UTILIZATION OF CAPTURED CO_2 FOR IMPLEMENTING CCUS IN ROMANIA

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Abstract. The promotion of the Carbon Capture and Utilisation (CCU) technology relies on the priorities of the European Commission that includes the Circular Economy as a major challenge (European Commission, 2018).To this end, under the EU Research and Innovation Programme (Horizon 2020), the Commission will demonstrate the opportunities for moving towards a circular economy at European level with large-scale innovation projects. Romania is part of this program, and is trying to implement CCU technologies in near future. While Carbon Capture and Storage (CCS) technologies are well known, studied and are starting to be implemented, the usage of captured CO_2 is less taken into account at present. These technologies involve the participation of more entities in several industrial branches, and the result is often only capturing CO_2 in a cycle, which eventually is reaching to the atmosphere but later and after being used in some technological processes.

Key words: captured CO_2 utilization, CO_2 utilization options, CO_2 chemical conversion, CO_2 biological conversion transformations of CO_2

1. INTRODUCTION

Carbon capture and storage (CCS) alone is a technology directed to CO_2 abatement by storing CO_2 captured from stationary industrial installations in suitable geological sites and preventing its release into the atmosphere.

CCU technologies instead are directed towards CO_2 abatement and also to converting captured CO_2 into useful products which can be valued and sold. Compared to CCS alone, CCU has already a business case. The CO_2 supply is guaranteed by various industries that will continue to emit CO_2, other than the energy industry (cement, steel, chemicals, glass etc.). One major problem of CCU could be that conversion of CO_2 to various products is energy intensive due to thermodynamic stability of CO_2 (Cuéllar-Franca, Azapagic, 2015).

However, CCU alone cannot realistically fix all emissions due to the large volumes involved and the potentially relatively low markets for individual products. Global CCS Institute (2011) concluded that only a few per cent of total emissions could be utilized. Still, CCU can be a reasonable solution in countries or regions where CO_2 geological storage is not allowed or is confronted with a lack of public acceptance, as well as in countries with no geological storage capacity.

Different CCS and CCU options are summarized in Fig. 1.

The present paper intends to make a comprehensive review of different CCU technologies and options that will form the basis for evaluating CCU options that could be suitable for Romania. In Romania there is already a market, although relatively low, for CO_2 and the major emissions of CO_2 (more than 100 kt CO_2 per year) from stationary industrial installations have reached a total of more than 37 Mt of CO_2 (ANPM, 2018).

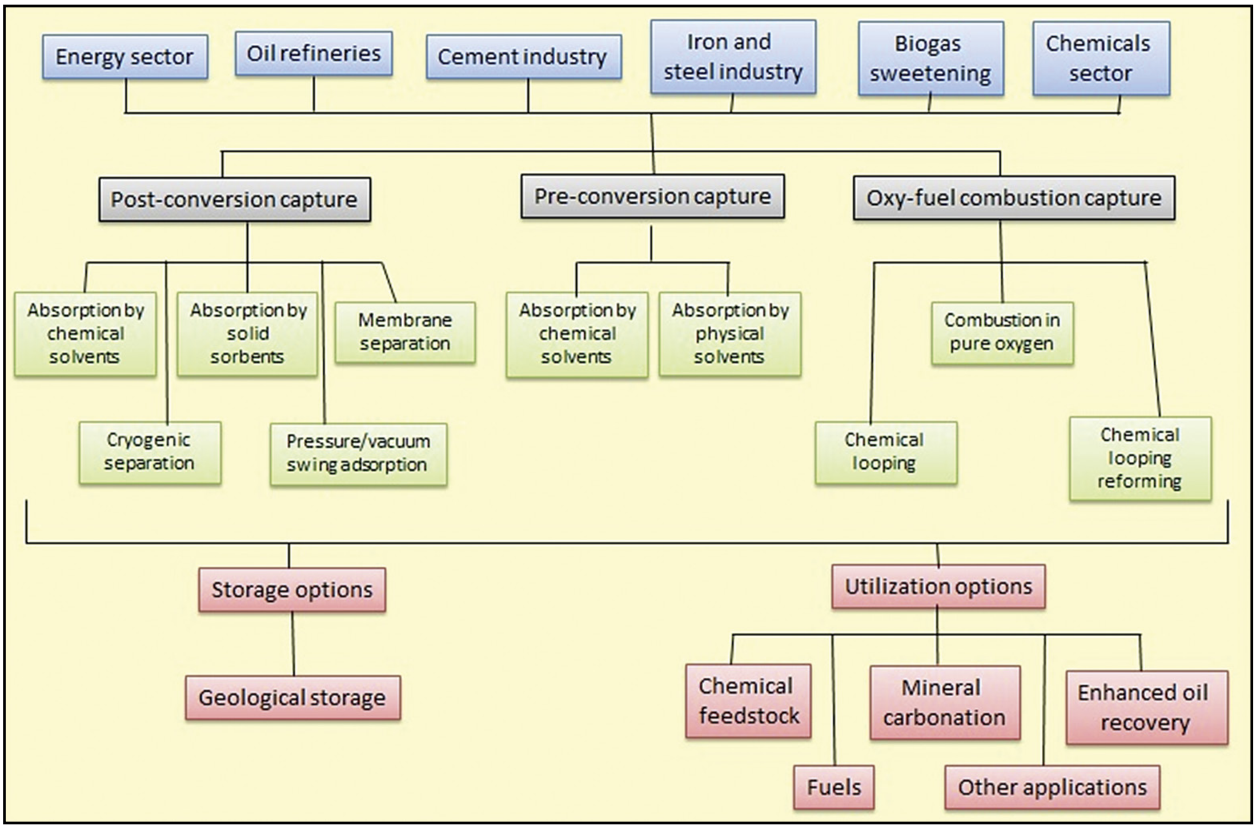

Fig. 1. Diagram showing various capture, storage and usage options of CO_2 (modified after Cuéllar-Franca, Azapagic, 2015)

2. DIRECT UTILIZATION OF CAPTURED CO_2

CCU applications are diverse and associated with many industries. Figure 2 presents the utilisation options for captured CO_2 and their association with specific industries.

Talking about CCU options, the two forms of CO_2 utilization are usually considered, directly or through conversion. Examples of direct utilisation of CO_2 include its use in the food and drink industry, in the pharmaceutical industry, the horticulture and for enhanced recovery of hydrocarbons. The first three utilisations require a high purity CO_2 stream which can be derived for example from ammonia production (Cuéllar-Franca, Azapagic, 2015).

In the food and drink industry, CO_2 is commonly used as a carbonating agent, (ex: carbonation of beverages with high-purity CO_2), as a seal gas to prevent oxidation of the wine during maturation, as a solvent for the extraction of flavours, extracting fat from food and in the decaffeination process (Cuéllar-Franca, Azapagic, 2015). In the pharmaceutical industry, CO_2 can be used as a respiratory stimulant, as an intermediate in the synthesis of drugs, or in surgery, sterilization and blood tests. CO_2 is used in horticulture to maintain optimal CO_2 concentration and maximise plant growth rate. Carbon dioxide systems dramatically improve the growth and quality of greenhouse plants. Increased gas concentrations lead to larger, healthier and faster growing plants and lower operating costs, especially during winter, when heating costs can be reduced by up to 50%. Carbon dioxide replaces gas generators, saving fuel costs and eliminating harmful emissions.

One of the best known uses of CO_2 is in fire extinguishers proving itself very efficient to combat fires when water is inefficient, unwanted or unavailable.

Enhanced oil and coal-bed methane recovery (EOR and ECBM) are other examples of direct utilisation of CO_2 where it is used to extract oil from an oil field or natural gas from unmineable coal deposits, respectively (Cuéllar-Franca, Azapagic, 2015). This type of CO_2 utilisation can lead to permanent storage of CO_2 (Bennett *et al.*, 2014). Enhanced oil recovery using CO_2 injection or CO_2 flooding has been widely practiced for over 40 years (IEA, 2015) in several oil-producing countries including Norway, Canada and the USA. It is a mature technology which now focuses also to enhancing CO_2 storage, apart from recovery of hydrocarbons.

3. CHEMICAL CONVERSION AND UTILIZATION OF CAPTURED CO_2

Utilization of CO_2 through conversion processes is known and applied since the second half of nineteen century (Aresta *et al.*, 2013) comprising mature technologies such as synthe-

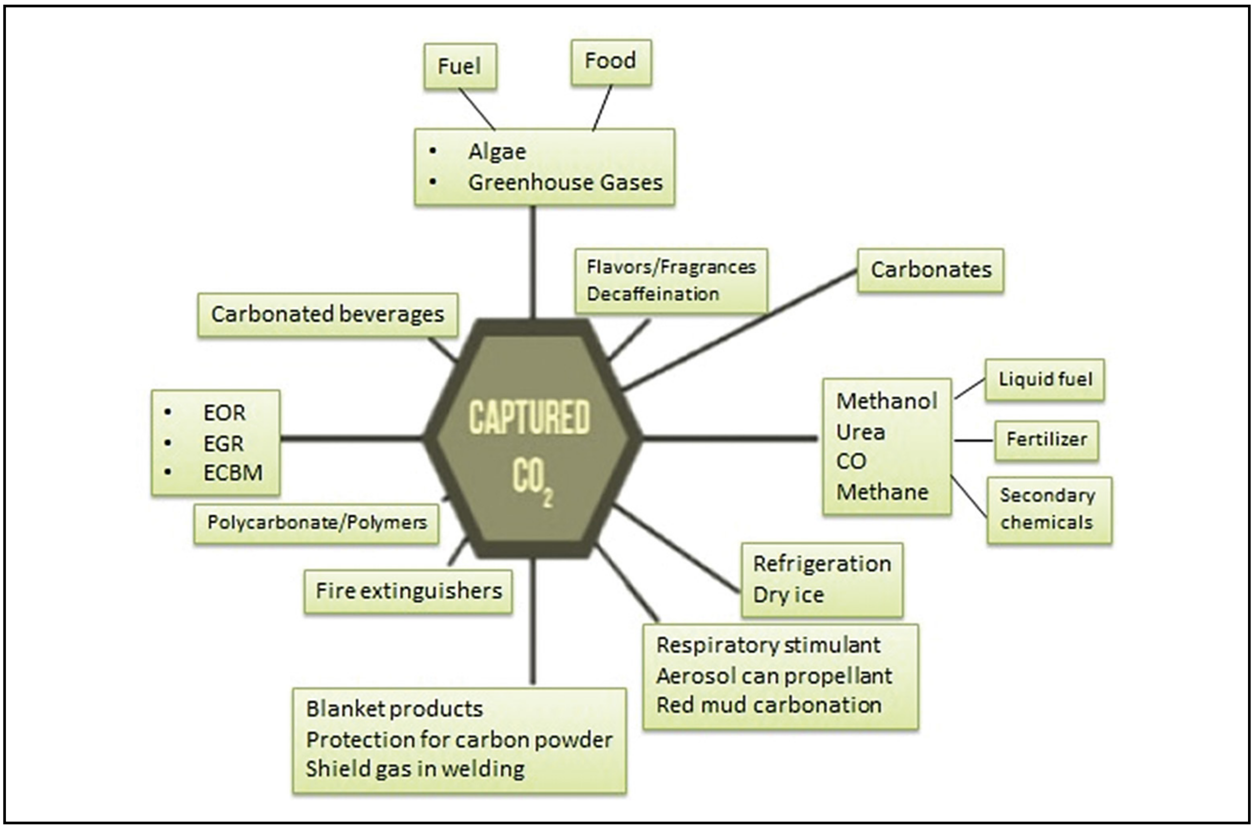

Fig. 2. Classification of CO_2 utilisation options (modified after European Comission, 2018)

sis of salicylic acid and urea production. New trends include mineral carbonation and production of biofuels using algae.

3.1. Conversion of CO_2 into chemicals and fuels

The conversion of CO_2 into chemicals and fuels can be accomplished by carboxylation or reduction reactions, leading to production of methane, methanol, syngas, urea and formic acid (Cuéllar-Franca, Azapagic, 2015). This type of conversion is very energy intensive and requires highly selective catalysts due to the low reactivity of CO_2.

3.2. Mineral carbonation

The concept of storage of CO_2 as calcium and magnesium carbonate minerals is commonly referred to as mineral carbonation (IPCC, 2005). In mineral carbonation, (captured) CO_2 is used with minerals (mostly calcium or magnesium silicates) to form Ca or Mg carbonates. As mineral feedstock, natural rocks that are rich in alkaline earth silicates can be used, such as woollastonite, olivine and serpentine which are available in large quantities in many places around the world and could lead to permanent storage of billions of tonnes of CO_2 (Bennett *et al.*, 2014). Mineral carbonation could be an alternative for long term geological storage, especially for regions where CO_2 underground storage is not possible. The main advantage of mineral carbonation is the formation of stable carbonates capable of storing CO_2 for long periods (decades to centuries), without the risk of CO_2 leakage as in CCS. Apart from natural minerals, for mineral carbonation, waste materials from cement and steel industry can be used providing also a way to recycle these products (Bennett *et al.*, 2014). There is also a drawback of this technology. It will require major dumps of the newly formed mineral masses to be built which uses space and has significant costs.

3.3. CO_2 absorption by microalgae to generate biomass

CO_2 can be used to cultivate microalgae for the production of bio-oils and proteins, biofuels, chemicals, ingredients for food or cosmetics, soil conditioners or animal feed. Microalgae are microscopic, single-celled plants growing in fresh water or seawater. They use sunlight as their energy source, and CO_2 and inorganic ingredients, mainly N-compounds (NO_3^-, NH_4^+) and phosphates, for growth. They have the ability to fix CO_2 directly from waste streams such as flue gas as well as using nitrogen from the gas as a nutrient. Cultivation of microalgae can be carried out in open ponds and photo-bioreactors (Aresta *et al.*, 2013; Cuéllar-Franca, Azapagic, 2015). The CO_2 sequestering process consists in "bubbling CO_2 through algal cultivation systems" (Global CCS Institute, 2011) which together with sunlight and water increases productivity / biomass generation in the algae cultivation process.

The first step in transforming microalgae into fuels is harvesting and drying them. Their transformation can be accomplished by thermochemical or biochemical conversions.

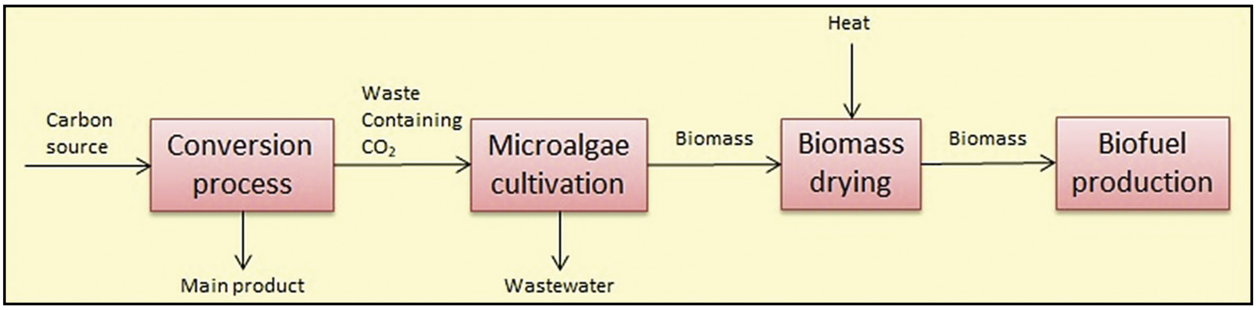

Fig. 3. Utilisation of CO_2 to produce biofuels from microalgae (after Cuéllar-Franca, Azapagic, 2015)

Thermochemical conversion consists of processes such as gasification, liquefaction and pyrolysis, processes in which heat and electricity are used. Biochemical conversion is based on biological and chemical processes, such as anaerobic digestion, fermentation and esterification.

The following diagram, Figure 3, shows the above mentioned.

Micro-algal biomass is a versatile raw material that can potentially be used as a source for a range of non-fuel and fuel products, including bio-oils and proteins, high value chemicals and ingredients, food and feed, fertilizers and fuels and as a result of their growth, oxygen is released into the atmosphere as shown in Figure 4.

4. CONCLUSIONS AND DISCUSSION

While CCS (carbon capture and storage) removes carbon from the economy, CCU (carbon capture and utilization) turns waste CO_2 emissions into valuable products that can be sold. By utilizing CO_2 it is possible to retain carbon within a cycle. Many different products could be obtained from captured CO_2 in industries like food, products, plastic, extractant, chemical, refrigerants, as well asfire suppression, fuel recovery and biological conversion chemicals.

Captured CO_2 can be used as a commercial product, either directly or after conversion. Its direct utilization is not widely used, except for EOR, because it requires in most cases a high purity of this gas, especially in the food industry, horticulture and pharmaceutical industry. Captured CO_2 is commonly used after conversion and till now the most used conversions methods include chemical transformation into fuels, CO_2 absorption by microalgae to generate biomass and mineral carbonation.

CCS technologies and CCU technologies have developed as a necessity for combating climate change, mainly due to accelerated increase of CO_2 emissions. These technologies are temporary solutions. CCS has the advantage of safe storage in underground natural CO_2 environments over a certain

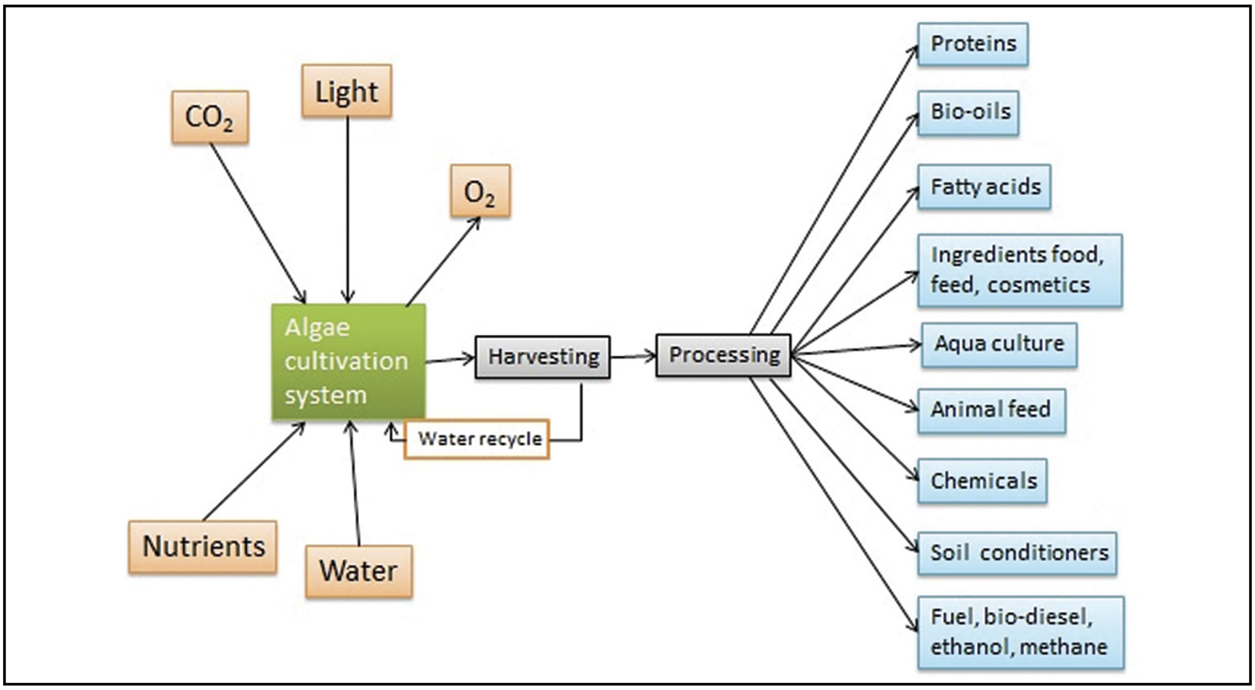

Fig. 4. Algae production process and product options (modified after Styring *et al.*, 2011)

period of time and CCU has the economic advantage, being an activity that generates other profits. The main disadvantages of CCU technologies refer to the release of CO_2 in the atmosphere after the end of product lifetime (e.g. through burning of fuels) diminishing the real carbon abatement and to the large energy consumption associated with the conversion processes. In order to eliminate these disadvantages and to mitigate climate change, future research should aim to develop materials and products for which the raw material is CO_2 and such products should have longer life to enable the storage of CO_2 in a longer cycle (Cuéllar-Franca, Azapagic, 2015).

REFERENCES

ANPM. 2018. Lista emisiilor de CO_2 de la instalatii stationare verificate pentru anul 2017.

Aresta, M., Dibenedetto, A., Angelini, A. 2013. The changing paradigm in CO_2 utilization, Journal of CO_2 Utilization, Volumes **3–4**, 2013, Pages 65-73, ISSN 2212-9820,https://doi.org/10.1016/j.jcou.2013.08.001.

Bennett, S., Schroeder, D., McCoy, S. 2014. Towards a framework for discussing and assessing CO_2 utilisation in a climate context. Energy Procedia **63** (2014) 7976 – 7992

Cuéllar-Franca, R.M., Azapagic, A., 2015. Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts. J. CO_2 Utilization **9**, 82-102

Styring P.,Jansen D.,de Coninck H., Reith H., Armstrong K. 2011. Carbon Capture and Utilization in the gree economy using CO_2 to manufacture fuel, chemical and materials. Report no. 501. The Centre for Low Carbon Futures 2011 and CO_2, Chem Publishing 2012. ISBN: 978-0-9572588-1-5.

Global CCS Institute, Parsons Brinckerhoff. 2011. Accelerating the uptake of CCS: industrial use of captured carbon dioxidehttps://www.globalccsinstitute.com/publications/accelerating-uptake-ccs-industrial-use-captured-carbon-dioxide

IEA. 2015. Storing CO_2 through Enhanced Oil Recovery. Combining EOR with CO_2 storage (EOR+) for profit. https://www.iea.org/publications/insights/insightpublications/CO2EOR_3Nov2015.pdf

IPCC,2005: IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

European Commission. 2018. Carbon Capture and Utilization. Available at: http://s3platform.jrc.ec.europa.eu/carbon-capture-and-utilization