlled using an isothermal water bath. During the experiment the solution was stirred by an electromagnetic magnet at a constant speed of 1,000 rpm. A Trison instrument was used and data was logged for temperature and, in order to agree with the carbonates pH range (8-11), it was measured by the same instrument. Both precipitant and solvent carbonated solutions were previously prepared and then 100 mL of each were poured into the reaction vessel. Each test was divided into 3 parts: precipitation reaction; centrifugation to separate the liquid and the solid product; drying. The extended procedure followed is explained below:

- The amount required to meet the specifications indicated previously in Table 9.2 for each reactant were poured in 200 mL separated vessels (Figure 9.1)

Figure 9.1. Vessel with reactant.

- Once this amount was introduced, the glass is thickened with distilled water up to 100 mL. After the two solutions were prepared, the beakers are placed on a thermal stirrer each and a magnet is introduced into both to promote agitation. Both solutions were stirred for 15 minutes previous to the precipitation reaction.
- The heating device is then operated, in addition to the stirring (set up above) and the desired temperature is controlled with a mercury thermometer whose lower zone is kept in contact with the liquid solution (Figure 9.2).
- After the temperature desired is reached in both solutions, they are poured and mixed in a 600 mL beaker whose temperature is controlled (Figure 9.2). In this moment the reaction time is started until the end of the test in agreement with Table 9.2.
- Once the reaction time finished, the product result is duly extracted from the beaker and taken to a centrifuge where the separation phase starts.

Figure 9.2. Precipitation reaction.

- For the centrifugation process, the liquid sample is poured into four centrifuge tubes (Figure 9.3). Once the sample with approximately the same amount of sample was introduced into each tube, they were inserted into the centrifuge (Figure 9.4).

Figure 9.3. Centrifuge tubes.

Figure 9.4. Centrifuge.

- Then the mix was centrifuged for 15 minutes at 400 rpm. Once the centrifugation was finished, the liquid product suspended in the upper part was removed from the centrifuge tubes and poured into a canister for later analysis. The solid product stayed at the bottom of the tube as can be seen in Figure 9.5.

Figure 9.5. Solid product at the bottom of the centrifuge tube.

- In order to avoid possible liquid impurities in the final solid product, a washing step was carried out. This step consisted on mixing the solid product contained in the centrifugation tubes with ultra-pure water and centrifuge for 15 minutes again at the same speed. Afterwards, the process was repeated for 3 times.
- To dry the solid sample, all test tubes were taken to an oven at a temperature of 105°C during 24 hours (Figures 9.6 and 9.7).

Figure 9.6. Oven with the samples.

Figure 9.7. Samples to be dried.

- After this time interval, the tubes were weighed with the solid inside, which were previously weighed empty to obtain the amount of solid sample by difference. Finally, the solid is removed from all the test tubes and poured into a canister to proceed with its analysis and thus verify the purity (Figure 9.8).

Figure 9.8. Final solid product after its extraction from the centrifuge tubes.

9.3.2.2. Physicochemical characterization

Inductively coupled plasma (ICP) optical emission spectroscopy (ICP-OES): the equipment consists of an atomic emission spectrometer with inductively coupled plasma, with the ability to perform axial and radial measurements. In addition, it consists of a refrigerant, a sampler and an extractor hood at the top. The model used for the analysis is the Agilent Technologies 5100 ICP-OES. The analysis procedure is based on the continuous introduction of the liquid sample, which, when passing through a fogging system, forms an aerosol that is transported by the argon gas towards the plasma torch.

Due to the high temperatures generated in the plasma, the analytes were atomized and ionized generating atomic emission spectra in characteristic lines.

The solid obtained by filtration was dried at 105°C.The solid was then characterized by means of SEM, XRD and Raman spectroscopy to corroborate the formation of the carbonate and get some insights on its main features

Raman measurements of the powders samples were recorded using a Thermo DXR2 spectrometer equipped with a Leica DMLM microscope. The wavelength of applied excitation line was 532nm ion laser and 50x objective of 8-mm optical was used to focus the depolarized laser beam on a spot of about 3 μm in diameter.

A JEOL JSM6400 operated at 20 KV equipped with energy dispersive X-ray spectroscopy (EDX) and a wavelength dispersive X-ray spectroscopy (WDS) systems was used for the microstructural/chemical characterization (SEM with EDS and WDS).

X-ray diffraction (XRD) analysis was completed by an X'Pert Pro PAN analytical instrument. The 2θ angle was increased by 0.05º, with a 450 time per step over a range of 10-90º. Diffraction patterns were then recorded at 40 mA and 45 kV, using Cu Kα radiation (λ=0.154 nm).

9.4. Results

In this section the results obtained in the precipitation experiments are analyzed in deep. For a proper study and comparison of the results obtained in each precipitant/carbonated solvent tested, first the result obtained with each pair are presented separately by precipitant (sections 9.4.1.-9.4.4) Later in section 9.4.5 an extensive discussion and comparison among the pairs is presented. Each sub-section is organized as follow: first, the results obtained employing Na_2CO_3 as carbonated solvent are exposed; then these results are compare to those obtained with K_2CO_3; finally, the physiochemical characterization of the solid samples are presented for sake of discussion and comparison.

9.4.1. $Ca(OH)_2$ results

Figures 9.9-9.11 show the precipitation efficiency curves resulting from precipitation experiments carried out with Na_2CO_3 - $Ca(OH)_2$ pair (giving $CaCO_3$ as solid product) at different reaction times, temperatures and molar ratios, respectively. The test here explained correspond to test 1-25 from Table 9.2.

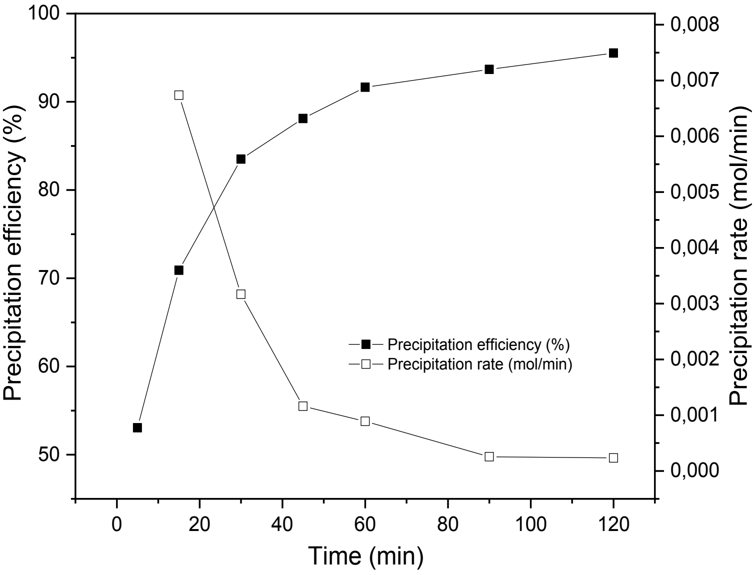


Figure 9.9. Precipitation efficiency vs time for Na_2CO_3 - $Ca(OH)_2$ pair.

Figure 9.9 shows the effect of the reaction time in the precipitation phenomenon. As depicted in the plot, precipitation efficiency varies from 53% to 83% approximately from 5 min to 30 min of reaction time, and later, the slope of the curve changes drastically, passing through 91% regeneration efficiency at 60 min, until achieving a 95% of precipitation at 120 min. This means, in fact, that in a hypothetical real reactor, a duplication of its volume will be necessary to achieve an increase of 4% approximately (from 30 min to 60 min). As can be seen, from 60 min to 120 min, less than 0.001 mol $CaCO_3$ is precipitated per minute. Thus, to operate at 120 min residence time is not worthy from a plant design point of view. The intersection of the two curves (precipitation rate and precipitation efficiency) indicates an interesting and very likely optimum operational point where a fair balance between both tendencies can be reached.

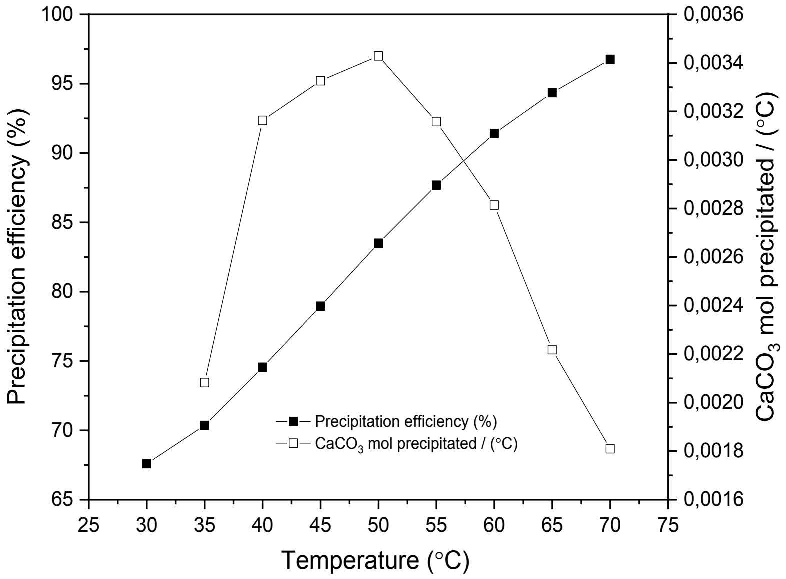


Figure 9.10. Precipitation efficiency vs temperature for Na_2CO_3 - $Ca(OH)_2$ pair.

As for the temperature influence, Figure 9.10 shows the effect of different temperatures in the precipitation studies. Temperature effect reflects a linear trend showcasing a direct correlation between precipitation efficiency and process temperature. Indeed, in the best case scenario (at 70 °C) it can reach 97% of precipitation efficiency. Normalizing the precipitation capacity by the incremental temperature (empty symbols in the Figure) maximum is obtained at around 50 °C which somehow indicates that the increment in temperature has a stronger impact on the precipitation efficiency in the low-medium temperature range. This is an important result to be highlighted from an energy consumption perspective, as a temperature of 50 °C could be easily achieved through low-cost and/or renewable energy sources such as solar.

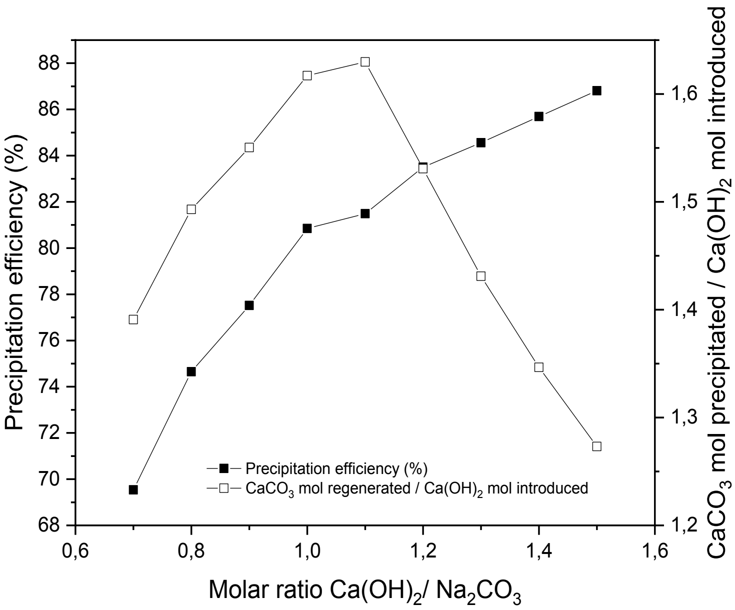


Figure 9.11. Precipitation efficiency vs molar ratio for Na_2CO_3 - $Ca(OH)_2$ pair.

Molar ratio inlet carbonate/precipitant agent is another important parameter to consider in the precipitation process. As can be seen in Figure 9.11, precipitation efficiency is favored by an increase of the molar ratio. Nevertheless, this increase of molar ratio promotes a higher quantity of Ca^{2+} ions that should be removed before recirculating the absorbent to the absorption tower in order to prevent accumulation of $Ca(OH)_2$ which eventually may lead to fouling phenomenon in the absorption tower. In parallel, as can be observed in Figure 9.11, $CaCO_3$ mol regeneration per mol of $Ca(OH)_2$ introduced decreases upon increasing the molar ratio above a threshold value of R = 1.1. This value set an optimum operational point beyond which no further benefits are envisaged from the process point of view.

For sake of comparison between Na_2CO_3 and K_2CO_3 as carbonated solvents, Figures 9.12-9.14 plot the results obtained for both in selected operation points. For K_2CO_3 experiments, the results showed correspond to tests 72-78 from Table 9.2.

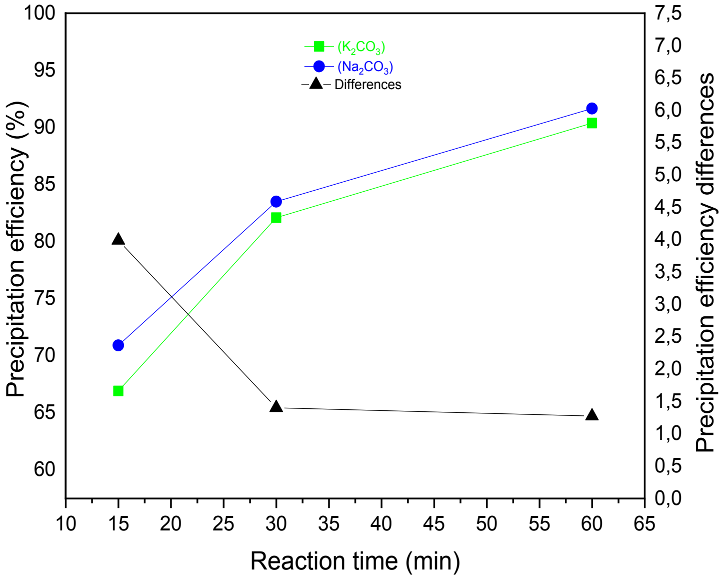


Figure 9.12. Comparison precipitation efficiency vs time for Na_2CO_3 - $Ca(OH)_2$ and K_2CO_3 - $Ca(OH)_2$ pairs.

The evolution of precipitation efficiencies during the reaction time is shown in Figure 9.12. Curiously, when employing K_2CO_3 as carbonated solvent, precipitation efficiencies are to be lower than those of Na_2CO_3. This result is in good agreement with separated previous studies [296] and may be caused by the higher stability of K_2CO_3 in comparison to Na_2CO_3. Given these circumstances, it may be better to employ NaOH instead of KOH in the absorption step. However, as discussed previously, KOH was proven to be a better solvent for CO_2 removal [141,378] and the differences in the precipitation stage can be overcome by increasing the reaction time. At 60 minutes, the differences between Na_2CO_3 and K_2CO_3 precipitation efficiencies are much lower than that at 15 minutes

(1.27% vs 3.99%). In any case, an almost 4% of difference in regeneration efficiency could be industrially assumed as long as the overall economic balance results positive.

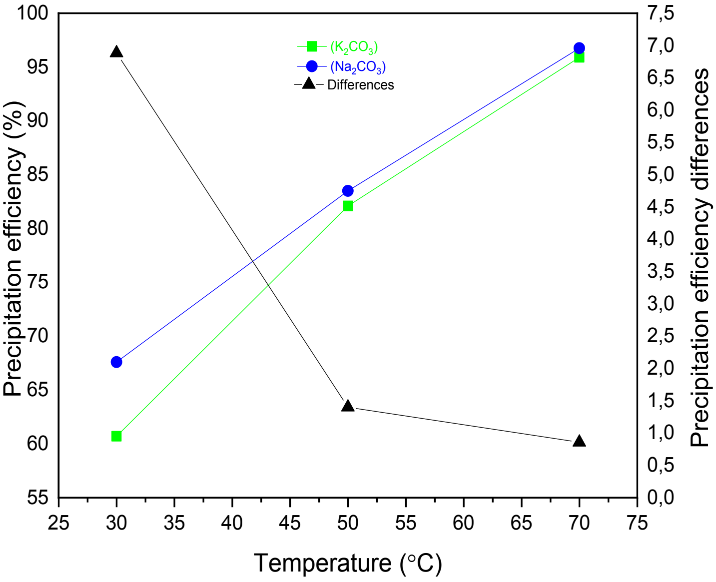


Figure 9.13. Comparison precipitation efficiency vs temperature for Na_2CO_3 - $Ca(OH)_2$ and K_2CO_3 - $Ca(OH)_2$ pairs.

Figure 9.13 reflects the strong impact of temperature in the precipitation efficiencies. It seems clear that in the low temperature range both solutions behave differently while at the high temperature window similar behavior was identified. In particular, at 30ºC a 6.88% of precipitation efficiency difference is obtained, whereas at 70ºC this value drops to 0.86%. This again can be ascribed again to the greater stability of K_2CO_3 compared to Na_2CO_3. In a hypothetical industrial application, in the case of choosing a temperature around 50°C, a high precipitation efficiency would be achieved for both hydroxides, without significant discrepancies between them. This is a remarkable finding that deserves to be featured, since as previously addressed, a process temperature as low as 50°C is feasible to achieve by the employ of renewable energy, being an important advance from an energy consumption perspective.

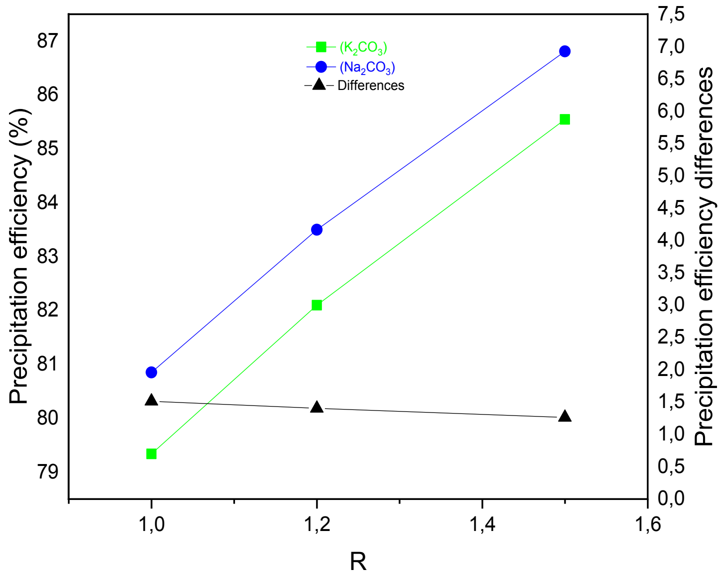


Figure 9.14. Comparison precipitation efficiency vs molar ratio for Na_2CO_3 - $Ca(OH)_2$ and K_2CO_3 - $Ca(OH)_2$ pairs.

The impact of precipitant/reactive molar ratio is depicted in Figure 9.14. As shown in the plot, both Na_2CO_3 and K_2CO_3 precipitation are favored when the molar ratio increases. Nevertheless, Na_2CO_3 precipitation efficiency is always higher than K_2CO_3 precipitation capacity at every studied value of R. In addition, the differences in regeneration efficiencies remains consistently steady across the studied R range. Contrary to the observations for the other reaction parameters, it seems that the impact of R in the performance is rather constant and the two families of solvent do not display similar behavior when tuning this parameter. Assuming 80% of precipitation efficiency as an acceptable result in an industrial case, an R value of 1 would be required to meet this value employing Na_2CO_3. However, a R=1.2 would be necessary for K_2CO_3, what promotes a higher amount of free calcium ions that need to be eliminated before recirculating the resulting aqueous KOH solution in order to prevent fouling in the absorption tower. In other words, it can speculate that KOH is more prone to produce solid fouling in the absorption column thus leading to higher operational cost in terms of shut-down / clean-up /star-up cycles.

Once precipitation efficiencies differences have been compared, the purpose of this section is to contrast both $CaCO_3$ obtained from K_2CO_3 and Na_2CO_3. The analyses were carried out over the tests number 1 and 72 (T=50ºC, R=1.2, t=30 min), which were selected as standard tests as previously explained. At the same time, these two samples were compared with commercial $Ca(OH)_2$ and $CaCO_3$. Figure 9.15 shows the representative FTIR spectra of the studied samples for sake of comparison. $CaCO_3$ is characteristic of monoclinic structure inside P21/c group [379,380]. As can be seen in Figure 9.15, both $CaCO_3$ represented are quite similar to commercial $CaCO_3$, suggesting an almost pure calcium carbonate was obtained [381]. A strong characteristic peak of $CaCO_3$ polymorphs is shown at 874 cm^{-1} wavenumber [382]. This peak is presented by both $CaCO_3$, so it could be an indication of $CaCO_3$ purity.

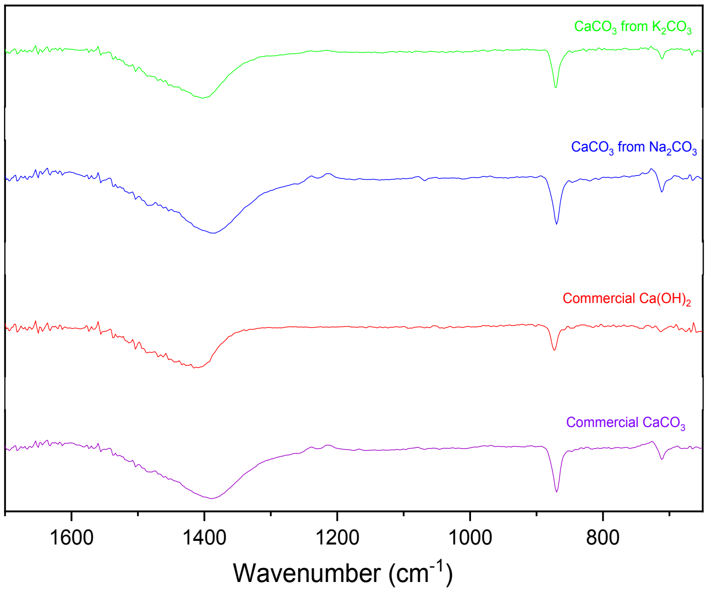


Figure 9.15. FTIR spectra for CaCO$_3$ from Na$_2$CO$_3$-K$_2$CO$_3$ in comparison with Ca(OH)$_2$-CaCO$_3$ commercial samples.

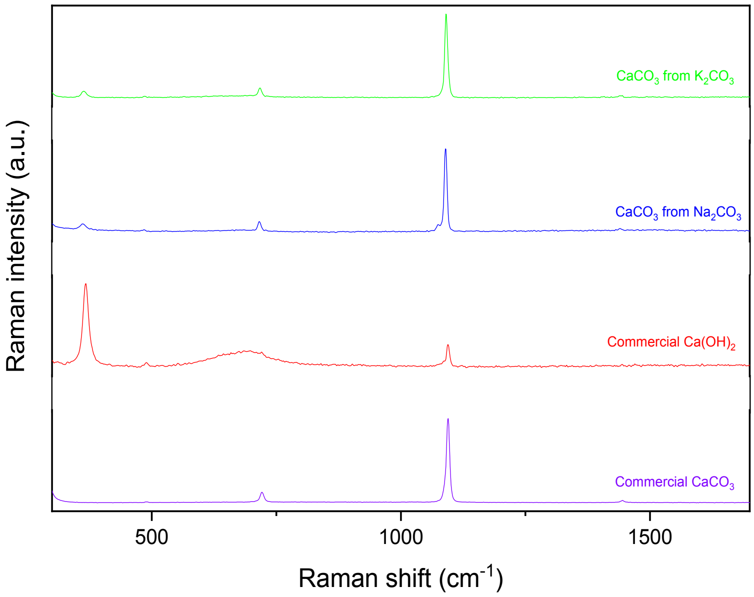


Figure 9.16. Raman spectra for $CaCO_3$ from Na_2CO_3-K_2CO_3 in comparison with $Ca(OH)_2$-$CaCO_3$ commercial samples.

In order to investigate the purity of the selected samples, Raman spectra are represented in Figure 7.16. In this analysis, it is easier to identify a weak peak of remaining $Ca(OH)_2$ at around 300 cm^{-1} in both carbonates spectra. This result agrees with those discussed previously in precipitation efficiencies obtained, where 100% efficiency is never achieved indicating some leftovers of $Ca(OH)_2$ in the obtained solids. In fact, the high intensity Raman mode of the carbonates spectra at around 1150 cm^{-1} again reveals the major contribution of $CaCO_3$ in the obtained solid. To corroborate Raman experiments and further gather information regarding the crystalline structure of the solids, Figure 9.17 shows XRD patterns of the studied samples. Herein it can be clearly observed that some contamination of $Ca(OH)_2$ remains in both $CaCO_3$, denoted by the diffraction peak at 34 degrees. Nevertheless, as announced before, this phase is present in very small concentrations in comparison with $CaCO_3$ as intended from the low intensity peak demonstrated by the obtained carbonates. Overall, the two XRD patterns of the obtained $CaCO_3$ are quite similar to that of the commercial $CaCO_3$ further confirming the predominance of this crystalline phase in the solid composition. Concretely, the XRD pattern exhibited by our solid product is characteristic of calcite phase. Comparing both $CaCO_3$ obtained from K_2CO_3 and Na_2CO_3, the first one presents a different peak at around 32 degrees. This seems to be a minor contribution of vaterite phase formed in good agreement with previous reports [383]. It is relevant to mention that such a secondary phase – vaterite – is only formed when KOH is used as a capturing solution in the tower what points out the impact of the alkaline cation not only in the regeneration efficiency of the upgrading process but also in the structure of the obtained solid. This result need to be further confirmed in subsequent analysis since it could be a strange point in the solid sample.

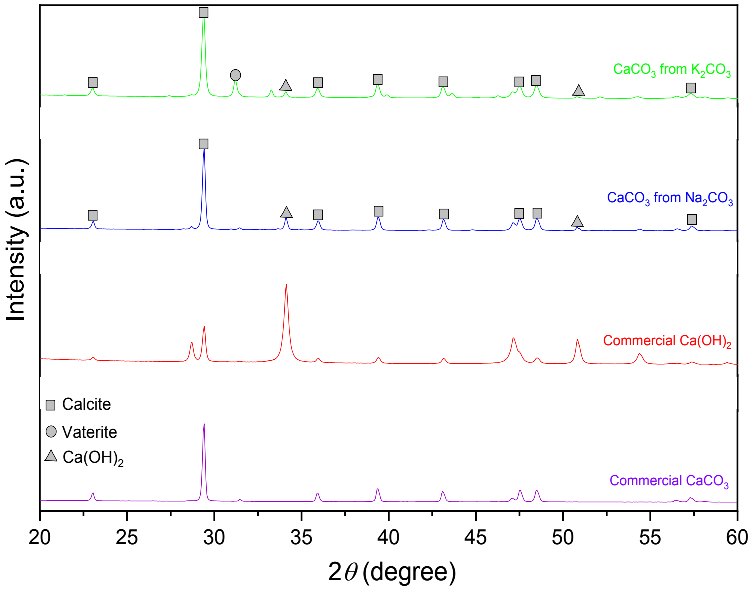


Figure 9.17. XRD patterns for $CaCO_3$ from Na_2CO_3-K_2CO_3 in comparison with $Ca(OH)_2$-$CaCO_3$ commercial samples.

Finally, SEM images were taken to get further insights into the precipitated carbonates morphology (Figure 9.18 and 9.19). $CaCO_3$ from Na_2CO_3, represented in Figure 9.18, seems to have a polymorphous calcite structure, as previously reported in a recent study [147]. On the other hand, $CaCO_3$ from K_2CO_3 (Figure 9.19), present a morphology dominated by calcite polymorphs. One main conclusion from the SEM images is that no significant morphology differences exist between both products.

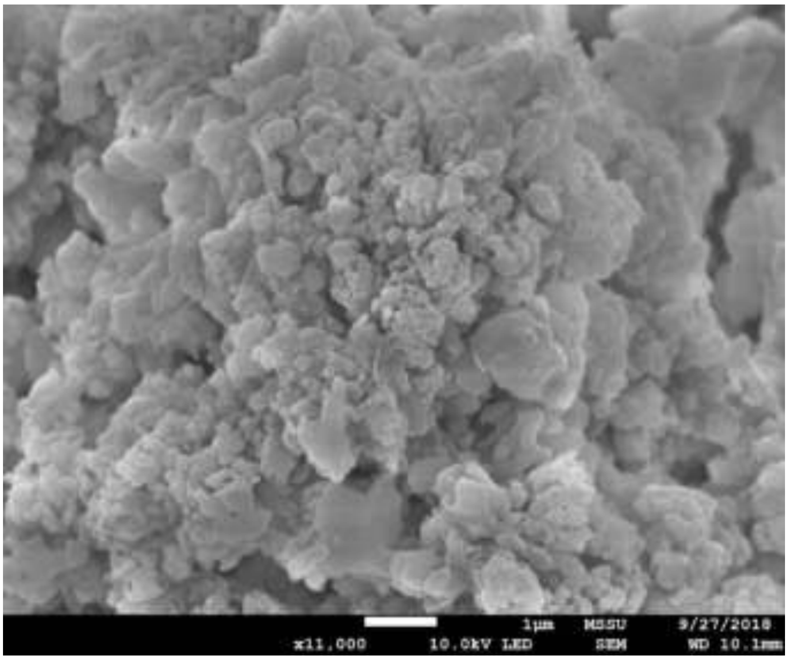


Figure 9.18. SEM image of $CaCO_3$ from Na_2CO_3.

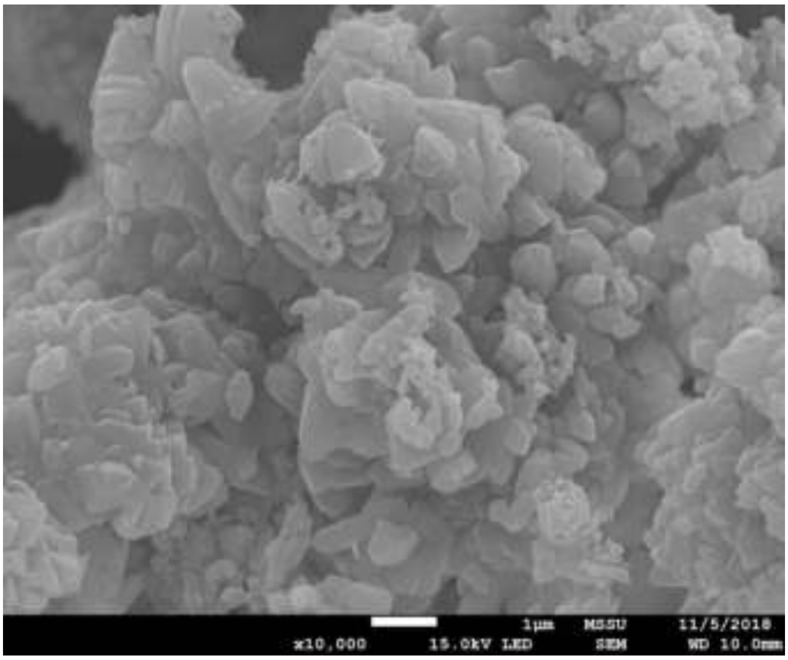


Figure 9.19. SEM image of $CaCO_3$ from K_2CO_3.

9.4.2. $CaCl_2$ results

Figures 9.20, 9.21 and 9.22, display the influence of the reaction temperature, molar ratio (R) variation and reaction time in the precipitation efficiency obtained with Na_2CO_3-$CaCl_2$ pair.

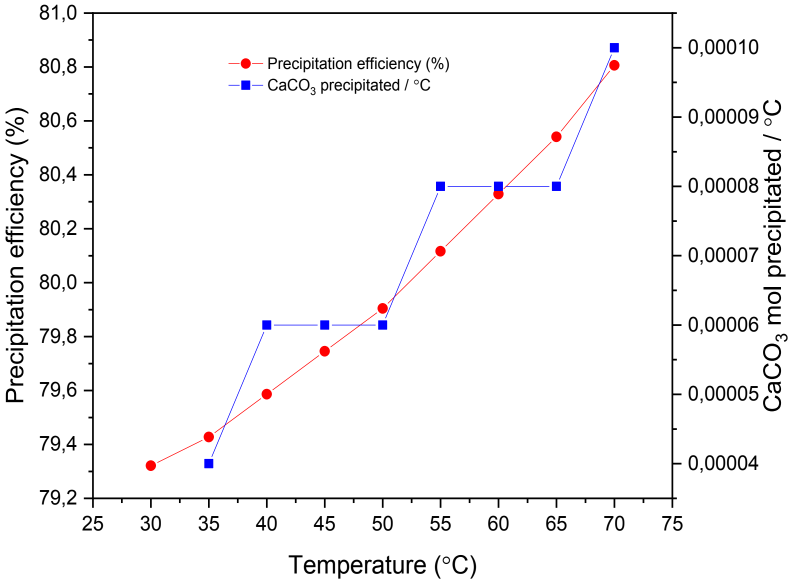


Figure 9.20. Precipitation efficiency vs temperature for Na_2CO_3 - $CaCl_2$ pair.

As shown in Figure 9.20, there is not much difference between regeneration efficiency at 30°C and 70°C (less than 2%). It means that good results could be obtained at room temperature making the process much less energy intensive than traditional alternatives such as CO_2 absorption with MEA or AMP [135,175,384]. This result matches well with previous investigations dealing with carbonate driven CO_2 capture alternatives [385,386]. Regarding $CaCO_3$ moles precipitated per degree of temperature increase, it is observed that generally the trend is positive in the studied range, which indicates positive effect of the temperature in the precipitation. However, the increase is considerably small – even inappreciable in some points - an aspect that agrees with the results obtained for PCC efficiency.

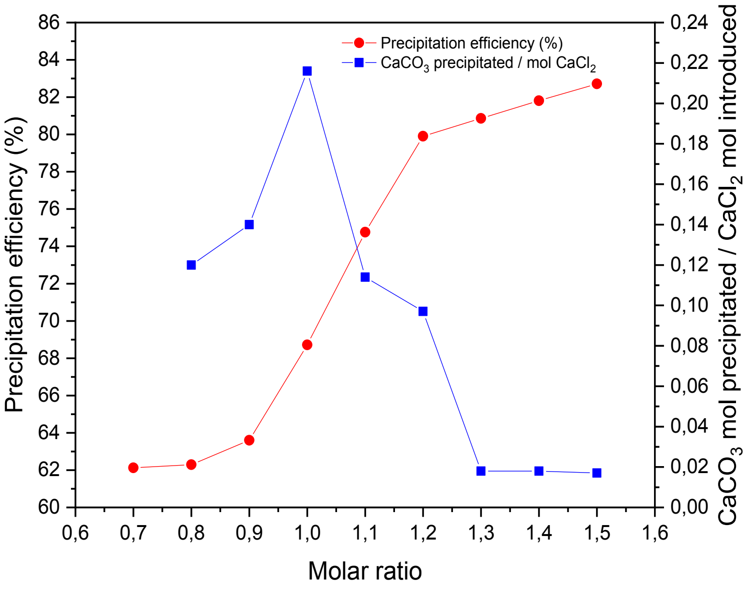


Figure 9.21. Precipitation efficiency vs molar ratio for Na_2CO_3 - $CaCl_2$ pair.

Interestingly, the molar ratio between the reactants seems to play a major role in the process. Figure 9.21 clearly demonstrates that the best point to operate the reactor is an R value of 1.2. Indeed, a reasonable value of precipitation efficiency is obtained at this point and further improvement beyond this threshold may not compensate the cost of the reagents. Also, the amount of free calcium remaining in the NaCl solution formed could be easily removed in a previous BMED stage by altering pH with the addition of small quantities of aqueous NaOH. Further relevant information concerning the process yield can be inferred from Figure 9.21. Following the squared symbols curve it seems clear that a better utilization of each $CaCl_2$ mol is obtained at R=1 since in this point the curve reaches the maximum. However at this ratio the net precipitation yield, is not as good as it is at R=1.2, which represent a good balance in terms of precipitation efficiency and reactant utilization and seems to be an ideal starting point for further studies seeking an industrial implementation.

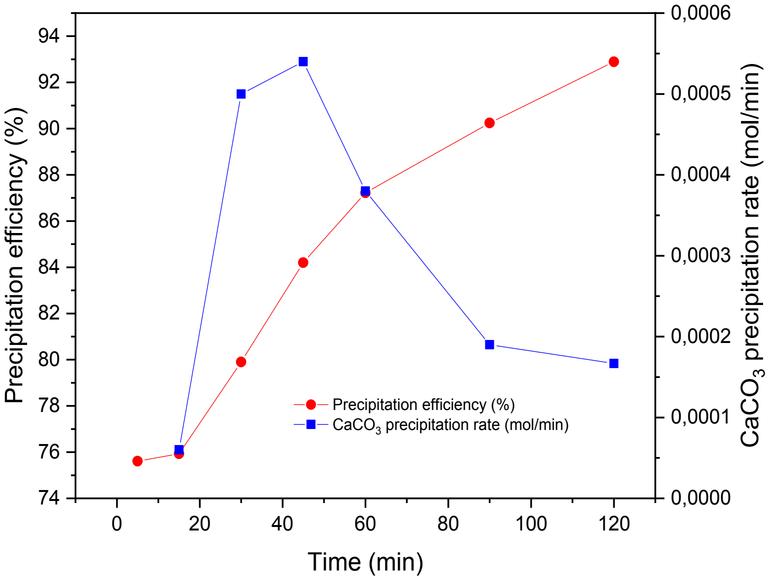


Figure 9.22. Precipitation efficiency vs time for Na_2CO_3 - $CaCl_2$ pair.

Finally, the evolution of $CaCO_3$ precipitation efficiency during the reaction time was studied. As shown in Figure 9.22 a remarkable improvement can be obtained from 15 minutes (75.93%) to 60 minutes (87.22%), but doubling the reaction time to 120 minutes only produces a minor impact (5% enhancement) on the overall efficiency. Such a reaction time increment would result in doubling the size of a potential industrial reactor in a realistic application and therefore it is not recommended given the subtle efficiency improvement. From the squared symbols plot we can infer that the maximum precipitation rate is achieved at 45 minutes (84.19% yield), with a remarkable decrease beyond this point suggesting that 45 min is a suitable operation point from a general process efficiency perspective.

As in the previous section, a comparison of the main selected points was made between Na_2CO_3 and K_2CO_3 as carbonated solvents. The results obtained are quite similar to the previous ones, being the precipitation efficiency always higher when using Na_2CO_3. The results are represented in Figures 9.23-9.25.

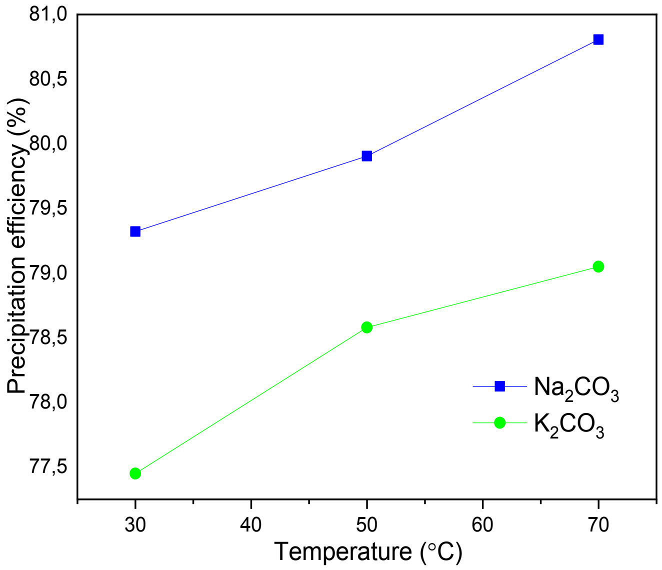


Figure 9.23. Comparison precipitation efficiency vs temperature for Na_2CO_3 - $CaCl_2$ and K_2CO_3 - $CaCl_2$ pairs.

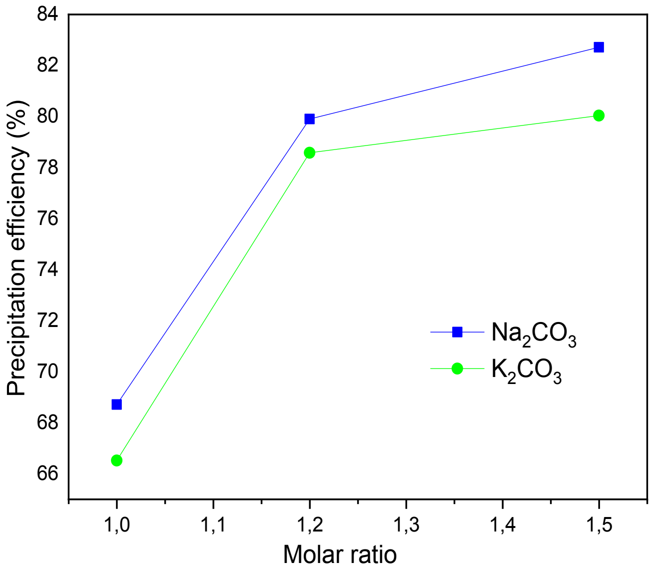


Figure 9.24. Comparison precipitation efficiency vs molar ratio for Na_2CO_3 - $CaCl_2$ and K_2CO_3 - $CaCl_2$ pairs.

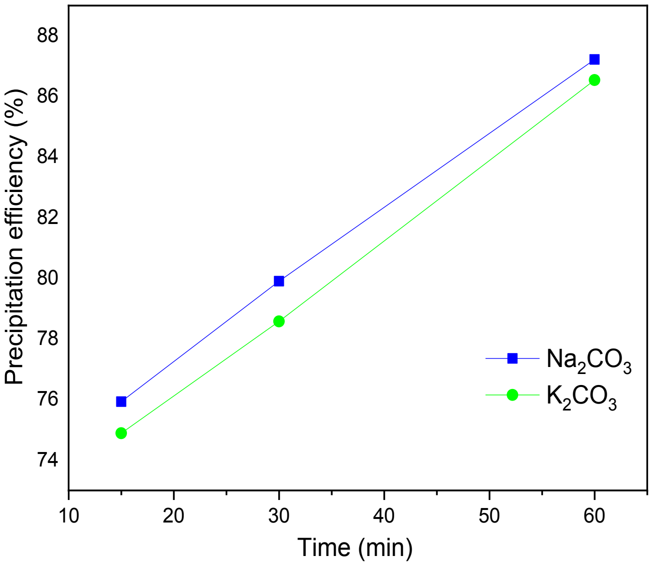


Figure 9.25. Comparison precipitation efficiency vs time for Na_2CO_3 - $CaCl_2$ and K_2CO_3 - $CaCl_2$ pairs.

Regarding the physicochemical analysis, a combined Raman, XRD and SEM was carried on the obtained precipitated samples in order to check their purity. The curves obtained were practically identical for both carbonated solvents. For sake of clarity and analysis, only Na_2CO_3 sample from test number 26 was chosen to compare with commercial samples. Commercial standards samples of $CaCO_3$ were also studied for sake of comparison. Figure 9.26 represents the Raman spectrum of the $CaCO_3$ obtained for the test corresponding to 30 minutes, 50ºC and R=1.2, in comparison with the spectrum of a standard $CaCO_3$ sample. The strongest band of $CaCO_3$ appears at 1100 cm^{-1} [375,380]. As can be seen in Figure 9.26, both $CaCO_3$ and standard $CaCO_3$ show this peak, as well as another characteristic band at 700 cm^{-1}, confirming that the precipitated sample is completely $CaCO_3$. This is an interesting observation since the result presented in the previous section reported an uncompleted precipitation and the presence of impurities such as hydroxides when $Ca(OH)_2$ are used [147]. It seems that calcium chloride is a suitable option as precipitator to favor full and neat $CaCO_3$ formation.

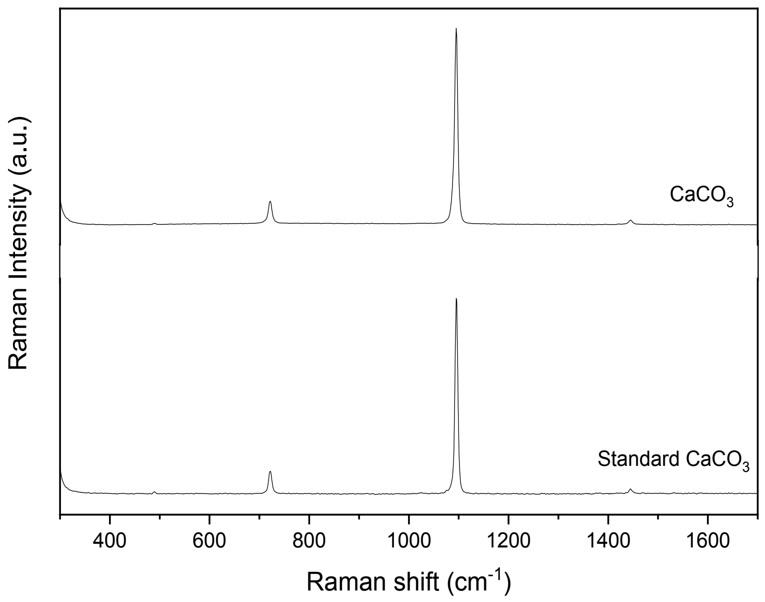


Figure 9.26. Raman spectra for $CaCO_3$ from Na_2CO_3 in comparison with standard $CaCO_3$ sample.

Once confirmed that the solid samples obtained are $CaCO_3$, it is important to investigate the crystal polymorphs in which the precipitation has resulted. $CaCO_3$ can be obtained in three main crystal polymorphs form: calcite, aragonite, and vaterite [379,380]. The type of $CaCO_3$ polymorphs are difficult to distinguish by routine Raman spectroscopy. For this reason, a XRD analysis was conducted. Figure 9.27 shows X-Ray diffraction patterns of the $CaCO_3$ obtained precipitated (same sample used for the Raman study). According to previous studies, the type of $CaCO_3$ obtained correspond to calcite, the most stable form of $CaCO_3$ [379,387]. Calcite present an intense and narrow diffraction peak at around 28 degrees, as well as less strong reflections at 23, 36, 39, 43, 47 and 48 degrees. Also, as can be seen in Figure 9.27 the XRD diffraction pattern of the obtained $CaCO_3$ matches perfectly that of the reference $CaCO_3$ indicating that both samples present the crystalline structure of calcite and they are both free of impurities.

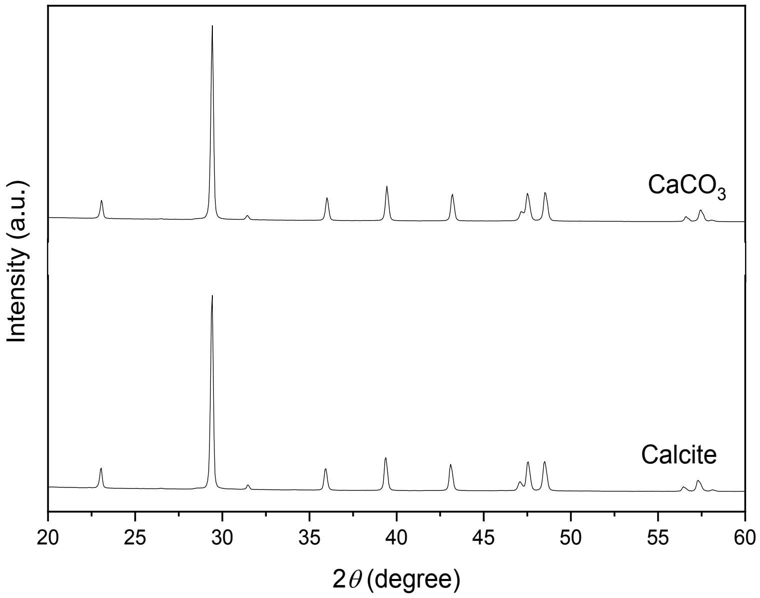


Figure 9.27. XRD pattern for $CaCO_3$ from Na_2CO_3 in comparison with standard calcite sample.

Further physicochemical information about the nature of the precipitated carbonates was obtained via scanning electron microscopy. Selected SEM images were taken showcasing the morphology of the solid samples. Previous reports in literature pointed out the tetrahedral morphology of calcite. Indeed, as it can be observed in Figure 9.28, $CaCO_3$ samples obtained in our experiments show this typical shape, what in general terms confirms the previous XRD and Raman results validating the purity of the precipitated samples.

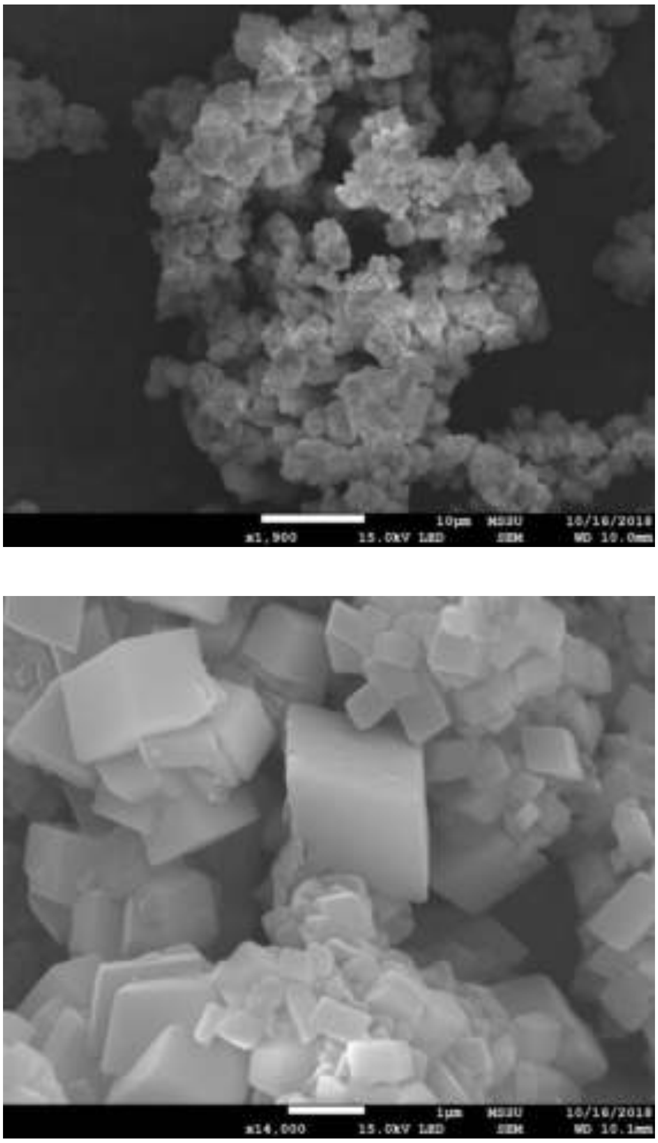


Figure 9.28. SEM images of $CaCO_3$ from Na_2CO_3.

9.4.3. $Mg(OH)_2$ results

This section analyzes the results obtained with the use of $Mg(OH)_2$ as a precipitation agent. As will be seen below, the results employing $Mg(OH)_2$ were much lower than the previous precipitants, so this section directly shows the Figures for the comparison between Na_2CO_3 and K_2CO_3 (tests 51 to 57 and 86 to 92 in Table 9.2). Figures 9.29-

9.31 show the precipitation performance results obtained by varying the time, temperature and molar ratio, respectively. It is observed that the efficiency results are significantly lower than those provided by the two precipitation agents previously studied. Although it may seem surprising because of the similar basic character of $Ca(OH)_2$ and $Mg(OH)_2$, this result coincides with similar studies present in the literature and is due to the greater precipitating nature of Ca ions with respect to Mg ions. This will be studied in deep in the discussion section 9.4.5.

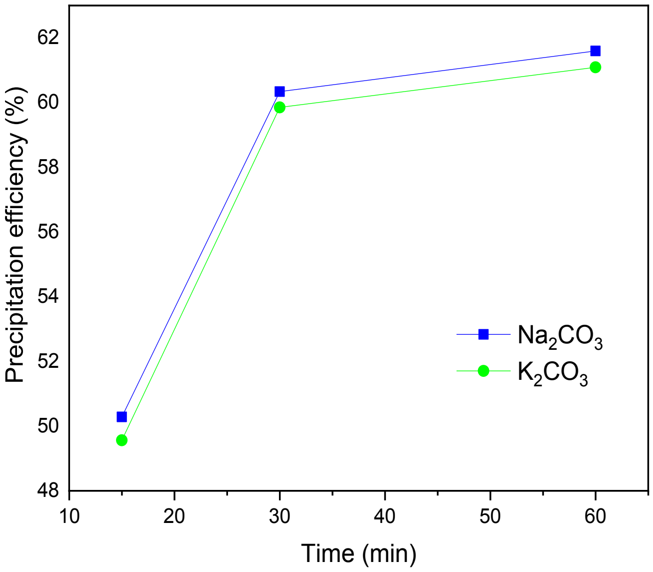


Figure 9.29. Comparison precipitation efficiency vs time for Na_2CO_3 – $Mg(OH)_2$ and K_2CO_3 - $Mg(OH)_2$ pairs.

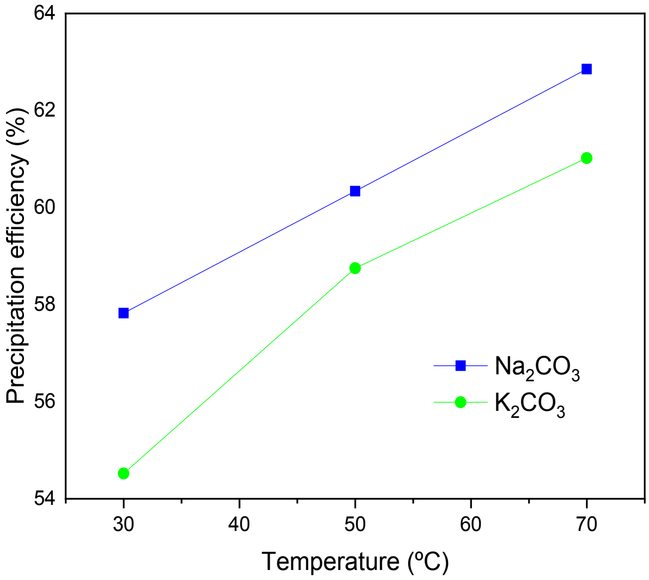


Figure 9.30. Comparison precipitation efficiency vs temperature for Na_2CO_3 – $Mg(OH)_2$ and K_2CO_3 - $Mg(OH)_2$ pairs.

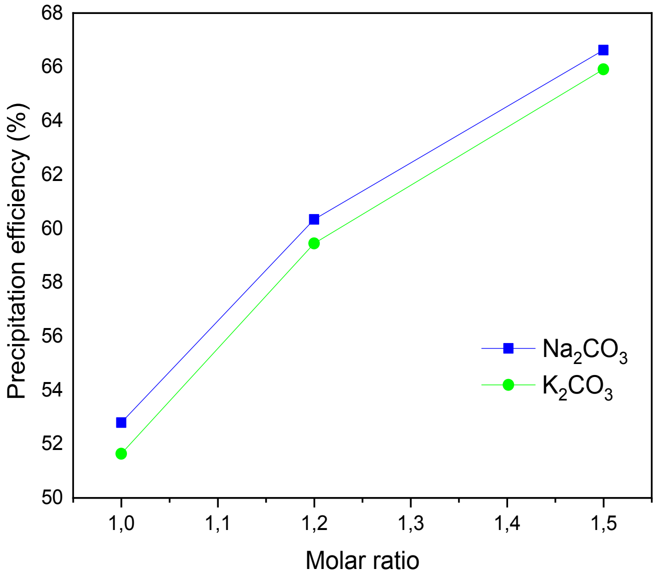


Figure 9.30. Comparison precipitation efficiency vs molar ratio for Na_2CO_3 – $Mg(OH)_2$ and K_2CO_3 - $Mg(OH)_2$ pairs.

A deeper analysis of $Mg(OH)_2$ as precipitant agent is not worthy since the precipitation efficiencies obtained are much worse than with the previous precipitants studied. Nevertheless, to provide a wide range of information and be able to compare properly in section 9.4.5, below the physicochemical analysis of the solid samples obtained is presented. Figures 9.31-9.34 reflect the results of FTIR, Raman, XRD and SEM analysis.

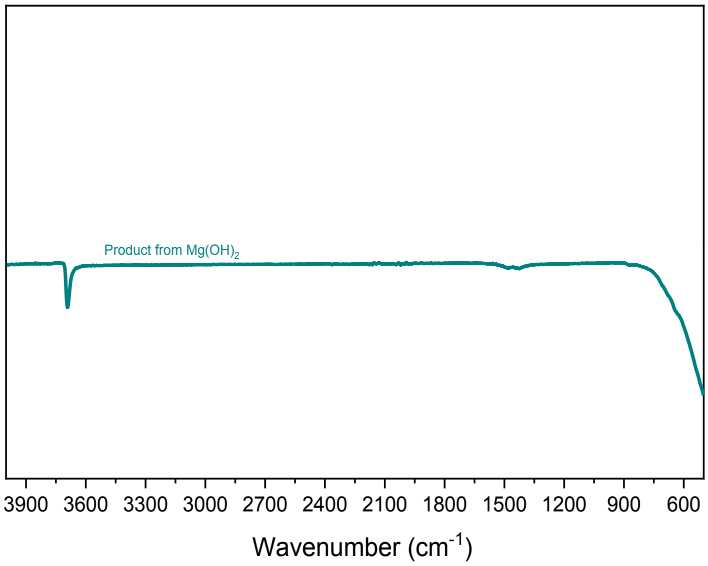


Figure 9.31. FTIR spectrum of the product obtained from Na_2CO_3 – $Mg(OH)_2$ pair.

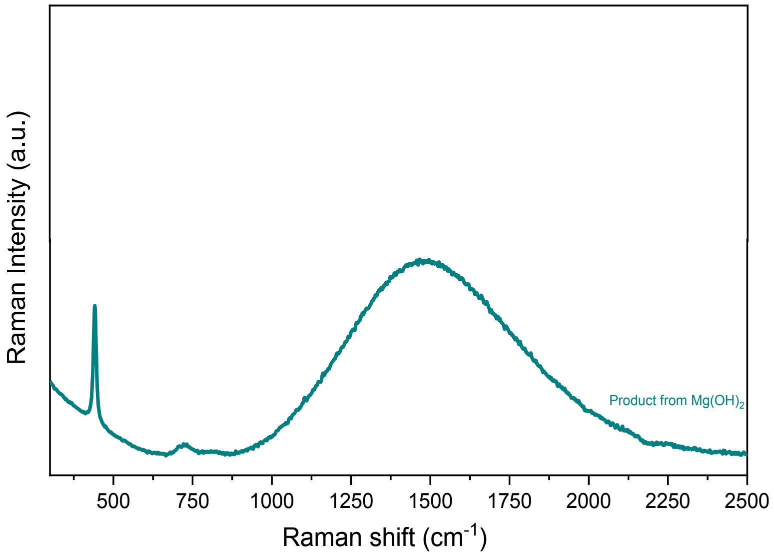


Figure 9.32. Raman spectrum of the product obtained from Na_2CO_3 – $Mg(OH)_2$ pair.

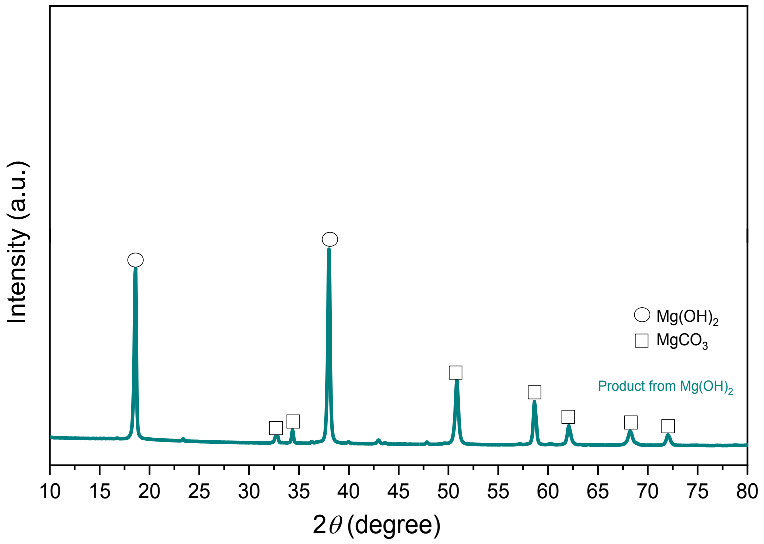


Figure 9.33. XRD pattern of the product obtained from Na_2CO_3 – $Mg(OH)_2$ pair.

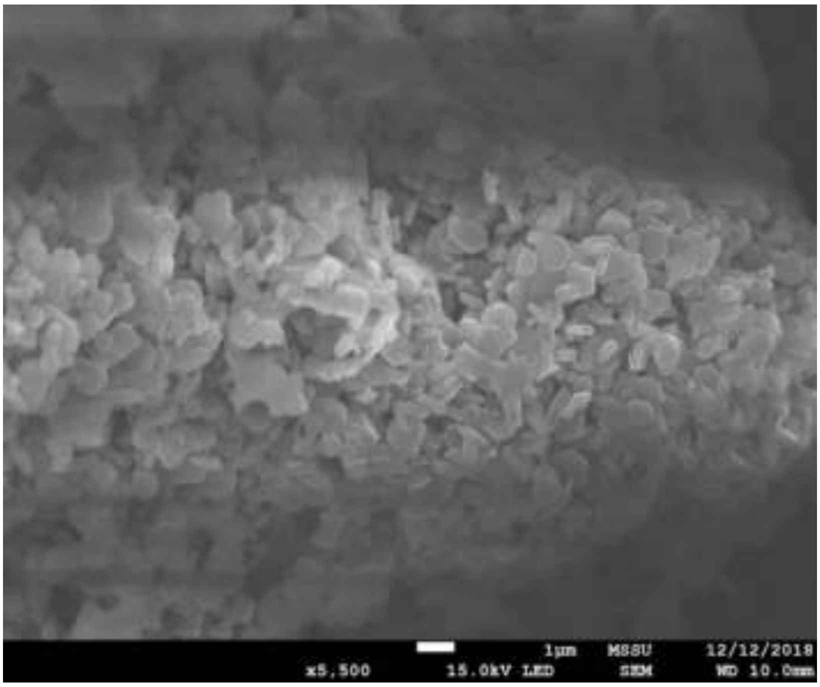


Figure 9.34. SEM image of the product obtained from Na_2CO_3 – $Mg(OH)_2$ pair.

FTIR of the product obtained from $Mg(OH)_2$, the presence of a typical $Mg(OH)_2$ band at around 3700 cm^{-1} indicates a poor $MgCO_3$ purity. The Raman spectrum showed in Figure X by the product from $Mg(OH)_2$ shows high presence of hydroxide ions recognizable at 400 and 1500 cm^{-1}. Inasmuch this result does not reject the possibility of an existing carbonate phase in the final product. Indeed, $MgCO_3$ typical strong bands could be hidden by the intense band at 1500 cm^{-1} presented also by $Mg(OH)_2$. In the case of XRD analysis, this time a mix of both species $Mg(OH)_2$-$MgCO_3$ is presented in the pattern. The most characteristic peak of $Mg(OH)_2$ is noticed at 18° as well as at 51° for $MgCO_3$. Inasmuch the morphology presented by the product obtained from $Mg(OH)_2$, SEM analysis of Figure 9.34 reflects a polymorph agglomerate structure previously seen in hydrated magnesium carbonate by other authors [388]. Indeed, the appearance of this morphology explains why there is not a clear carbonate phase in the results previously obtained by means of FTIR, Raman and XRD. Hydrate magnesium carbonate contains high quantity of OH ions which could hide carbonates peaks or bands [388].

9.4.4. $MgCl_2$ results

Figures 9.35-9.37 depict the results obtained in our experiments by the variation of temperature, molar ratio and reaction time. Similar trends than in previous precipitant were obtained, hence a deeper discussion comparing with other previous work was also included in this point. For example, Figure 9.35 reveals the trends of the precipitation efficiency when varying the reaction temperature. In agreement with previous works, this trend seems to be positive and the precipitation efficiencies are quite similar than those observed employing organic alcohols as CO_2 carriers [389]. This is a very important fact as the market price of our reactants is quite low compared to that of the organic alcohols typically employed in this process. The precipitation efficiency for 30°C was 75.13% which means that good results can be obtained at room conditions, what is an important advantage respect to current ongoing industrial processes for CO_2 mineralization. Increasing the temperature from 30°C to 50°C is not worthy inasmuch only a 3% of improvement is obtained. However, there is a remarkable increase from 75.13% to 82.07% when rising up the temperature from 30°C to 70°C. Thus, an increase of more than double the initial temperature value would be necessary for a substantial improvement of the overall precipitation efficiency. Even under the maximum temperature tested in our experiments this process is much more feasible in terms of energy consumption compared to traditional methods. Nevertheless, this parameter needs to be optimize since 50°C can be easily obtained by means of renewable energies whereas 70°C would be a more challenging situation to be achieved exclusively using sustainable resources. Comparing with previous similar studies in terms of temperature, our innovative process has proved to be more feasible due to the higher efficiencies obtained. For instance at 30ºC our precipitation efficiency was 75.13% while less than 70% was obtained in a similar study with organic alcohols as solvent [386].

Morene et al also performed comparable experiments at ambient temperature using steel slags as precipitator agent [390]. They obtained around 60% of equivalent efficiency which again reflects a poorer precipitation capacity compared to our results. Air pollution control residues were employed in [151], obtaining 65.1% efficiency for 55ºC whereas in our work 78.28% precipitation efficiency was obtained at 50ºC with $MgCl_2$ residues. In summary from the temperature perspective (and ultimately energy savings in the process) there are obvious advantages of our approach over previously reported strategies.

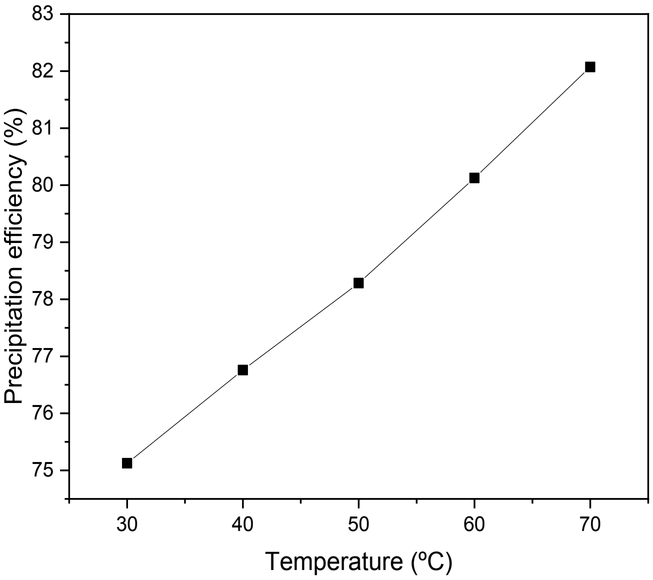


Figure 9.35. Precipitation efficiency vs temperature for Na_2CO_3 - $MgCl_2$ pair.

Figure 9.36 shows again a positive trend of precipitation efficiency regarding the variation of molar ratio. This could be due to a major proportion of chloride ions enhancing their reaction with sodium and thereupon providing more free carbonates which triggered the precipitation of $MgCO_3$. Interestingly, the molar ratio indeed has a stronger effect than reaction temperature in the precipitation efficiency. This wide difference can be observed when increasing the R value from 1 to 1.2, where the precipitation efficiency was enhanced from 69.44% to 78.28%. When an R value of 1.5 was tested, 82.70% precipitation efficiency was obtained. This last increase did not show to be as effective as the first one since less than 4% of enhancement was achieved. Moreover, upon this value a higher chloride concentration in the NaCl solution would be obtained. This could unbalance the pH of the solution making necessary a pre-treatment before employing it in a potential industrial process thus increasing the overall running cost.

Similar studies varying parameters equivalents to R also showed positive trends upon incrementing R value [359,386,391]. Organic alcohol N235 was used as solvent and showed around 45% efficiency with molar ratio equal to 1. At 1.5 molar ratio little more than 60% was obtained [386]. In our work almost 70% was obtained for this R=1 and more than 80% with R=1.5 hence Na_2CO_3 has been demonstrated to be better solvent for carbon mineralization. Similar conversions were obtained in [391] but with $CaCl_2$ instead of $MgCl_2$. Employing air pollution control residues at R=1.2 resulted in 65.1% efficiency whereas as previously commented 78.28% was obtained in our study.

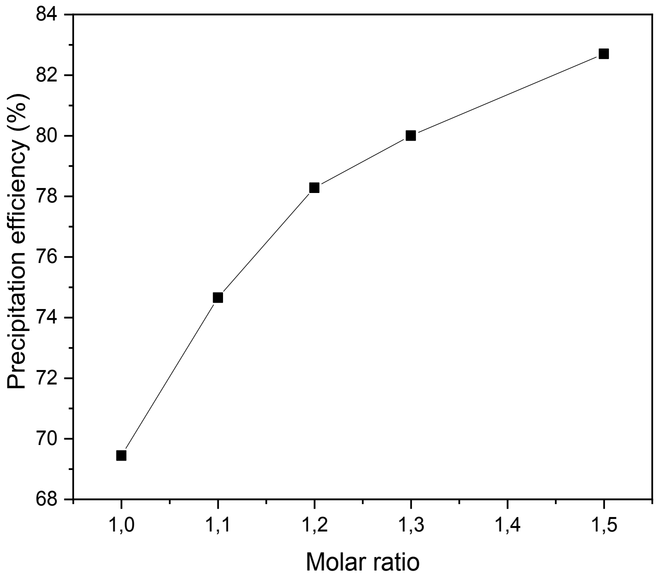


Figure 9.36. Precipitation efficiency vs molar ratio for Na_2CO_3 - $MgCl_2$ pair.

Again the influence of the reaction time is quite remarkable on precipitation efficiency comparing to the effect of temperature variation. As shown in Figure 9.37 a noticeable improvement was obtained from 15 minutes (73.23%) to 60 min (85.23%). Even if this means a reactor size four times bigger, a possible enhancement of 12% would be a reason of optimization regarding a potential industrial application. Furthermore, in a potential industrial process other configurations could be tested, such as continuous stirred tank reactor (CSTR), to obtain a higher reaction time which could minimize the investment costs of the reactor. Additionally, the results obtained at 30 min (78.28%) could be an optimum trade-off between precipitation efficiency and reactor size. In comparison with previous studies there are remarkable differences regarding reaction time. Probably these discrepancies are originated by the different precipitator agent employed in each study. Baciocchi and co-workers reported *ca.* 90% efficiency of the carbonation reaction in terms of KOH regeneration for 1 hour-experiment [359]. On the other hand, 50% of conversion was obtained with steel slag as precipitator at 30 minutes

[390]. Thus, our innovative system has proved to be in line with Baciocchi's work and almost 30% better in terms of precipitation capacity than the work by Morone et al.

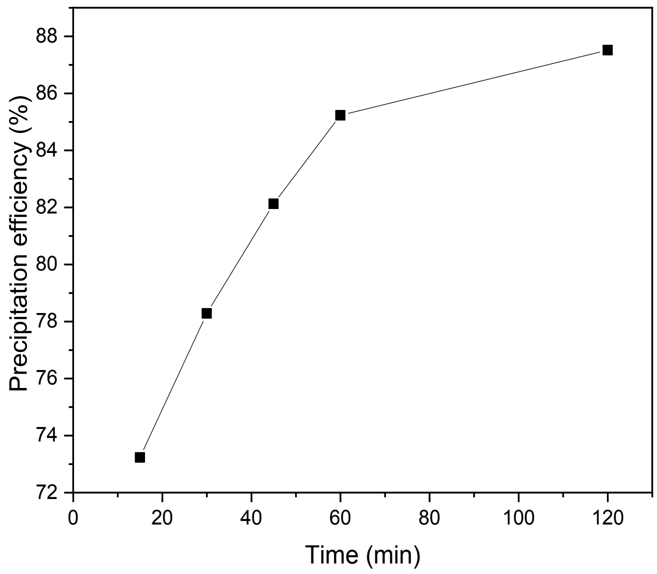


Figure 9.37. Precipitation efficiency vs time for Na_2CO_3 - $MgCl_2$ pair.

As in previous sections with other precipitant agents, Na_2CO_3 and K_2CO_3 were also compared for $MgCl_2$ pairs. In this section more points were selected to compare since as discussed above the outcomes from this precipitant are remarkable. Figures 9.38-9.40 reflect the results obtained.

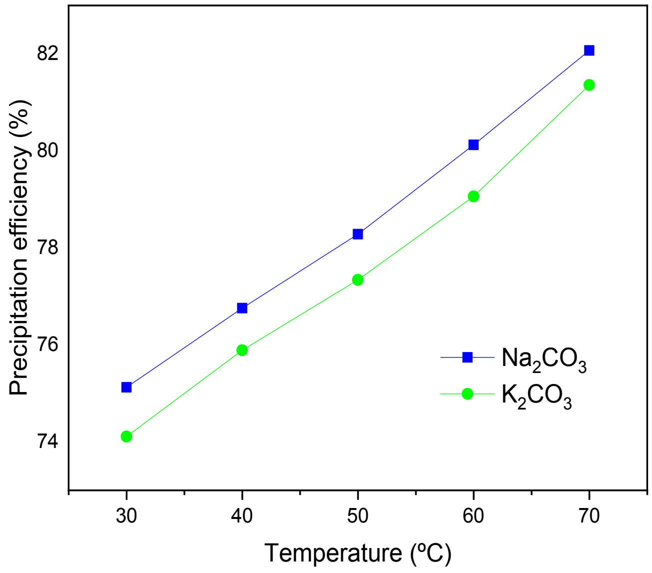


Figure 9.38. Comparison precipitation efficiency vs temperature for Na_2CO_3 – $MgCl_2$ and K_2CO_3 - $MgCl_2$ pairs.

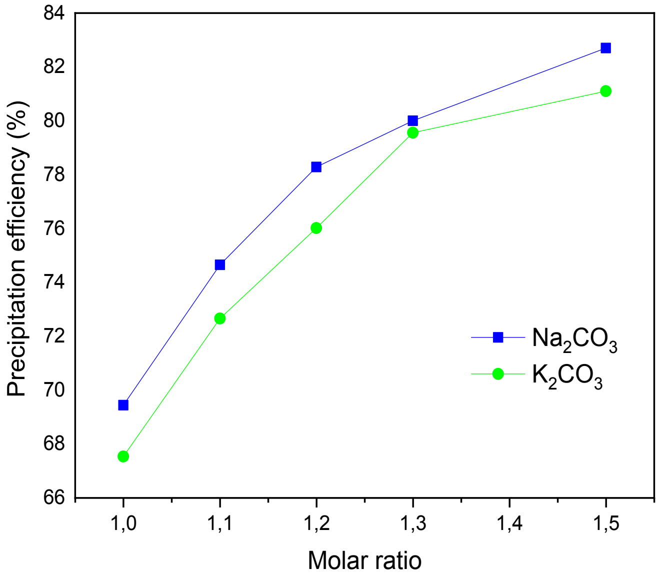


Figure 9.39. Comparison precipitation efficiency vs molar ratio for Na_2CO_3 – $MgCl_2$ and K_2CO_3 - $MgCl_2$ pairs.

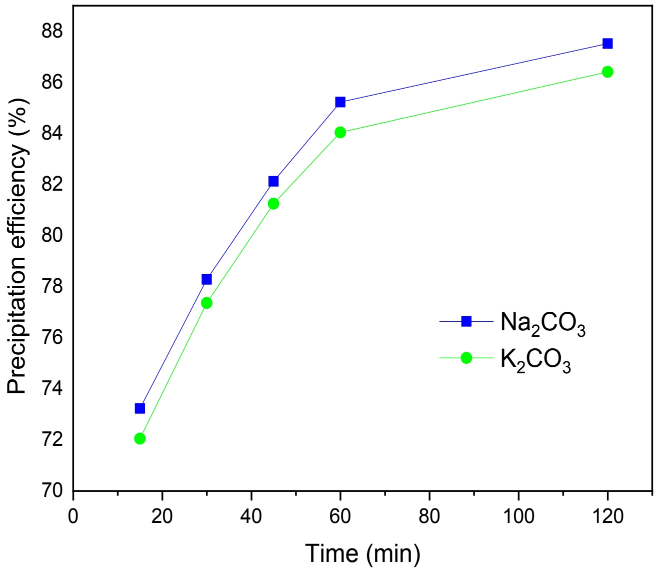


Figure 9.40. Comparison precipitation efficiency vs time for Na_2CO_3 – $MgCl_2$ and K_2CO_3 - $MgCl_2$ pairs.

Regarding the physicochemical characterization of the solid samples, both carbonated solvents presented a very similar structure. The purity and the quality of the resulting precipitate determines its market opportunities and could be a plus for the proposed strategy. The white powder obtained as precipitated samples was characterized by means of Raman, XRD and SEM in order to determine its physicochemical properties. Firstly, Raman was adopted to ascertain whether a carbonate phase was presented in our samples. Figure 9.41 represents selected Raman spectra for our experiments indicating undoubtedly the formation of the carbonate phase. Indeed, the presence of a strong band at 1100 cm^{-1} characteristic of carbonates confirms this statement [392]. Thus, the presence of this band means that the predominant compound presents in our sample is $MgCO_3$. Furthermore, another characteristics weaker bands are presented at around 480 and 740 cm^{-1} [361,393]. Hence these results confirmed that the mineralization reactions entirely met our hypothesis. Nevertheless, due to the multiple existing carbonate phases as well as particle shapes and morphologies, the use of standalone Raman does not allow to confirm the crystal structure and purity of the resulting solid.

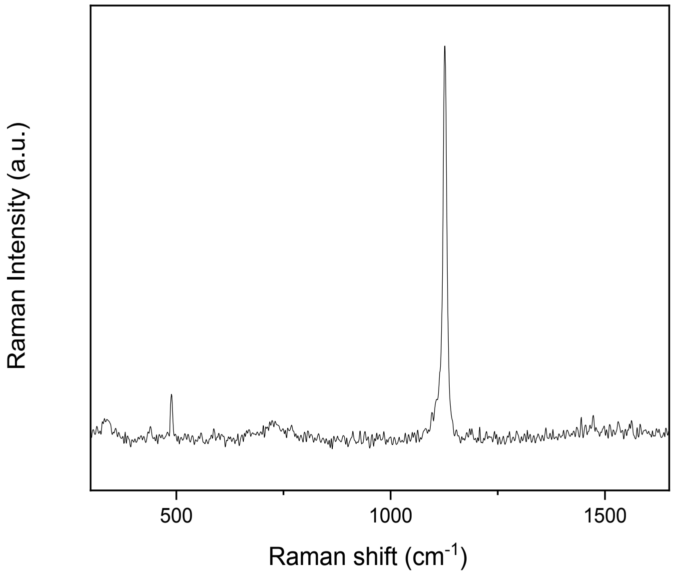


Figure 9.41. Raman spectrum of the product obtained from Na_2CO_3 – $MgCl_2$ pair.

For this purpose XRD and SEM were conducted in our study. Once confirmed that the solid samples obtained are $MgCO_3$, it is important to investigate the crystal polymorphs in which the precipitation has resulted to assess their commercial value. $MgCO_3$ can be obtained in multiple crystal polymorphs form such as for example Magnesite, Barringtonite, Nesquehonite, Dypingite, and Hydromagnesite. Hydromagnesite, typically known as Hydrated Magnesium Carbonate (HMC), can be split in two main categories according to the number of water molecules attached in their empirical formula - Light Hydrated Magnesium Carbonate (LHMC) with $4H_2O$ molecules and Heavy Hydrated

Magnesium Carbonated (HHMC) which contains $5H_2O$ molecules [388]. Figure 7.42 shows the XRD patterns of the $MgCO_3$ samples obtained during the standard test. According to previous studies, this XRD pattern agrees fairly well with that of the HHMC samples. As can be seen, there are some peaks characteristics of Dypingite (e.g. 15, 31 or 33 degrees) as well as diffractions attributed to Nesqueonite (e.g. 22 or 52 2Ɵdegrees) and some of them which appear in both diffractograms Dypingite-Nesqueonite (D-N in Figure 9.42) of these species [388,394–396]. As previously documented, these products present a variety of commercial applications and can be used as inorganic filling agents [397], filler pigment in paper [398], or to produce cement and basic refractory bricks [399] reinforcing the commercial viability of the biogas upgrading strategy coupled with added value by-product generation proposed in this work.

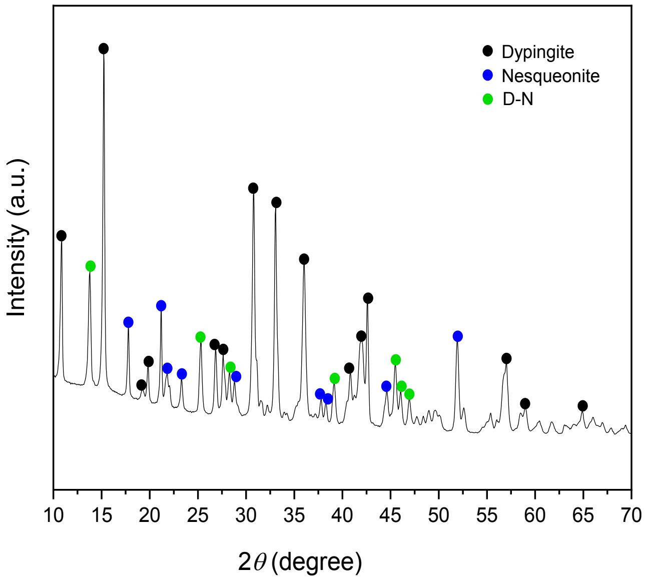
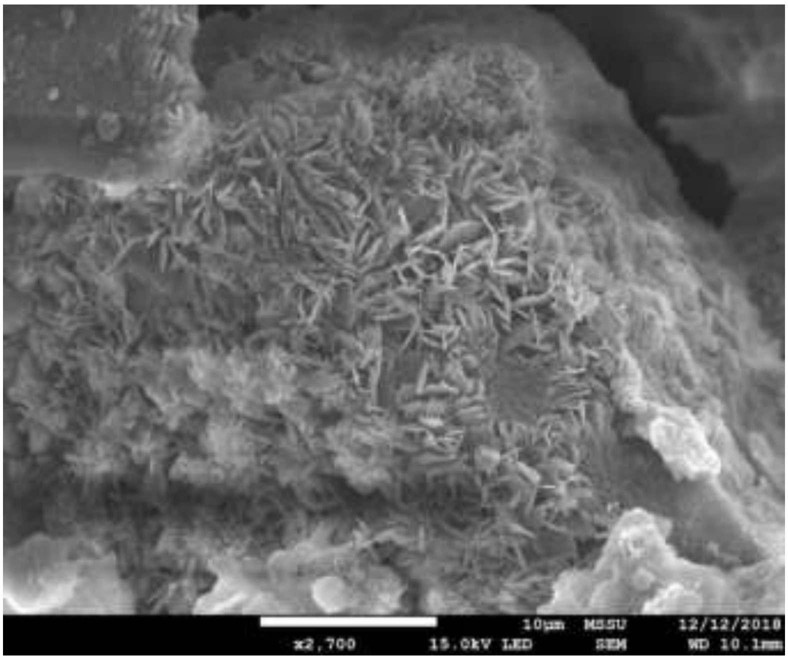


Figure 9.42. XRD pattern of the product obtained from $Na_2CO_3 – MgCl_2$ pair.

In order to examine the morphology of the solid samples to complement the results provided by XRD, SEM images were taken of the selected samples. Figure 9.43 shows

HHMC typical morphology in which Dypingite shape alike aggregated plate crystals are recognized as in previous studied by other authors [386,388]. Nevertheless, the presence of some Nesqueonite portion can be seen in the needless shapes in some parts of the sample, confirming our previous XRD results. Thus, the products of our innovative process present different morphologies and sizes, which could make them useful in various industrial applications.



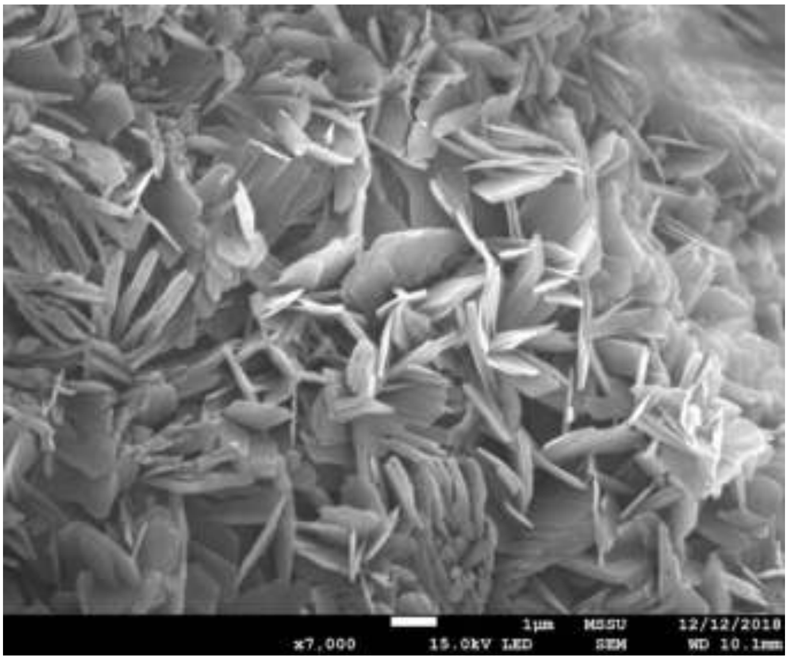


Figure 9.43. SEM images of the product obtained from Na_2CO_3 – $MgCl_2$ pair.

9.4.5. Precipitant agents' comparison

The precipitant agents tested and whose results were explained in deep in sections 9.4.1-9.4.4, present comprehensive differences regarding the precipitation efficiencies obtained. Therefore, a proper comparison to evaluate the most suitable precipitant agent is needed. In this sense, it seems clear than K_2CO_3 pairs give lower precipitation efficiencies than Na_2CO_3 pairs. This fact can be seen in the sections above indicated. Nevertheless, among every pair tested of Na_2CO_3-precipitant, it is not clear which one is the best for this application. Figure 9.44 collects the results of each standard test for Na_2CO_3-precipitant pairs.

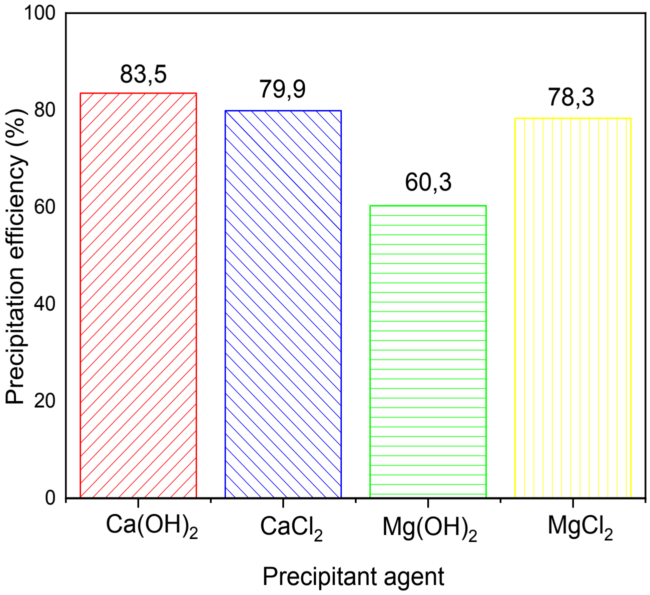


Figure 9.44. Results of the standard test for each precipitant agent (pairs with Na_2CO_3 as carbonated solvent)

As can be seen, the best results were obtained by using $Ca(OH)_2$ as precipitant agent. Nevertheless, the other hydroxide compound tested as precipitant does not show similar results. The fact that generally $Mg(OH)_2$ get lower precipitation efficiencies is a phenomenon which need some explanation. This fact is probably owing to the dehydroxilation phenomenon which occurs in $Mg(OH)_2$ and does not take place in $Ca(OH)_2$ carbonation reaction because of the different solubility of both species [400,401]. Dehydroxilation phenomenon of $Mg(OH)_2$ consist on the liberation of hydroxide agents (water release) to produce MgO and therefore to react with CO_2 to produce $MgCO_3$. It seems that in the present of an aqueous solution, this phenomenon is diminished. Nevertheless, at the temperature and pressure conditions tested in this work, the phenomenon cannot be completely overcome. The increase of temperature – pressure conditions will lead to higher operational cost in a hypothetic industrial application, which will result in less competitiveness of this technique. Therefore, in agreement with the results presented in this study, $Ca(OH)_2$ should be employed instead $Mg(OH)_2$ to overthrow this phenomenon.

To analyze the differences among hydroxides and salts, $Ca(OH)_2$ and $CaCl_2$ pairs will be discussed. In this sense, no remarkable differences were found on precipitation efficiencies. Nevertheless, the final solid product from $Ca(OH)_2$ presented some impurities which has a considerable impact on $CaCO_3$ price. Generally speaking, there are many potential applications for $CaCO_3$ calcite and its market price depends on the purity obtained, being around 100€/ton for less refined $CaCO_3$ [402], and *ca.* 350 €/ton for the finest $CaCO_3$ batches [403]. As a matter of practical example, calcium carbonate is employed as a paper filler and coating in the paper industry to its natural brightness [404,405]. In the paints sector, its lower price compared to titanium oxide favors the utilization of calcite as coating for paints manufacturing [404]. Also its economic viability makes $CaCO_3$ a very versatile chemical with multiple applications including adhesive and sealant production or as filler plastics in polymers industry [406,407]. Given the importance of the final solid product purity, below both products from $Ca(OH)_2$ and $CaCl_2$ are further physicochemically compared. $CaCO_3$ coming from the precipitation reaction of CO_2 in a liquid solution and $Ca(OH)_2$ or $CaCl_2$ is commonly known as precipitated calcium carbonate (PCC).

The first step of the physicochemical comparison was to corroborate the formation of the carbonate phase in the collected samples. For this purpose, Figure 9.45 represents both FTIR spectrum for $CaCO_3$ from $Ca(OH)_2$ and $CaCl_2$ as precipitant agents in comparison with a commercial $CaCO_3$ solid sample.

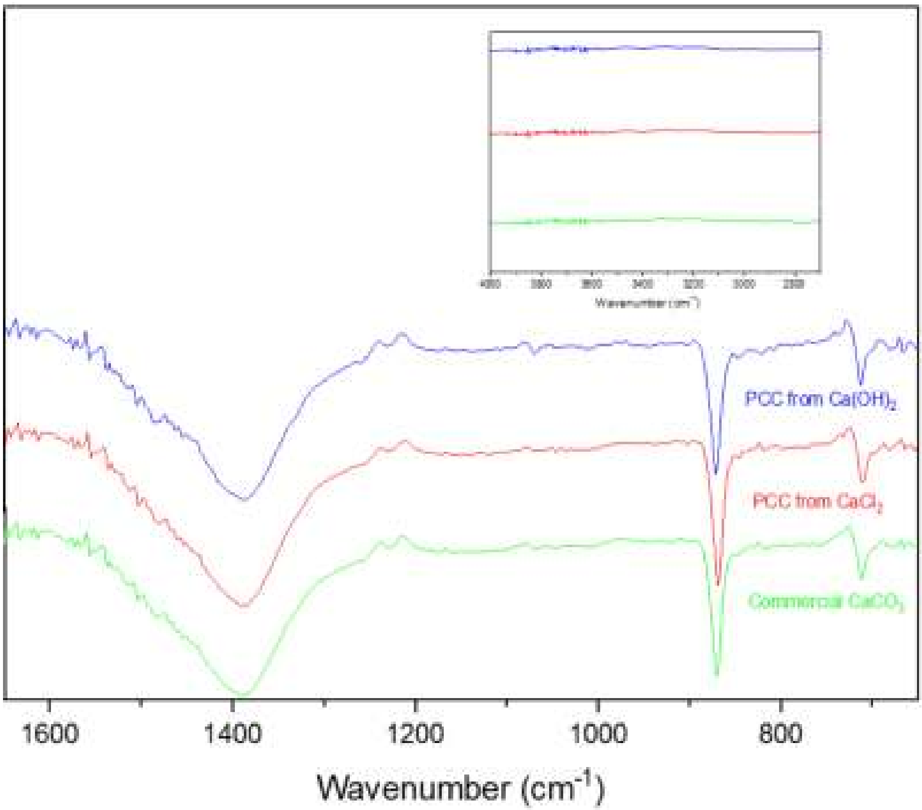


Figure 9.45. FTIR spectra of the products from $Ca(OH)_2$-$CaCl_2$ in comparison with commercial samples of $CaCO_3$.

Typically, a strong band of $CaCO_3$ spectra appears at around 1400-1500 cm^{-1} as well as a weaker peaks at 876 cm^{-1} and 715 cm^{-1} [408]. These are easily identified in every spectra of Figure 9.45, so it is possible to conclude that the carbonate phase is presented in both studied samples. According to the vibration bands at 715 cm^{-1} are indicative that calcite is the predominant crystal type in the investigated $CaCO_3$ samples, although it will be confirmed later by XRD [409]. Previously, in [408], FTIR spectra for different $CaCO_3$-$Ca(OH)_2$ mixtures were studied, obtaining strong vibrations at around 3600 cm^{-1} which are characteristic of hydroxyl groups. Indeed, only when pure $CaCO_3$ was measured, the produced spectra did not show this peak, inferring the peak at this value suggests the presence of hydroxide ions from $Ca(OH)_2$. In the Figure 9.45 inset, the data corroborates that there is no presence of these hydroxides, meaning that the purity of the $CaCO_3$ samples obtained is relatively high. Nevertheless, is not possible by means of this technique to distinguish the complete absence of $Ca(OH)_2$ in the represented spectrum. There may be some remnants of $Ca(OH)_2$ in the samples that would appear also at approximately 1400-1500 cm^{-1}, as in $CaCO_3$ spectra [408]. It is also possible to confirm that there is no $CaCl_2$ remaining in the inset of Figure 9.45, as there is no peak at 3200 cm^{-1}, characteristic of $CaCl_2$. To distinguish possible residual $Ca(OH)_2$, Raman spectroscopy was employed. Furthermore, this technique was useful to corroborate a carbonate phase in the collected samples, which can be seen in Figure 9.46 that represents both the PCC Raman spectrum from $Ca(OH)_2$ and $CaCl_2$ precipitant agents in comparison with a commercial $CaCO_3$ solid sample.

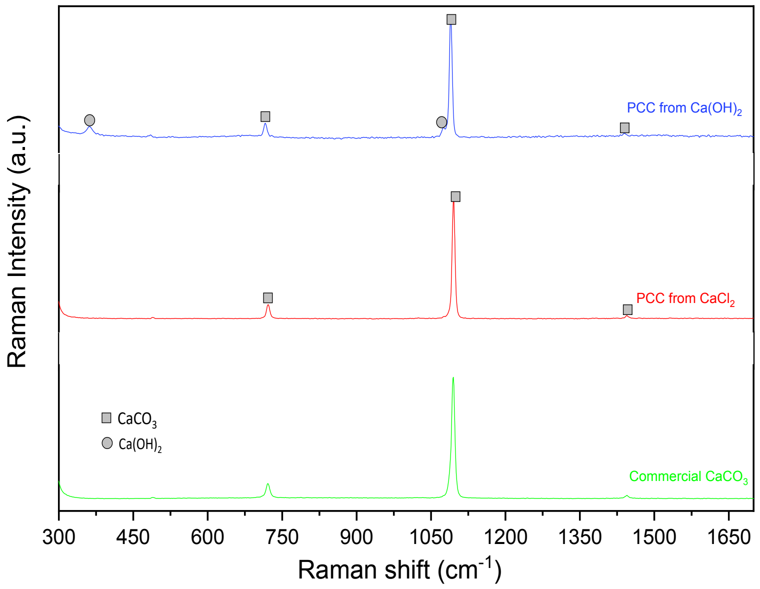


Figure 9.46. Raman spectra of the products from $Ca(OH)_2$-$CaCl_2$ in comparison with commercial samples of $CaCO_3$.

$CaCO_3$ shows a monoclinic structure that belongs to the P21/c group [380]. The main characteristic band of $CaCO_3$ polymorphs appears at around 1100 cm^{-1} and *ca.* 700 cm^{-}

^{1} and is typically ascribed to this monoclinic type of structure [379,380]. Figure 9.46 shows that these two peaks are presented in both PCC spectra for PCC from $Ca(OH)_2$ and $CaCl_2$, confirming the successful precipitation process due to the formation of the carbonate phase. The appearance of a band at 400 cm^{-1} and 1086 cm^{-1} are characteristic of $Ca(OH)_2$ that must be due to a small amount of $Ca(OH)_2$ remaining present in PCC from $Ca(OH)_2$ sample as this does not appear in the PCC from $CaCl_2$ spectrum. This was distinguished by the Raman vibration mode at *ca*. 400 cm^{-1}, which belongs to the most characteristic intense band of commercial $Ca(OH)_2$ as confirmation of our previous hypothesis [410]. The absence of this peak in PCC from $CaCl_2$ spectra confirms a pure $CaCO_3$ employing $CaCl_2$ as a precipitant agent, proving that by using this innovative process, it is possible to obtain PCC with a purity of 100% by removing CO_2 from biogas streams.

Once $CaCO_3$ was confirmed as the only species for PCC from $CaCl_2$ and predominant species for $Ca(OH)_2$ by both FTIR and Raman measurements, XRD analysis was carried out to distinguish which crystal morph of $CaCO_3$ has been obtained. The future use of the final $CaCO_3$ obtained depends on the morph, so that makes the crystal structure of the final product extremely important for both precipitant agents. There are three types of $CaCO_3$ crystal morphs: calcite, vaterite, and aragonite [375]. In terms of thermodynamics, the most stable form is calcite, followed by aragonite with vaterite being the least stable [383]. Figure 9.47 represents XRD patterns of the PCC obtained from both sources in comparison with commercial $CaCO_3$ calcite.

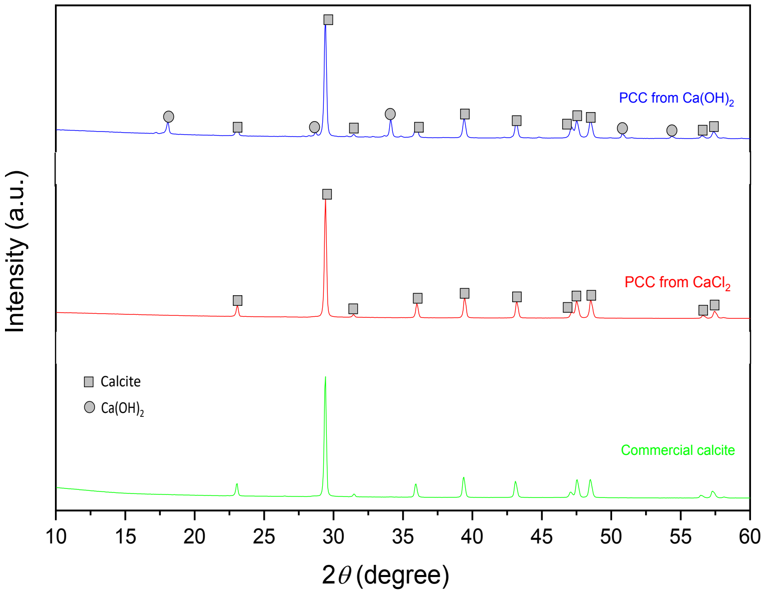


Figure 9.47. XRD pattern of the products from $Ca(OH)_2$-$CaCl_2$ in comparison with commercial samples of $CaCO_3$.

The analysis of the obtained XRD patterns, confirms that the calcite morph has been produced, the peaks being in accordance with previous references studied [383,411]. The main peaks of calcite appear at 28°, 39°, 43° and 48°. All of these peaks can be seen in both XRD patterns of PCC from $Ca(OH)_2$ and $CaCl_2$. Nevertheless, it seems that PCC from $CaCl_2$ pattern is more consistent with commercial calcite than PCC from $Ca(OH)_2$, due to the strong presence of $Ca(OH)_2$ within the sample, the peaks for which appear at 18°, 28°, 34°, 51° and 55° [412]. Characteristic $CaCl_2$ peaks appear at 13° and 18° [413] and as can be seen on the relevant XRD plot in Figure 9.47, there is no presence of any residual $CaCl_2$ as the mentioned peaks are not present. These results agree with both Raman and FTIR analyses presented previously in this work.

Calcite has five different structural shapes: rhombohedral, rhomboscalenohedral, scalenohedral, scalenorhombohedral, and spheroidal [414]. Rhombohedral or scalenohedral shapes are widely employed as filler in paper industry, due to an enhancement produced in the optical properties of paper sheets [414]. Confirming the different shapes of the obtained samples is therefore very important when considering future applications and is possible through SEM analysis. SEM images are useful to gain further insights on the structure of the samples. Multiple images of the obtained samples were taken to ensure homogeneity. Figures 9.48 and 9.49, showcase representative examples of the SEM micrographs. Again the presence of $CaCO_3$ is confirmed with the typical morphology of calcite as previously observed by Altiner et al. [379]. In their study, several PCC structures are shown and strictly compared, obtaining similar results to those presented in this work regarding the morphology of the different solids obtained. As can be seen in Figure 9.48, PCC from $Ca(OH)_2$ presents a polymorph form with a mixture of different morphologies. On the contrary, Figure 9.49 shows a rhombohedral form of the particles, again highlighting the purity of the $CaCO_3$ obtained in the form of calcite and making the product very valuable from a commercial point of view discussed above.

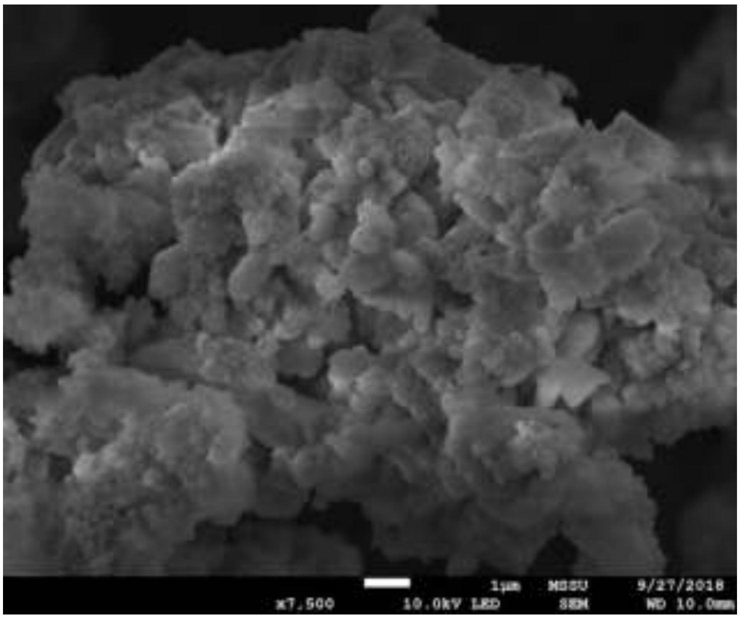


Figure 9.48. SEM image for the product obtained from $Ca(OH)_2$.

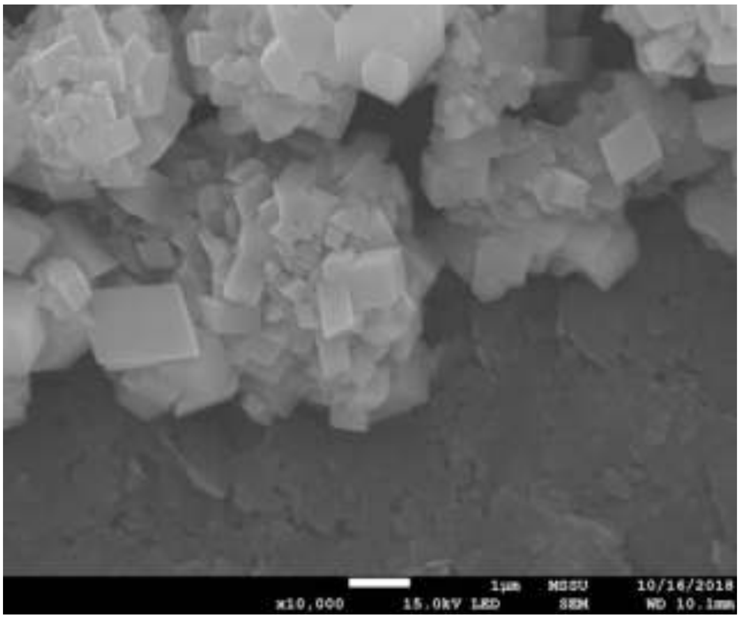


Figure 9.49. SEM image for the product obtained from $CaCl_2$.

9.5. Conclusions

The following conclusions have been obtained from the experimental study presented in this chapter:

- Temperature, molar ratio and time were tested as main parameters of the potential precipitation process. Temperature clearly affects the precipitation efficiency obtained with hydroxide precipitant agents, whereas its effect with salts as precipitant agents is not noteworthy. Molar ratio influence was assessed and probably 1.1-1.2 is a reasonable value to work on, for the reasons previously explained. Reaction time showed to be optimum between 30-45 minutes.
- The best precipitation efficiencies were obtained by the use of $Ca(OH)_2$ as precipitant agent. Nevertheless, the final solid product showed some impurities which are mainly remaining OH^- ions. This diminish the potential economic value of the final solid product in the market.

- The best product purity was obtained by the employ of $CaCl_2$ as precipitant agent. Moreover, the precipitation efficiencies obtained were quite acceptable at room temperature which is less energy intensive than traditional process for CO_2 capture.
- The use of $Mg(OH)_2$ as precipitant agent did not provide remarkable results, both in terms of precipitation efficiency and of final product quality. Therefore, this precipitant agent may be discarded.
- $MgCl_2$ as precipitant agent gave good results both for precipitation efficiency and for product quality. Nevertheless, the final product needs a further study since a mix of different $MgCO_3$ structures was obtained and its applicability could be reduced.

LIST OF PUBLICATIONS

1) **Baena-Moreno, F.M.**, Rodríguez-Galán, M., Vega, F., Vilches, L.F., Navarrete, B. *Review: recent advances in biogas purifying technologies.* (2019) International Journal of Green Energy, 16 (5), 10.1080/15435075.2019.1572610
2) **Baena-Moreno, F.M.**, Rodríguez-Galán, M., Vega, F., Alonso-Fariñas, B., Vilches Arenas, L.F., Navarrete, B. *Carbon capture and utilization technologies: a literature review and recent advances.* (2019) Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 41, 10.1080/15567036.2018.1548518
3) **Baena-Moreno, F.M.**, Rodríguez-Galán, M., Vega, F., Reina, T.R., Vilches, L.F., Navarrete, B. *Regeneration of sodium hydroxide from a biogas upgrading unit through the synthesis of precipitated calcium carbonate: An experimental influence study of reaction parameters.* (2018) Processes, 6 (11), 10.3390/pr6110205
4) **Baena-Moreno, F.M.**, Rodríguez-Galán, M., Vega, F., Ramirez-Reina, T., Vilches, L., Navarrete, B. *Understanding the influence of the alkaline cation K^+ or Na^+ in the regeneration efficiency of a biogas upgrading unit.* (2019) International Journal of Energy Research, 10.1002/er.4448
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6) **Baena-Moreno, F.M.**, Price, C.A.H., le Saché, E., Pastor-Pérez, L., Sebastia-Saez, D., Reina, T.R. *Physicochemical comparison of precipitated calcium carbonate for different configurations of a biogas upgrading unit*. (2019) Journal of Chemical Technology and Biotechnology, 94, 10.1002/jctb.6013
7) **Baena-Moreno, F.M.**, Rodríguez-Galán, M., Vega, F., Reina, T.R., Vilches, L.F., Navarrete, B. *Converting CO_2 from biogas and $MgCl_2$ residues into valuable*

magnesium carbonate: A novel strategy for renewable energy production. (2019) Energy, 180, 10.1016/j.energy.2019.05.106

8) **Baena-Moreno, F.M.**, Rodríguez-Galán, M., Reina, T.R., Zhang, Z., Vilches, L.F., Navarrete, B. *Understanding the effect of Ca and Mg ions from wastes in the solvent regeneration stage of a biogas upgrading unit*. (2019) Science of the Total Environment, 691, 10.1016/j.scitotenv.2019.07.135
9) **Baena-Moreno, F.M.,** Sebastia-Saez, D., Rodríguez-Galán, M., Vega, F., Vilches, L.F., Navarrete, B. *Biogas upgrading through naoh chemical absorption: Understanding the hydrodynamics of a packed tower for a regenerative-sustainable process.* (2019) European Biomass Conference and Exhibition Proceedings,
10) **Baena-Moreno, F.M**., Vega, F., Pastor-Pérez, L., Reina, T.R., Navarrete, B., Zhang, Z. *Novel process for carbon capture and utilization and saline wastes valorization.* (2020) Journal of Natural Gas Science and Engineering, 73, 10.1016/j.jngse.2019.103071
11) Zhang, N., Pan, Z., Zhang, Z., Zhang, W., Zhang, L., **Baena-Moreno, F.M.**, Lichtfouse, E. *CO_2 capture from coalbed methane using membranes: a review*. (2020) Environmental Chemistry Letters, 18, 10.1007/s10311-019-00919-4
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18) **Baena-Moreno, F.M.**, Pastor-Pérez, L., Zhang, Z., Reina, T.R. *Stepping towards a low-carbon economy. Formic acid from biogas as case of study.* (2020) Applied Energy, 268, 10.1016/j.apenergy.2020.115033
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20) **Baena-Moreno, F.M**., Sebastia-Saez, D., Wang, Q., Reina, T.R. *Is the production of biofuels and bio-chemicals always profitable? Co-production of biomethane and urea from biogas as case study.* (2020) Energy Conversion and Management, 10.1016/j.enconman.2020.113058
21) **Baena-Moreno, F.M,** Zhang, Z., Zhang, X.P., Reina T.R. *Profitability analysis of a novel configuration to synergize biogas upgrading and Power-to-Gas.* (2020). Energy Conversion and Management, 10.1016/j.enconman.2020.113369

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Preliminary abstract

Herein a novel path to integrate CO_2 capture and utilization in an urban wastewater treatment plant is proposed. The reduction of CO_2 emissions is clearly beneficial for our society, and the consecution of commercial materials from this waste is a key point for the development of new circular economy strategies. The proposal here developed synergize biogas upgrading and carbon capture and utilization. Furthermore, the process proposed allows to integrate this stage to concentrate nutrients from anaerobically digested sludge centrate, hence favoring process integration and intensification. The emission of these nutrients is a current environmental problems of wastewater treatment plants, hence its concentration is a key point to improve the performance of post-treatments. The synergy showed presents high novelty and it has not been seen to date. The theoretical aspect involved the scale-up of the process and the design of the process including auxiliary stages. Furthermore, the process is techno-economically analyzed in terms of profitability, evidencing the economic advantages of the novel process proposed.