# A Preliminary bibliographic review on Carbon Capture and Utilization

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Recent events and reports from multiple worldwide sources clearly indicate that the issue of Climate Change has already reached a state of emergency, throughout the globe and especially in the West. Awareness about the danger of environmental deterioration seems to have finally permeated almost completely all levels of modern societies, after countless summits, conferences, public speeches, and official statements of political leaders, have taken place for the last 20 years. The scientific community has already overwhelmingly and almost unanimously accepted **[1],[2],[3]** that human intervention in nature has been the major determining factor of Climate Change. Interestingly, besides the wide agreement among the scientific world, with regards to human intervention as the major causative factor of this menacing phenomenon, a minority of the population, a limited number of think tanks, and various other "pockets of resistance" are still in denial, yet not in unawareness, about the claim (which is almost certainty), that humans have already inflicted very significant damage in the biosphere, and will continue to do so, unless further measures are taken for the abatement and inversion of this dreadful situation. Probably several individuals are not in a position to even remotely visualize the impacts of the climatic changes, regarding their immediate environment, their lives, and their daily habits. The same cannot be said about the majority of the non-expert population, as it is proven among various recent surveys **[4]**, with special reference to developed-world countries. It is therefore rather safe to assume that changes in technology, labour market, established practices, traditions, and various other aspects of human life, are anticipated to be accepted by the majority, as absolutely necessary, in the same manner that currently implemented innovations (such as electric and hybrid cars, emission trading schemes, or carbon taxes) have been materialized without significant hindrances.

Climate Change has the form of global warming. The increase in the temperature on the surface of the Earth, that has been recorded during the last 120 years, is caused overwhelmingly by the production of greenhouse gases, among which, the greatest percentage accounts for carbon dioxide ($CO_2$). The enormous quantities of this triatomic molecule, that are emitted by industry and transportation, pose a great peril for nature and its inhabitants – among them humans – as they retain larger quantities of heat within the atmosphere. The mechanism has been identified and it is well understood. The cumulative quantity of atmospheric $CO_2$ increases rapidly, and the predictions of the anticipated response in terms of average temperature are alarming. Furthermore, the response may be even more intense, and it can take place sooner than the probabilistic models predict. It is therefore imperative, that large-scale measures have to be implemented for the reduction of atmospheric $CO_2$.

In this poster paper, a general outline of the most recent advances in this thematic is attempted to be properly and succinctly presented, according to carefully selected bibliography. The literature sources have been selected and evaluated, according to the higher reliability standards.

The current publication should be considered as preliminary, to a fully comprehensive study that is about to be published soon.

The accumulation of unprecedently high volumes of $CO_2$ in the atmosphere has created a major call for the development of carbon, capture, storage and utilization technologies, and has spurred a wide campaign of research around this topic. The problematic nature of this continuous accrual of $CO_2$ quantities in the atmosphere, is directly linked to the nature of the molecule itself. Carbon dioxide can be mainly detected in its gaseous form, while in terms of chemical reactivity, it can be considered mostly inert, as a highly oxidized species **[5]**. Despite of the great capacity of all major carbon sinks (vegetation, aquatic bodies), the majority of carbon dioxide molecules, after being emitted, will most likely linger in the atmosphere, and for a very capable amount of time. The average lifetime of a single molecule is calculated at approximately 100 years.

The consequence of this fact is that the radiative forcing of the atmosphere, or in simple terms its capacity to contain Sun-derived thermal energy, is steadily increasing, leading thus to the rise of the average temperature of the terrestrial environment.

Therefore, it is understandable that the physical and chemical nature of $CO_2$, must be thoroughly studied, in order to conceive and develop technologies that will be able to successfully confront the seemingly ever-growing problem.

Carbon capture storage and sequestration, bearing the acronym "CCS" was the first technological approach to $CO_2$ abatement effort. In this context, various methods of isolating pure carbon dioxide were deployed, aiming primarily on point sources of massive $CO_2$ emissions, as for example coal/hydrocarbon-based power plants, or industrial units of considerable emitting capacity, as for example cement-producing plants. Around this concept, the various technologies were divided in three main categories; post-combustion, oxyfuel combustion, direct capture, and the most advanced approach of pre-combustion [6] (Integrated Gasification Combined Cycle (IGCC) Power Plants, Natural Gas Reforming, Hydrogen Production – all of them including the production of syngas). It is considered that GWP (global warming potential) can be significantly reduced by the use of any of capture technologies [6],[7]. Preferable capturing techniques are based on the fundamental mechanisms of absorption, adsorption, and mineralization (acid-base reactions). Research and use of various components, such as membranes for separation, cheap and effective sorbents [8] presenting high affinity with $CO_2$, and also cryogenic separation, is advancing, by the careful manipulation of a multitude of regulating parameters.

The storage of captured quantities involves the transportation of $CO_2$-rich streams via piping systems, and sequestration in the most secure possible spaces. An immense amount of research has been devoted particularly to the sequestration methods, the most prominent of which is directed towards the use of fossil fuels/ hydrocarbon reservoirs, due to their great spatial capacity, and to the isolated environment that they can provide. The applied technologies can be separated in enhanced oil recovery (which involves the dissolution of $CO_2$ in hydrocarbons, and increased oil/natural gas production, with concomitant recycling of the injected $CO_2$), or permanent sequestration, which involves injecting ample quantities of sequestered $CO_2$ from the atmosphere, inside depleted/exhausted fossil fuel reservoirs, and sealing them for long-term storage. The use of natural reservoirs (except of hydrocarbon reservoirs, saline underground aquifers should be also included) is considered as a first-line effective measure for the achievement of short-to-midterm goals according to the 2015 Paris Agreement, having already achieved high readiness level (TRL>6) [9]

Carbon capture and storage has been deemed to be of limited value, at least when taking into consideration the extent of intervention required, to achieve the Herculean feat of restoring pre-industrial levels of atmospheric $CO_2$, and consequently averting Climate Change. It appears also to present a pattern of diminishing returns, in the long term, regarding its abatement capacity.

More recently, another strategic approach for controlling $CO_2$ emissions, which is referred to as "Carbon Capture and Utilization" with the acronym "CCU". The rationale overrunning this brand-new assortment of novel technologies, is based on the treatment of $CO_2$ as a chemical reagent, which can be directly used in the production of various valuable commodities such as chemicals, polymers, fuels, or inorganic carbonate salts. The production of methanol, formic acid, urea, and dimethyl-ether (DME), are among the most promising technologies in CCU [10]. Generally, the main difference between the CCS and the CCU is that in the former technological applications, the carbon dioxide molecule does not react with other substances, and keeps its form intact, while the latter involves chemical reactions, so the molecular structure of $CO_2$ is disrupted, and its constituents (and particularly the carbon atom) are incorporated in newly formed compounds. Because it became evident that each of these main strategies, will inevitably be insufficient, if they remain uncomplemented by other synergistic actions. Therefore, in the most recent bibliography, the new term "Carbon capture, utilization and storage" (acronym: CCUS) has emerged as a wider concept, which combines both storage and utilization aspects [11]. According to this new premise, "integrated systems" that bring together storage and utilization, are increasingly becoming one of the main subjects of research in environmental science.

Despite this new integrated perspective, technologies that account for the utilization of $CO_2$ as feedstock for the production of a wide variety of materials, is considered the most advanced – and difficult to develop – part of emission treatment systems. The chemical utilization domain faces many limitations, yet it is considered as the most promising path for a comprehensive framework of actions to mitigate and revert Climate Change.

The main limitations can be again traced back to the physical and chemical properties of the molecule itself. $CO_2$ is an especially stable – from a thermodynamic point of view – molecule, with a low level of energy, being the product of the complete oxidation of carbon [12]. In addition to the oxidation state, the geometry of the molecule (linear, with two double bonds), increases its stability even more. Therefore, the conversion of $CO_2$ into high value (which in many cases means higher energy density, as with synthetic fuels) useful products, requires significant amounts of energy, so that the reduction of carbon into less oxidized states, and accordingly to higher levels of energy can be achieved. A notable exception to this rule, is the thermodynamically favourable nature of the neutralization reaction with alkaline species, under room conditions, although increased rates of reaction typically require certain amounts of energy input (usually in the form of heat). The acidic nature of $CO_2$, and its tendency to react with bases almost spontaneously, has attracted attention, as a high potential technology for the treatment of large volumes of industrial alkaline residues, with simultaneous consumption of $CO_2$. [10]

While the case of mineralization, poses an attractive perspective for facile $CO_2$ utilization, the conversion reactions to other chemicals require significant amounts of energy. The energy is usually provided in the form of electricity, where $CO_2$ is reduced in electrolytic cells, to products with additional value. In this domain, various technologies are being tested, including electrochemical, thermocatalytic, biochemical, and photocatalytic methods, processes that produce methanol, fomic acid, hydrocarbons, urea, and other large-volume commodities. [10]

The efficient and economically viable deployment of such technologies, requires also very extended involvement of catalysts. The empirical study has designated certain substances (mainly metal oxides) as potent catalysts for many of the aforementioned conversion reactions. Catalysis is a decisive factor in the total cost of these processes, as the application of the most suitable catalyst, can curb significantly the energy demand. Extensive research regarding the catalysts, has been noted by various sources. [12],[10],[13] Despite the need for catalysts, the research is mostly oriented towards the use of electricity as the most convenient energy carrier. The main advantage provided by electricity, must be considered through the prospect of incorporation of renewable energy sources into the electrical grid [6]. The renewables have already been massively connected to the electrical grid, and the rate of their contribution to the total energy balance is increasing rapidly, while new renewable energy units are installed, all around the world. The renewable-derived energy is a key determinant in the successful utilization of $CO_2$. Production of fuels, synthesized from carbon dioxide utilization processes, with energy provided by renewables, results in net-zero fuels, a class of products that are anticipated to gain great significance in the near future, due to the versatile nature of these fuels.

Finally, it must be mentioned that significant and persistent research has been devoted to biological utilization systems, with algal ponds being the current state of the art. There have been estimations recorded in the bibliography, that 1 kg of algal biomass can metabolize 1.83 kg of $CO_2$ [10],[14]

A relatively recent and very conclusive study, highlighting the still malleable nature of the CCUS concept, provided an estimation that setting the $CO_2$ price at high levels (40$ - 80$ per tonne) can be a most significant driver towards the research and development pertaining to these systems [14] (It must be noted that the price of carbon dioxide in the EU trading system was approximately at 26€ per tonne $CO_2$, in 2019 – when the paper was published – while currently, the EU carbon permits have escalated to approximately 95€ per tonne. This marked difference reveals the rapid changes that take place in carbon finance and legislation, which are anticipated to impact directly the purely technological aspect of the $CO_2$ abatement issue)

A few conclusions can be drawn from this preliminary study:

Regarding the assessment of the prospects of integrated systems, it is almost unanimously supported among highly reliable literature sources, that the first section (storage) of these systems, is technologically better understood, and there is limited margin for further development, while the second section (utilization) has substantial margin for development. [13]

Regarding the associated costs of these systems, there is agreement about the complexity of developing cost-effective technology with significant output, yet the most prominent factors affecting this issue, have been mostly identified.

Regarding the dynamics in the development of CCUS technologies, it is unanimously recognized that the already established capacity of $CO_2$ removal is still at very low levels (order of magnitude of a few dozen of Mt $CO_2$/year removed, while the global emission figures are estimated approximately at 37 Gt $CO_2$/year), but in spite of the currently meagre productivity of CCUS integrated systems, the great menace that is posed by Climate Change, is anticipated to constitute a literally tremendous stressor towards the rapid development, scaling, and implementation of all the aforementioned environmentally clean technologies, so that the goals of Paris Agreement, will be sooner or later met.

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