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CARBON DIOXIDE UTILIZATION: A COMPREHENSIVE REVIEW

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ABSTRACT

Carbon dioxide (CO_2) is regarded as one of the main green house gases (GHGs) that is causing global warming and forcing climate change. CO_2 sequestration is widely recognized as an important option to reduce increasing levels of atmospheric carbon dioxide concentrations. However, CO_2 storage technology is receiving criticism for allowing continued use of fossil fuels. CO_2 utilization technology is fast emerging as a practical solution that involves recycling of CO_2 to various important industrial compounds and feedstock materials bringing concepts of organic chemistry to be the core climate change mitigation measure. This review article communicates current trends, challenges and advances in CO_2 utilization that exploits concepts of organic chemistry.

Key words: Sequestration, Utilization, Climate change, Carbon dioxide, Decarbonization.

INTRODUCTION

With ever increasing levels of carbon dioxide, climate change is one of the most pressing challenges for the future development of energy systems. CO_2 concentration has increased by 40% from 278 ppm to 390.5 ppm in 2011 exceeding the natural range of last 650,000 years (180-300 ppm)[1]. Efforts to mitigate the greenhouse gas emissions have traditionally focused on avoiding the production of carbon dioxide by reducing the use of fossil fuels, typically referred to as 'CO_2 abatement'[2,3]. However, fossil fuels are relied to produce at least 80% of global energy demands and 61% of greenhouse gas (GHG) emissions are linked to energy production, delivery and use. Consumption of fossil fuels produces nearly 30 petagram of CO_2 annually[4]. These figures clearly reveal that fossil fuels are dominant source of global primary energy demand and will likely remain so far the rest

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of the century. Until now, all of this carbon dioxide was released in the atmosphere as it was considered largest natural sinks for any additional carbon dioxide. Since industrial revolution, CO_2 content in the atmosphere has risen and it is predicted that CO_2 content is rising by 2 ppm every year suggesting that more than two-third of CO_2 does not stay in the atmosphere[5]. That is when the only alternative to CO_2 abatement comes across as economically viable option is to capture CO_2 emissions, sequester or utilize them in carbon reservoirs other than the atmosphere[6-8].

The burying problem

Management of GHGs using carbon sequestration technologies has been proposed to complement mitigation strategies that improve energy efficiency or increase the use of non-fossil energy sources[9,10]. CO_2 sequestration features in climate change policy documents of many countries as a cornerstone of their mitigation strategies and is widely explained and promoted as a part of technologies for decarbonization. Carbon sequestration implies transfer of atmospheric CO_2 into other long-lived global pools including oceans (oceanic sequestration), pedologic, biotic and geological strata (terrestrial sequestration) to reduce the net rate of increase in atmospheric carbon dioxide. For every ton of carbon taken from the ground, another ton of carbon has to be stored permanently and safely away from the mobile carbon pool. There is a need to justify that the term ‘storage’ rather than ‘disposal’ in the fact that storage needs to be maintained and be responsible for keeping carbon out of the mobile carbon pool. Hence, the term can be redefined as ‘capture and secure storage’ of carbon that would otherwise be emitted to or remain in the atmosphere[11]. US EPA has proposed to exclude carbon dioxide from the legislation governing hazardous waste[12], provided storage complies with the rules established under Safe Drinking Water Act[13]. With this change in purview, it is now essential to view carbon dioxide as a commodity than a waste by-product.

Though CO_2 sequestration technology has risen meteorically in recent years, it is not immune to serious challenges. Carbon reservoirs, like oceans and soil are not necessarily permanent. This poses a challenge of how to quantify the benefits of temporary carbon storage, for example on the time-scales of decades or centuries. The important technological challenges include:

(a) Issue of permanence of the carbon sequestered in trees and soils[14].

(b) Issue of verifying sufficient storage capacity for carbon dioxide[14].

(c) Sequestered CO_2 may leak back into the atmosphere from the storage sites[15-17].

Apart from the above challenges, there exist non-technical challenges primarily consisting of:

(a) Global need for significant financial investments to bring numerous commercial-scale demonstration projects on-line in the near future[18].

(b) Establishing an adequate legal and regulatory framework to support broad carbon storage chain deployment, including dealing with long-term liability, building public understanding, awareness and acceptance[19].

Rationale of CO_2 Utilization

Rather than burying CO_2 underground, companies are now exploiting organic chemistry and developing processes that use CO_2 emissions as chemical starting materials. Research efforts to investigate alternatives to sequestration options are already well advanced[20]. Recently, Danish Government has proposed a move to zero reliance on fossil fuels by the year 2050[21,22]. Carbon utilization emerges as a practical alternative to divert CO_2 from the transport and storage route and zero reliance on fossil fuels. Carbon utilization has been identified by the Engineering and Physical Sciences Research Council (EPSRC) in their Grand Challenges looking towards a sustainable chemical economy by 2050[23]. 'Carbon dioxide utilization' (CU) is quite a different concept than storage technology. Storage technologies target reducing atmospheric carbon dioxide by trapping it into remote environments or by fixing it in long-living (hundred years or more) compounds. On the other hand, utilization technologies prevalently avoid CO_2-emissions and reduce fossil carbon extraction by recycling carbon. Quite obviously, most of the compounds into which CO_2 is converted, if used, will release CO_2 on a time scale from months to years. The only exception is polymeric materials that may last for decades (polycarbonates) or longer (polyurethanes as insulating materials). Nature utilizes CO_2 to produce myriad substances that are consumed by humans and animals. Some industrial processes aim to accelerate the utilization of CO_2. Technology of CO_2 utilization explores ways to change the basic characteristics of the CCS supply chain. There are essentially three pathways for utilizing CO_2 viz,

(a) Use of CO_2 as a chemical feedstock.

(b) As a fertilizer for algae production leading to further CO_2 emission reductions through the sustainable application of algae.

(c) Mineral conversion of carbon dioxide.

Various utilization technologies are developing that have the potential to reduce CO_2 emissions both directly and by reducing use of fossil fuels. However, much greater reductions are possible through wider adoption of such technologies. Applications of CO_2 utilization whether technological, biological, or chemical, for effective reduction in its emission into the atmosphere, the processes must comply with certain conditions, namely:

(a) New process must reduce overall CO_2 emissions;

(b) It must be less energy - and material-intensive with respect to the on – stream processes that it aims to replace;

(c) It must employ safer and eco-friendly working conditions with economic viability.

Understanding CO_2 Chemistry

CO_2 is colorless, odorless gaseous molecule with two oxygen atoms and a carbon atom at the center assuming linear geometry. It exhibits no absorption in the UV-Vis region but exhibits absorption maximum at 175 nm and is IR sensitive due to active dipole interactions of certain molecular vibrations. CO_2 is a non-polar, chemically unreactive molecule under standard conditions and hence persists in the atmosphere. CO_2 can be activated due to Lewis basicity of the O-atom and C-atom is electrophilic. Reactions of CO_2 are dominated by nucleophilic attack on C-atom using electron donating reagents and/or electrophilic attack on O-atom. It has high thermodynamic stability ($-\Delta H_f$ = -394 kJ/mol). It occurs naturally through combustion of carbonaceous materials and volcanic activity, but is also a major pollutant from anthropogenic utilization of carbonaceous materials. Because of the enormous quantities of CO_2 emitted through anthropogenic activities, it is necessary for these processes to be diverse because of supply chain requirements and global capacity. Converting CO_2 into fuels and complex chemicals through cleaving of the C-O bond requires hydrogen and the latter can be produced with use of renewable energy resources for effective green chemistry. As a consequence of its low reactivity, if carbon dioxide has to be converted into economically valuable products there is a need to reduce activation energy for the reaction using catalysts.

The nature of carbon in CO_2 is in the oxidized form and hence many of the reactions are reduction-type, either through the addition of hydrogen or electrons. The exceptions are CO_2 insertion reactions where there is no overall change in oxidation state. It was viewed that reactions involving CO_2 are thermodynamically impractical. Today, many chemical reactions have been studied that involves use of catalysts and increased temperature. Though such conditions facilitate reactions utilizing CO_2, it also results in significant process energy.

In order to reduce the carbon footprint and optimize energy balances, it is essential that the required energy comes from renewable zero carbon emission sources such as solar, wind, geothermal, hydro supplies. While catalysts can play a significant role in reducing the activation energy and the total energy required for a reaction, it is likely that there will also need to be a considerable energy input to make it viable. Thermodynamics of CO_2 conversion, for example, Gibbs free energy of CO_2 and related substances, many reactions exhibit positive change in enthalpy ($\Delta H > 0$) and thus are endothermic. In other words, low energy input, active catalysts, and effective reaction conditions are necessary for conversion of CO_2 to chemicals. One feasible and thermodynamically practical route is to use CO_2 as a co-reactant to react with another substance that possesses higher Gibbs free energy, for example, hydrogen and methanol.

Trends in CO_2 Utilization

Besides photosynthesis, a nature's way to utilize carbon dioxide, this technology finds its origin in chemical industries including synthesis of soda Solvay[24], Na_2CO_3, salicylic acid[25,26] and urea a process that is now more than 140 years old[27]. During the same time period, copolymerization of CO_2 with propene marked the development of first catalytic industrial application of carbon dioxide[28]. Later, coordination of CO_2 to metal center could promote its reduction to carbon monoxide in milder conditions rather than harsher condition required by free CO_2 molecule was demonstrated[29]. Applications of CO_2-transition metal complexes as electrocatalysts have been investigated[30]. Further developments included applications of CO_2-metal complexes as catalysts in functionalization of organic molecules[31]. Even with great academic efforts for CO_2 utilization was traced, there was a missing link of exploiting these processes in a real industrial scenario. The reason is that conditions required to apply these processes did not seem practicable in well established production plants. This resulted in apparent decrease in the interest of carbon dioxide chemistry in early 2000s. However, this situation changed in early 1990 with noteworthy introduction of supercritical fluids[32]. Chemical utilization of CO_2 to formic acid, urea, polycarbonates, polyurethanes, methanol, acrylates and their polymers have been extensively studied[33]. CO_2 utilization involves either its direct use or its conversion to useful chemicals. In general, there are two classes of reactions that can be distinguished for the conversion of CO_2 into other chemicals[34]. In carboxylation reactions, entire CO_2 moiety is incorporated into molecular or polymeric compounds containing moieties like –COOR (carboxylates, esters, lactones), N-COOR (carbamates), NCO (isocyanates or ureas), and ROCOOR (carbonates). In all such cases, the product will have a higher C/H ratio than the parent compound, and the reaction will be energetically favourable[35]. In reduction reactions, CO_2 is reduced to other C1- (CO, CH_3OH) or CN-molecules used as fuels. Fig. 1 shows industrially important transformations of CO_2 that have been reported to date.

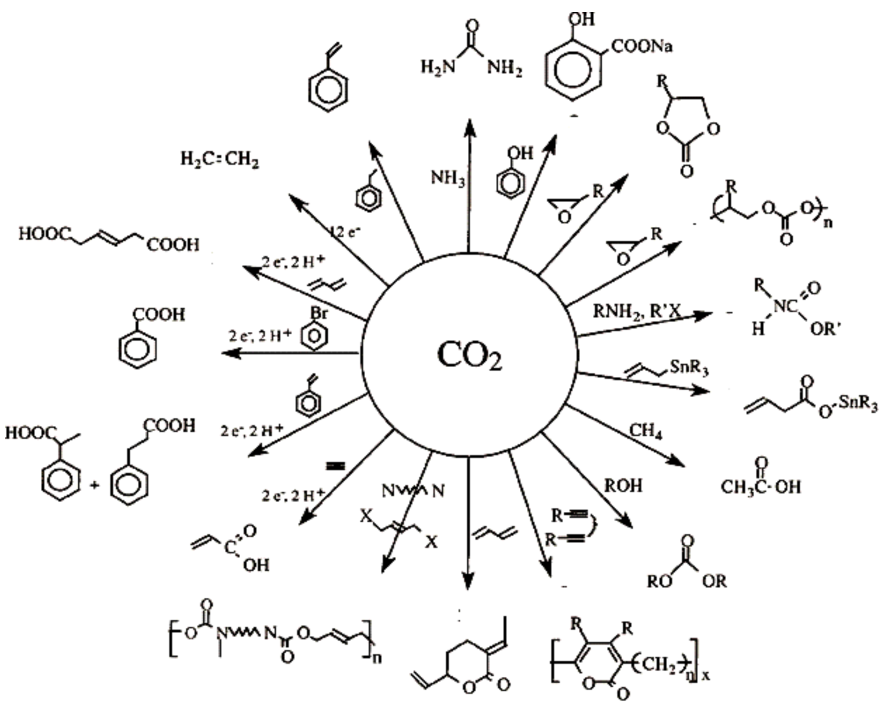

Fig. 1: Chemical reactions for utilization of CO_2 moiety

It is only recently that efforts have been focused on diversifying the portfolio of reactions[36]. Table 1 presents the major companies involved in exploitation of carbon dioxide to chemically viable products[37].

Table 1: Major companies developing chemical syntheses utilizing CO_2

	Chemical processes/Syntheses	Company
(i)	Captured CO_2-catalyst for the production of ethylene oxide (C_3-PEO)	RTI International, USA
(ii)	Converting CO_2 into chemicals and fuels using clean, domestic sources of energy	Liquid Light, USA
(iii)	Coupled CO_2 and wastewater treatment process to create High value Gas/Oil field chemicals	British Columbia University, Canada
(iv)	Dimethyl carbonate production (DMC) from captured CO_2 and CH_3OH	E3Tec Service, LLC, USA

Cont…

	Chemical processes/Syntheses	Company
(v)	Direct catalytic synthesis of acetic acid from CO_2 and CH_4	Gas Technology Institute, USA
(vi)	Conversion of CO_2 into polyol feedstocks for polyurethane plastics	Bayer Material Science with CAT Catalytic Center in Aachen, Germany

Advances and Challenges in CO_2 Utilization

Reuse of CO_2 could be a massive opportunity in CO_2 utilization. It could exploit a currently untapped resource and contribute to reducing GHG emissions and be a major driver of innovation and growth. CO_2 utilization should not be regarded as an alternative technology to CCS but a complementary technology to update the overall technology. Number of barriers still exist that slow down the advancement of these CO_2 utilization technologies, such as –

(i) CO_2 utilization is much less supported as compared to other energy-related technologies;

(ii) Fossil fuel plants are still benefited currently by energy regulations;

(iii) CO_2 utilization technologies that can result in net CO_2 reduction at commercial scale are yet to be demonstrated.

As seen in Table 1, many companies are working towards utilizing carbon dioxide. Many advances and innovations have been witnessed in CO_2 utilization. Recently, Novomer utilized CO_2 as a feedstock for polymers and plastics. It involves a catalyst (Novomer Catalyst) to create Polypropylene carbonate (PPC) polymers through co-polymerization of CO_2 and suitable epoxides. It results in polymers containing more than 50% CO_2 by weight[38]. CO_2-containing polymers can be tailored for preparing polymeric materials ranging from solid plastics to soft, flexible foams, depending on the size of the polymer chain. Skyonic Corporation has developed a mineralization process for scrubbing industrial flue gases. It uses an electrochemical method to make a low concentration sodium hydroxide solution from salt and water. This then scrubs CO_2 and other chemicals from exhaust gases and produce high purity sodium bicarbonate. Electrolysis also produces hydrogen and chlorine gases. By producing low concentration NaOH solutions, Skymine process uses much less electricity than commercial hydroxide production processes. The process also removes sulfur oxides, nitrogen dioxide, mercury and other heavy metals from flue gas streams, and hence can potentially replace existing scrubber technology. Solid carbonates initially formed in the process also provide an option for carbon sequestration that avoids pipelines and concerns about CO_2 leaking back into the atmosphere, but that alone does not necessarily make a profit[39]. CO_2 Solutions' Inc technology addresses the high-cost barrier to Carbon Capture & Sequestration created by conventional solvent-based CO_2 capture processes. The technology, inspired by nature, utilizes extremely powerful enzyme catalyst carbonic anhydrase, which efficiently manages CO_2 in humans and other living organisms to boost the productivity of solvent scrubbers used to capture carbon dioxide[40]. Phycal produces oil by introducing algae initially grown in isolation into ponds. The ponds contain nutrients and have waste CO_2 injected into them at a rate set to maintain a steady pH and optimal algal growth rate. When the algal culture has reached optimal density, it is continuously harvested at a rate that maintains the culture density, put into closed reactors, and fed sugars derived from food and beverage industry waste streams and inedible plant biomass feedstocks.

Heterogeneous catalytic conversion of CO_2 to organic raw materials is gaining particular interest due to its better stability, durability and simplicity in separation, handling along with simpler reactor design[41]. The demerits of catalytic CO_2 conversions include use of large amount of catalysts, high temperatures and pressures with longer reaction times. Various plasma techniques along with catalysts have been reported but, the energy demand for reaching a plasma state predominantly restricts the plasma process in an industrial setup[42,43]. It is known that Nature utilizes CO_2 to produce myriad substances that are consumed by humans and animals. Considerable effort is being made to mimic these biological processes. The most noteworthy work is recently envisioned that includes developing artificial leaves to remove ambient CO_2 from the air to prepare fuels[44]. Currently, energy balances are being worked upon for CO_2 fixation capacity of an algal system and exhibits numerous advantages over other plant feedstock in CO_2 capture and utilization such as greater photosynthetic conversion, lesser to no land use, higher production of feedstocks and effective bioremediation, zero CO_2 emission at the end-cycle. Complete up-scale of industrial setting of microalgae utility is under process[45]. Electrochemical and photo-electrochemical conversion routes is currently coming to fore in the next decade. Electrochemical conversion promises to be deployable in many systems, because of its low footprint, its scalability, lower energy requirements and its ability to produce many end products. Photo-assisted electrochemical reduction of CO_2 in water represents an interesting technology that allows the efficient use of residual or intermittent energies with conversion of large volumes of CO_2 into chemicals or fuels[46]. Recently, a new carbon-capture polymer was reported that cross-linked benzene with formaldehyde dimethyl acetal using Friedel-Crafts alkylation that outperforms other CO_2 sorbents like zeolites and metal–organic frameworks under high pressure conditions[47].

CONCLUSION

Treating CO_2 as a raw material represents a sea change in the approach to limiting carbon dioxide pollution. Rather than punish fuel consumers through a punitive carbon tax, carbon dioxide utilization offers the possibility that capturing and sequestering CO_2 could be a profitable enterprise setting off a virtuous cycle of ever improving carbon management techniques. By mimicking Nature and combining biotechnology and chemistry, it may be possible to bring about the discovery of new technologies with a greater use of biomass, substitution of fossil-carbon and quasi-zero-emission technologies. One major exploitation of the concept that 'Nature makes and organic chemists re-shape' may bring about important benefits that have not yet been fully identified. The 'inorganication' of CO_2 is a technology that may, at least potentially, be used to store large volumes of CO_2 over the long term, in the form of 'safer' chemicals. Of course, such an approach would be feasible in situations where residual inorganic oxides and sludge from industrial processes could be used for the CO_2 fixation. It is essential that industry, international and national funding organizations all support research investigations in CO_2 chemistry. In this way, it will be possible to investigate a wider variety of applications and consequently producing the greatest benefit to Society in general.

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