

The Strategy on Adaptation to Climate Change using CO₂ Capture and Recycle

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Abstract

In 2015, Paris Agreement regarding climate change warns us that human species will be exposed to a severe danger if people cannot solve the problem of climate change. MOFs present a solution to this problem, promising a more environmentally friendly and efficient alternative, capturing more CO₂ and requiring less energy to regenerate. The structural tunability of MOFs allows them to be optimised for the specific type of CO₂ capture to be performed. Thus, it is most effective strategy to retrieve emitted CO₂ and recycle it. Rather than just capturing the existing CO₂, it is a fundamental alternative to build a technique that can recycle the captured CO₂.

Keywords : Climate Change, MOF (Metal-Organic Framework), CO₂ pyrolysis, Photodissociation of carbon dioxide (CO₂)

Introduction

We all know that the cause of climate change is constant release of green-house gases. We all need to work together in order to reduce the amount of green-house gas for a sustainable development of humans. People need to especially reduce the concentration of CO₂ in the air. The counterattack of climate change will surely arrive. The problem of climate change could be solved with the power of modern technology. If we constantly put effort into solving the problem of climate change, it will be solved in 50 years[1]. As long as a modern scientific civilization continues, effluence of CO₂ will continue as well. This research’s goal is to discover the potential of modern science regarding capturing and recycling of CO₂.

Is the concentration of CO₂ the cause of change in climate?

The concentration of CO₂ in the earth’s atmosphere now exceeds that of 400ppm. Global climate change has rapidly become one of the most prominent environmental and energy policy issues of our age. we are contributing greatly to the accumulation of so-called greenhouse gases (GHGs) in the atmosphere, which trap heat and block outward radiation[3]. Now there is an opinion which asserts that there is no scientific evidence that the greenhouse effect is not caused by the increase of concentration of CO₂ in the atmosphere[2]. It means that there is an opposing argument that there is no correlation between CO₂ in the atmosphere and change in climate.

However, there is historical evidence that there is a correlation between constant increase in the concentration of CO₂ after the Industrial Revolution and the increase of atmospheric temperature. Therefore, it can be concluded that the increase of concentration of CO₂ is the cause of climate change as below(Figure 1)

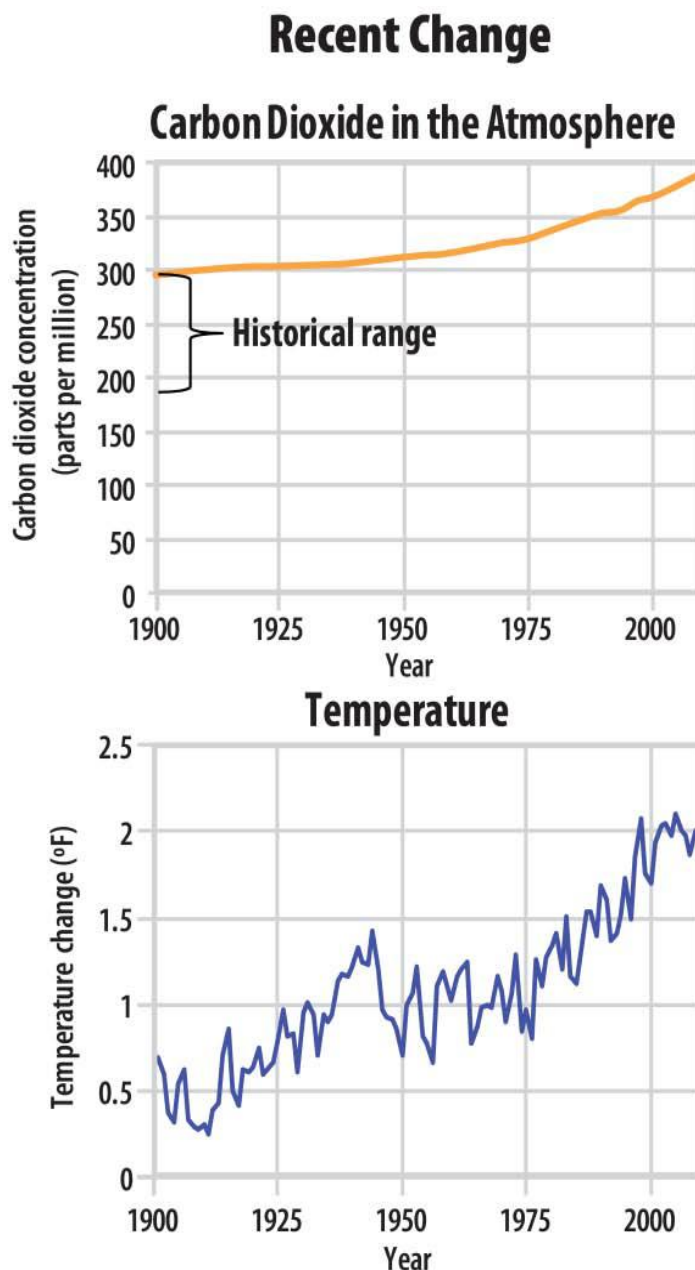


Figure 1: Source: U.S. EPA. *A Student’s Guide to Global Climate Change.*
 url: <http://www.epa.gov/climatechange/students>.

Various methods for reducing the concentration CO₂

The places where most amount of CO₂ is emitted are factories and transportations. The best way to reduce CO₂ concentration is to prevent CO₂ from being emitted into the atmosphere. If one equips car's exhaust system or factory's stack with CO₂ gas collecting facilities, it can prevent the release of CO₂. This is the most certain way to prevent CO₂'s release beforehand. However, as it takes tremendous amount of money, it is nothing but impractical and ideal means. Next thing we can think of is to retrieve the existing CO₂ in the air. Currently, there are researches on storing CO₂ in an underground chamber. However, underground space is limited, and this method takes too much construction costs. Also, there is a risk of soil contamination as well. CO₂ in the earth's atmosphere is used for plant's photosynthesis. Usually, people call the Amazon the lung of the earth. There is no problem with effusing amount of CO₂ that plants on the Earth can absorb. Effusion of CO₂ beyond that leads to an increase in the concentration of CO₂ in the atmosphere. To rephrase it, the problem of climate change will be solved when emission of CO₂ per hour is equal to an the amount that plants intake CO₂. Thus, a development of technique that retrieves excess of effusion of CO₂ is necessary. It is technically feasible to capture CO₂ from flue gases and store it in geologic formations. CCS(carbon capture and storage)would reduce the *effective* carbon intensity of energy by directly removing CO₂ from flue gases and industrial processes and preventing its release to the atmosphere[3]. CCS technologies are currently not widely used as a way to avoid carbon emissions. It could be considered issues of cost for applying CCS technologies on a much larger scale[3].

What are the conditions for technique used for capturing CO₂?

We need a protocol for capturing CO₂. There are two big rules that we can think of. First is that we should be able to retrieve a large amount of CO₂ with a small amount of money. The other one is that the equipment must be small and have mobility. To be more specific, it is as below:

- It should be able to retrieve CO₂ on the ground. It takes more facility if it were to retrieve underground or in the air. Also, it is more costly. CO₂ should be retrieved on an atmospheric pressure and normal temperature. Or else, the technique would need extra facility for changing the pressure and temperature. If it takes more money, it will be less practical. If the technique for retrieving CO₂ takes a lot of electricity, more power plants will be needed as well. Then, the emission of CO₂ will be increased in order to decrease the amount of CO₂ which is a contradiction. Thus, the technique should require small amount of money. It will be better if the technique

can utilize solar energy. The equipment should be as small as possible. If we are to retrieve CO₂ with huge equipment, it would take a lot of space, become costly and less mobile. The equipment should be small in order to be mobile. If we can develop technology to capture and sequester the fossil fuel CO₂ in a cost-effective and environmentally sound manner, we will be able to enjoy the benefits of fossil fuel use throughout the next century[4]. Technological improvements in power generation and capture technology can lower the capture costs.

What are methods to retrieve CO₂ efficiently.

Nano-technology is the core technology for collecting CO₂ in the air. There are many gases in the atmosphere. By using nano-technology, people can choose to collect only CO₂. If one observes CO₂ molecule, it is a three-dimensional structure.

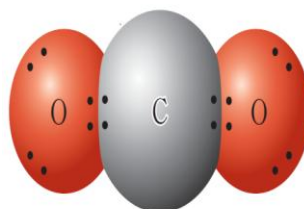


Figure 2: Structure of CO₂

Source : www.climate-change-knowledge.org

CO₂ always floats freely in the air as it is very light. It is same as small flour particle floating in the air. Thus, in order to capture CO₂ molecule, we need something with a nano-sized framework. In other words, we need something with a nano sized space where gas molecule such as CO₂ can freely travel. We need a nano-structured substance with porosity. Nanoscientists developed a porous material called MOF (Metal-Organic Framework) that can capture air particles. By using MOF, we can selectively capture CO₂, and MOF has an excellent trapping capacity. MOF has a covalent bond between metal ion and organic ligand. One MOF can capture one CO₂ molecule.

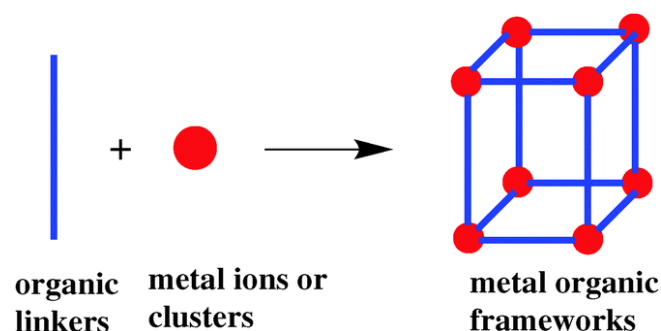


Figure 3 : MOF

Source : Amarajothi Dhakshinamoorthy et al, Metal-organic frameworks as solid catalysts for the synthesis of nitrogen-containing heterocycles, *Chem. Soc. Rev.*, 2014,43, 5750-5765, DOI: 10.1039/C3CS60442J

Recent extensive research into the design and synthesis of metal-organic frameworks (MOFs) has led to numerous practical and conceptual developments in that direction³⁻⁷. Specifically, the chemistry of MOFs has provided an extensive class of crystalline materials with high stability, tunable metrics, organic functionality and porosity⁵. Metal-organic frameworks (MOFs)^{1,2}, which are self-assembled from organic ligands and metal ions, are highly promising porous crystalline materials with the strong potential for gas separation, chemical sensors, catalysts and optical devices because of their large and accessible specific surface areas, uniform and tunable pore sizes, and diverse properties⁸.

In essence, reticular synthesis can be described as the process of assembling judiciously designed rigid molecular building blocks into predetermined ordered structures (networks), which are held together by strong bonding. It is different from retrosynthesis of organic compounds¹⁰, because the structural integrity and rigidity of the building blocks in reticular synthesis remain unaltered throughout the construction process—an important aspect that could help to realize fully the benefits of design in crystalline solid-state frameworks⁵. Thus, we need a structural substance that can connect multiple of MOF. That's where CNT (carbon nano tube) comes in handy. CNTs are efficient CO₂ adsorbents and possess potential applications for CO₂ capture.

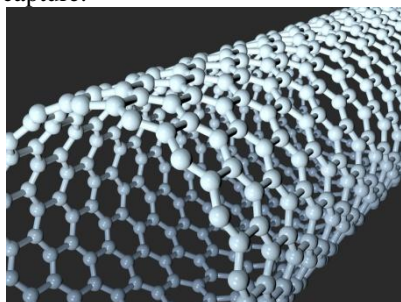


Figure 4: carbon nano tubes

Why is MOF appropriate

MOF is a porous substance. Porous substance has an inner hole with diverse size, and several functional groups can be attached. In order for CO₂ to be captured by MOF, it must have a reaction with MOF. This reaction occurs between MOF and functional group. Thus, in order to have more CO₂ captured, there must be a number of reaction, and for a number of reaction, there must be many functional groups as well. MOF is formed through fusion between metal ion and organic molecule.

Combination of metal ion and organic molecule is the structure of MOF⁶.

Metal-organic frameworks (MOFs) have attracted much attention as adsorbents for the separation of CO₂ from flue gas or natural gas⁷. Excellent adsorbent materials are the prerequisite of completing the operation smoothly and realizing high CO₂ load, Metal-organic frameworks (MOFs), as a class of physisorbents, possess remarkable gas adsorption ability⁷. They are self-assembled of metal ions and organic ligands that involve O and N⁷. In organic molecule, there are aromatic hydrocarbons. Benzene is one of typical aromatic hydrocarbons. Benzene has hexagonal structure, and it is possible to replace hydrogen in benzene with other functional group.

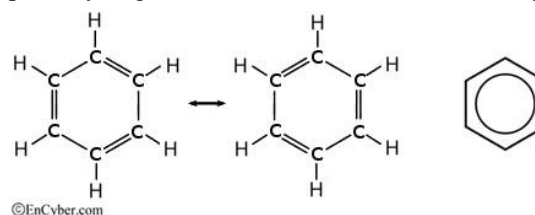


Figure 5 Benzene, C₆H₆. Source : www.chegg.com

One can create a structure of MOF with several functional groups by attaching aromatic hydrocarbon with another aromatic hydrocarbon and attaching functional group to that aromatic hydrocarbon. By using this method, intersection of aromatic hydrocarbon stem with functional group will occur. By using this intersection, there will be a space in between. By controlling the size of inner hole, we can collect CO₂ physically. By creating a hole that has a size of CO₂ molecule, one can selectively collect CO₂, and this hole can work as a filter. Size, volume and physical-chemical conditions of pore of MOFs could realize orient design by changing or modifying organic ligands, widely used in gases storage and separation of mixture gases in recent years⁷. Thus, it can prevent gas other than CO₂ from entering MOF and prevent CO₂ from escaping.

Why should MOF be fixated

MOF takes a form of tiny and light powder, and it can be blown away with a light breath. In order to increase the efficiency of capturing CO₂, MOF should be fixed on a single point. MOF is too light and small that it is hard to carry it around. Thus, there is a need to converge large amount of MOF into one lump. But, MOFs suffer from some limitations. One is their instability towards the solvent removal step performed during their synthesis⁹. Other drawbacks include their inability to provide strong, nonspecific interactions to retain small molecules of gas and the collapse of some MOF networks in the presence of humidity⁹. CNT(carbon nano tube) is a solution to this⁸. The main point in construction of MOF is to make a hole with a size of CO₂ molecule¹⁰.

Every MOF has a characteristic structure with mesopores and nanopores of different dimensions. These cavities of the structure are only accessible via windows whose

dimensions are also determined by the MOF structure, normally spanning from few nm or less than one[11]. To ensure the extensive use of MOF materials in industrial/large-scale applications, a key technology is to develop hierarchically structured bulk materials such as composites to overcome the above problems[12]. Recent studies about the composites of MOFs and different substrates, carbon nanotubes have been reported to address the shortcomings of MOFs[12]. In particular, incorporation of carbon nanotubes (CNTs) into MOFs can obtain better crystals and enhance the composite performance because of the unusual mechanical, thermoconductive, electroconductive and hydrophobic properties of the CNTs[12]. The size of CO₂ molecule is 3.3 Å, while the size of water molecule is 1.9Å. It is important to block absorption of water molecule and induce absorption of only CO₂. As a specific surface of clay of MOF gets bigger, the more CO₂ it will be able to absorb. MOF has flexible structure as it is formed between metal ion and organic ion. Thus, it is MOF's strongest point that the structure and its function can change accordingly with pressure, light, and temperature.

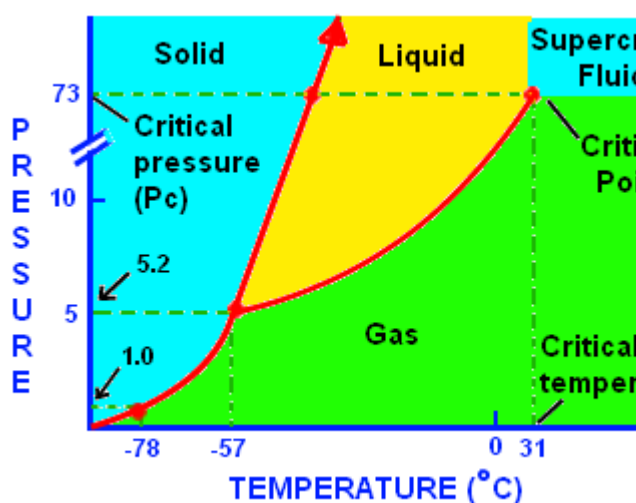
Why is CO₂'s reduction so hard to achieve

CO₂ is in a gaseous state in air pressure and room temperature. CO₂ is formed with two oxygen atoms and a single carbon atom. Thus, as CO₂ has covalent bond and double bond, bonding power is very strong. As carbon is oxidized, it gives four electrons to oxygen and CO₂ is created. This bond is broken at 1500°C. And in order to disassemble both oxygen atoms from a single carbon, the temperature must be over 5000°C. It takes a lot of energy to disassemble CO₂ by heat energy

To summarize the characteristic of CO₂ by using a phase diagram:

All three phases of CO₂ exist simultaneously at the triple point. All three phases of CO₂ exist simultaneously at the triple point. When the pressure is 1 atm, there is no temperature at which the liquid phase of CO₂ exists. CO₂ forms a supercritical fluid at temperatures less than 31 degrees Celsius. CO₂ is a gas under normal conditions of temperature and pressure. When the pressure is 5.1 atm and the temperature is more than -56.7 degrees Celsius, CO₂ exists as a solid.

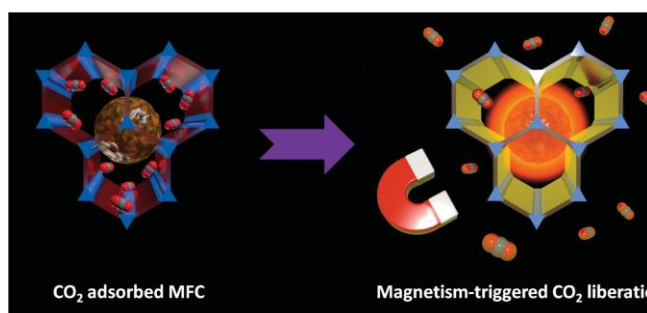
We cannot only continue to pile up CO₂ just because it takes a lot of money to reduce CO₂ as it will not be efficient as time passes. In order to save a storage space, liquefaction is one the solution. However, as it takes a lot of money and energy to liquefy CO₂, it is not economically wise as well. While a variety of technologies and methods have been developed, the separation of CO₂ from gas streams is still a critical issue[13]. Apart from establishing new techniques, the exploration of capture materials with high separation performance and low capital cost are of paramount importance[13]. The combination of CO₂ capture and conversion is an attractive strategy for efficiently reducing CO₂ emissions[14]. It is essential that the materials used in this strategy be able to capture and convert CO₂ at atmospheric pressure and room temperature with only heat from the surrounding environment to avoid the generation of new CO₂. Thus far, no material has been identified that satisfies these requirements[14]. For now, it is a best alternative to recycle the captured CO₂. The cyclic and thermal stability of MOFs during adsorption/desorption is very important when connected to practical application[13]. The cyclic CO₂ adsorption of MOF-5 prepared by microwave synthesis showed that the uptake capacity is invariably near 3.6 wt% when cycled between 30 and 300 °C at atmospheric pressure through 10 separate adsorption/desorption cycles[13]. CO₂ is a highly quadrupolar gas, whereas competitive sorbates in commonly concerned CO₂ capture separation, including N₂, CH₄, and H₂ are non-polar or weakly polar[13]. This means that there are profound differences in the interaction between these gas molecules and the pore surface of porous material, which can be taken advantage of when modifying the surface properties of MOFs to greatly enhance the adsorption and separation ability[13]. The surface properties of MOFs can be tuned not only by pre-design of ligands, metal-containing nodes, and MOF construction but also by post-modification of existing MOFs[13]. Open active metal sites located on the pore walls of aMOF provide an approach for the enhanced separation of (quadru)polar/non-polar gas pairs, such as CO₂/CH₄[13].] A photosensitive metal organic framework (MOF) -- a class of materials known for their exceptional capacity to store gases is a powerful and cost-effective new tool to capture and store, or potentially recycle, carbon dioxide[15]. The technology to release CO₂ when the light is shown to MOF is



[Figure 6] the phase diagram for CO₂: The animation shows the type of movement experienced by CO₂ molecules in a particular phase.

source : chemistry.tutorvista.com

already developed[15]. The inclusion of Fe₃O₄ magnetic nanoparticles (MNPs) within Mg-MOF-74 frameworks actually increased adsorption capacity in comparison to the native framework. When exposed to an alternating magnetic field, the MNPs within MFCs(magnetic framework composites) acted as “nanoheaters” to generate heat locally, triggering the release of the large majority of adsorbed CO₂ from MFCs (Figure 6)[6].



[Figure 7] : CO₂ liberation from MFC triggered by the application of an external alternating magnetic field.

Source : Reference 6.

Released CO₂ becomes a mixed gas between CO and H₂ by going through electrolysis process.

What is the most efficient way to decompose CO₂

Reducing CO₂ emissions is an extensive and long-term task. there are three possible strategies with this regard—reduction of the amount of CO₂ produced, storage of CO₂, and usage of CO₂[16]. The utilization of CO₂ as a feedstock for producing chemicals not only contributes to alleviating global climate changes caused by the increasing CO₂ emissions, but also provides a

grand challenge in exploring new concepts and opportunities for catalytic and industrial development[16]. Carbon capture and recycling (CCR) can be viewed as a way to introduce renewable energy into the chemical and energy chain, by storing solar, geothermal, wind, or other energies in chemical form[17]. CO₂ hydrogenation to methanol, DME(Dimethyl ether, CH₃OCH₃)

, and hydrocarbons appear already economically viable industrial processes if cheap sources of renewable H₂/electrochemical power are available[17]. CO₂ must be heated in order for it to be decomposed to CO. It is commonly deemed highly efficient if CO₂ is decomposed under 200°C. Currently, the technology to decompose

released CO₂ into CO, hydrogen, and oxygen under 200°C is being developed. Photosynthesis is a process of fixating CO₂ in the air. This process is similar to artificial photosynthesis. Reduction of CO₂ is turning CO₂ into something useful. We need a catalyst to facilitate the

reduction of CO₂. Au(gold), Ag(silver), and Zn are good CO₂ reduction catalysts, displaying a high current efficiency for CO₂ reduction, whereas Ni, Pt, and Fe are poor CO₂ reduction catalysts and mostly produce hydrogen[18]. Cu shows good current efficiency but less than Au, Ag, Zn. Because gold is expensive, nano silver catalyst for changing CO₂ into CO is being developed at the moment. There is a research that shows CO₂ can convert into CO fast is nano silver particle is distribute equally on top of carbon nanofiber. As it is cheaper to use silver while effective, it is appropriate to use silver as the catalyst. It could be produced CO with overvoltage that is only 60% of what is needed originally with silver nano particle. Overvoltage means that the electric energy that is being lost is high. So, for artificial photosynthesis with high efficiency, overvoltage should be low. In aqueous solution, when one induces a reducing reaction of CO₂, there is a problem of low efficiency in conversion because H₂ is created by reducing of H₂O[18]. When it is induced a reducing reaction of CO₂ using electrolysis with nana silver catalyst, it becomes a highly efficient conversion as it can save electricity[19]. As reducing reaction of CO₂ through electrolysis is possible in room temperature and normal pressure, it is less costly[18]. Moreover, it only requires water to do it. Even more, if it is possible to use solar energy for the energy needed for electrolysis, this technology will be semi-permanent; and problems with CO₂ can be solved. Let’s look at below to find out several methods to induce reducing reaction of CO₂ and examine specific steps for electrolysis.

CO₂ pyrolysis : CO₂ can be pyrolyzed into CO and O₂.

60% of CO₂ is disassembled in 2,500°C. CO that returns to atmosphere can cause toxic problems. Some of CO makes contact with oxygen in the air and reduced into CO₂ once more. Therefore, CO should be captured before emitted into the air and used as a substance for other products. Pyrolysis of CO₂ and capturing CO is technically very difficult due to high temperature and short time available[18]. As pyrolysis takes a lot of energy, it becomes a paradox. to create CO₂ in order to reduce CO₂. Also, this method is too costly.

It is to electrolyze CO₂ into CO and O₂ so that CO₂ is reduced to CO

Electrolysis: **CO₂ = CO + 1/2O₂**

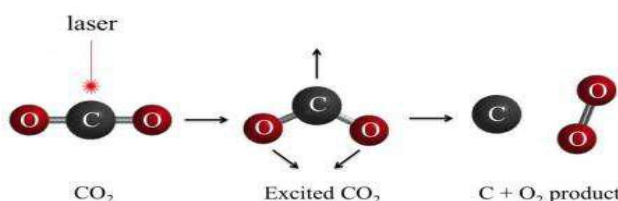
As the formula above states, CO₂ is separated into CO and O₂. However, as CO’s emission can be problematic due to its toxicity, it is better to turn it into fuel or organic chemicals. There are two ways for electrolysis: high temperature and low temperature. High temperature electrolysis should not be considered because it takes a lot of energy. It is said that low temperature electrolysis is the most efficient way[18][19].

In other words, electrolysis is considered prominent for its ability to reduce CO₂ and turn it into CO and formic acid. Low temperature electrolysis uses polyelectrolyte membrane, acidic aqueous solution, or alkaline aqueous solution as an electrolyte and should be operated less than 100 degree Celsius[18]. Compared to high

temperature electrolysis that uses solid oxide aqueous solution, low temperature electrolysis is less efficient[19]. However, low temperature electrolysis is easier to build a system and uses less energy comparably. As all raw materials needed for reducing reaction is water and CO₂, by recycling electrolyte, there is no emission of chemicals[19].

As the system is simple and can be modularized, the process is simple too and economical. If the electric energy needed for the reaction can be provided by renewable energy that does not produce CO₂, it can reduce the net amount of CO₂ in the air even more. By converting CO₂ into chemicals such as formic acid(HCOOH) or methanol, this technology can be used as a preservation technique for renewable energy[18]. Methanol is the most promising photo-reduced product of carbon dioxide because it can be transformed into other useful chemicals such as gasoline (petrol) using conventional chemical technologies, or easily transported and used as fuel in the automobile vehicles without major adjustments[20]. Effective conversion of CO₂ into HCOOH can be achieved using CR(Copper Rubeanate)-MOF in aqueous media by means of potentiostatic electrolysis[21]. It showed that the quantity of products on the CR-MOF electrode was greater than that of Cu metal electrode[21]. If one induces reducing reaction of CO₂ in aqueous solution, H₂ will be produced inevitably as H₂O will be reduced as well. By collecting H₂, it can be used as hydrogen fuel cell as well[19].

Photo-dissociation of CO₂: Photodissociation of carbon dioxide (CO₂) has long been assumed to proceed exclusively to carbon monoxide (CO) and oxygen atom (O). In the future, some Researchers would discover a way to tease oxygen molecules from carbon dioxide for nonbiological oxygen production in CO₂-heavy atmospheres as below(Figure 7)

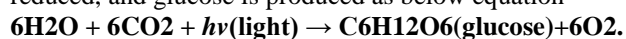


[Figure 8] : It shows that carbon dioxide can be split by vacuum ultraviolet laser to create oxygen in one step.

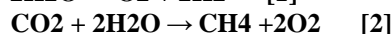
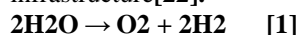
Source : <http://phys.org/news/2014-10-oxygen-molecules-carbondioxide.html>

Technology for photo-dissociation of CO₂ is environmental friendly in that it uses solar energy[20]. But, It is referred as an artificial photosynthesis over technology for photo-dissociation of CO₂. Generally, as a

lot of energy is required for the reduction reaction of CO₂, it is not really efficient. However, photo-dissociation that uses solar energy is innovative. Photo-dissociation is based on photosynthesis which synthesizes glucose from water and CO₂ by using solar energy. Photosynthesis consists of light reaction and dark reaction. During light reaction, plants use chloroplast to absorb light and dissolve water to create hydrogen and oxygen. During dark reaction, by using hydrogen, CO₂ is reduced, and glucose is produced as below equation



By imitating a photosynthesis that happens in nature, artificial photosynthesis is a research that tries to convert CO₂ and water into O₂ and liquid fuel using solar energy. The goal of artificial photosynthesis is to mimic the green plants and other photosynthetic organisms in using sunlight to make high-energy chemicals but with far higher efficiencies and simplicity of design for scale-up and large-scale production[22]. Target reactions were water splitting into hydrogen and oxygen (equation 1) and light-driven reduction of CO₂ by water to give CO, other oxygenates, or hydrocarbons. Methane is shown as the product in equation 2, but the ultimate target is liquid hydrocarbons to power our existing energy infrastructure[22].



Thus, artificial photosynthesis consists of two technologies. One is to create oxygen and hydrogen by decomposing water using solar energy. Other one is to convert CO₂ into a useful chemical.

CO₂ converts into CO and C₃O₂ (carbon suboxide) through photo-dissociation[23]. In photo-dissociation from CO₂ to CO requires UV photon. Condensed C₃O₂ polymer is recycled[23]. Photo-dissociation technique can not only be used for highly concentrated CO₂ in power plant but also be used with low concentrated CO₂ as well.

Conclusion

Recycling carbon dioxide is a great deal. Many scientists believe that it is not only worth the effort, but a crucial endeavor. It is necessary to do effort to clear the problem of the climate change using so-called "carbon negative" technologies. That means actually sucking the greenhouse gas out of the atmosphere and doing something productive with it. Several pilot projects on Recycling carbon dioxide (CO₂) in air are operating or under construction. In near future, Carbon Capture and Utilization could overcome many of the drawbacks of carbon capture and recycling.

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