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Biological Conversion of Carbon Dioxide to Value-added Chemicals

Owen James McGrath
omcgrath@mix.wvu.edu

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Biological Conversion of Carbon Dioxide to Value-added Chemicals

Owen J. McGrath

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Master of Science in Chemical Engineering

Jianli Hu, Ph.D., Chair

Charter D. Stinespring, Ph.D.

Jeremy S. Hardinger, Ph.D.

Department of Chemical and Biomedical Engineering

Morgantown, West Virginia

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Abstract

Biological Conversion of Carbon Dioxide to Value-added Chemicals

Owen J. McGrath

As Carbon Dioxide (CO₂) levels in the atmosphere continue to rise due to human intervention, there is increased urgency to take actions to mitigate the potential ramifications. Many countries have instituted a CO₂ tax and have provided funding to finding potential solutions to our growing CO₂ problem. Further investigating CO₂ capture, sequestration, and utilization is key to combating rising CO₂ levels and methods being investigated have increased substantially in recent years. Converting CO₂ into fuels and value-added chemicals provides a unique opportunity to create materials of value from a substance that is being subsidized to use as a feedstock, as well as taking steps towards being a “net-zero carbon emission” culture. Energy efficient conversion of CO₂ is crucial to achieve both environmental and economic benefits. Current methods being researched use enzymes to imitate the CO₂ metabolic process found in many organisms. This review will elucidate the current methods for using enzymes for capture, sequestration, and utilization of CO₂, as well as the expected future capabilities based upon ongoing research.

Table of Contents

Introduction.....	1
Carbon Dioxide Capture/Sequestration.....	4
Carbon Dioxide Utilization in Natural Processes.....	4
Value Added Products from Carbon Dioxide.....	7
Enzymatic Conversion of Carbon Dioxide.....	8
Single Enzyme Processes.....	9
Enzyme Network Processes.....	12
Electro/Photo enzymatic Processes.....	13
Enzyme Immobilization.....	13
Microbial Fermentation.....	14
Discussion.....	16
Future Work.....	19
Conclusion.....	19
References.....	21

Introduction

Carbon Dioxide (CO₂) is of critical importance to all life on earth; atmospheric CO₂ is the main source of carbon for biological processes. Plants and algae fix CO₂ into carbohydrates via photosynthesis, and aerobic organisms produce CO₂ during metabolic processes.

The rise in atmospheric CO₂ due to human intervention has been widely recognized as a growing problem, with potential ramifications for life on Earth. The rise of atmospheric CO₂ can be primarily attributed to the production of CO₂ from combustion of fossil fuels. The principal reason the rise of CO₂ in the atmosphere is concerning is due to CO₂'s behavior as a greenhouse gas. A greenhouse gas is defined as any gas that absorbs and emits infrared radiation [1]. Infrared radiation is electromagnetic radiation with a wavelength longer than visible light and is emitted or absorbed by molecules as they change their rotational and vibrational movement [2]. Sunlight provides about one kilowatt per square meter of energy at sea level. Of this energy, 500 watts are infrared radiation (450 watts of visible light and 50 watts of ultraviolet radiation make up the balance) [2]. Greenhouse gases absorb this infrared radiation, this in turn results in more energy being put into the atmosphere and causes an overall rise in average temperatures. This increase in energy absorption versus reflection changes the principal energy balance of the Earth.

CO₂ emissions have been increasing since around the time of the industrial revolution (1750) and levels are approximately 45% higher now (415 ppm) than CO₂ levels were then (280ppm) [3]. Historic CO₂ concentrations are shown in Figure 1 and growth rate of CO₂ emissions is shown in Figure 2. To combat the rise of atmospheric CO₂, this problem is being approached from multiple angles. To reduce the amount of CO₂ produced, reliance on fossil fuels is being reduced by utilizing more “green” energy (wind, solar, nuclear, etc.). Also, more

“renewable carbon” fuels (biofuels) are being researched and put into operation. CO₂ capture and sequestration are also being utilized to reduce emissions from burning fossil fuels. To reduce the amount of CO₂ already present in the atmosphere, direct air capture (the process of capturing CO₂ directly from the ambient air) and sequestration can be performed.

Figure 1: CO₂ atmospheric concentration over the past 40 years. The red points are the monthly averages, and the yearly averages are denoted by the black line. [3]

Figure 2: Growth rate of CO₂ emissions over the past 60 years. The black bars signify the average increase in CO₂ emissions for that decade. [3]

Utilizing CO₂ for chemical production has been practiced since the 1880's, namely in the production of urea [4]. Interest in using CO₂ in chemical synthesis waned during the 1900's, with carbon monoxide (CO) being the predominant method to supply carbon in the production of various chemicals and fuels.

One method for combating the rise of atmospheric CO₂ is implementing a “carbon tax”. This tax attempts to reduce emissions by placing a larger financial burden on entities that produce CO₂.

Carbon Dioxide Capture/Sequestration

CO₂ capture and sequestration are the most effective method we currently have for reducing CO₂ in the atmosphere. CO₂ capture is the process of capturing CO₂ produced from specific sources (such as the combustion of fossil fuels) by dissolution in a solvent such as monoethanolamine (MEA). This CO₂, once captured, is then stored in tanks for later use or sequestration; an example scrubbing process is shown in figure 3.

Figure 3: Process flow diagram of an example amine scrubber system [5]

Carbon Dioxide Utilization in natural processes

Carbon Dioxide plays a key role in some of the most basic forms of energy conversion in biological systems. There are six distinct cycles, with biological systems using one or more of these cycles to maintain homeostasis. These six cycles are shown in Figure 4. Of these six cycles, the most common is the Calvin cycle and is used by nearly all photosynthetic life. The

Calvin cycle has three distinct mechanisms for CO₂ utilization; CO₂ fixation, CO₂ reduction, and regeneration of the CO₂ receptor, which allows the cycle to repeat.

Figure 4: Six of the natural CO₂ metabolic cycles: (a) Calvin cycle, (b) Reductive citric acid cycle, (c) Reductive acetyl-CoA route, (d) 3-Hydroxpropionate cycle, (e) 3-Hydroxpropionate/4-hydroxybutyrate cycle, (f) Dicarboxylate/4-hydroxybutyrate cycle [6]

Value Added Products from Carbon Dioxide

Fuels

Investigating methods of deriving fuels from sources other than “fossil carbon” sources is a major field of study. Some of the most common fuels being investigated for production from CO₂ are methanol and ethanol.

CO₂ is a relatively low energy molecule, therefore, to build energy carrying molecules, such as fuels, energy must be added in some way. The difference in energy carrying capacity between CO₂ and carbon-based fuels is easily seen when comparing the Gibbs free energies of formation. The Gibbs free energy of formation for CO₂ and various relevant compounds is shown in Table 1.

Compound	Chemical Formula	ΔG_f° (kJ/mol)
Carbon Dioxide	CO ₂	-394.39
Carbon Monoxide	CO	-137.16
Ethanol	C ₂ H ₅ OH	-174.8
Methanol	CH ₃ OH	-166.6

Table 1: Gibbs free energy of formation of relevant compounds (at 25°C and 1 atm)[17]

The problem with converting CO₂ to various fuels is twofold: first, where does the additional energy come from, and second, where does the hydrogen that are in the composition of these fuels come from? The answers to these questions are different for organic and inorganic production methods.

For inorganic methods of producing CO₂, the energy source is typically in the form of heat. This heat can be supplied through various means, however if the aim is to reduce net carbon in the atmosphere, renewable energy sources such as wind, solar, and geothermal should be utilized. The typical source of hydrogen is diatomic hydrogen itself, with that hydrogen typically being supplied through methods such as steam methane reforming and water gas shift reaction.

For organic conversion methods, the energy source can come from a variety of methods, including ultraviolet radiation, electrical potential, or energy carrying molecules (ATP, GTP, and NADH) and may require a specific combination of those sources. The typical source of hydrogen is through an energy carrying molecule.

Feedstock chemicals that can be synthesized from CO₂ include carbon monoxide (CO), formate, bicarbonate, urea, and various carboxylic acids.

Enzymatic Conversion of Carbon Dioxide

Single enzyme processes for conversion of CO₂ to useful products are less common than enzyme network processes. In addition to typically requiring a complex system of enzymes working in tandem, these processes also require energy to be added, usually in the form of adenosine triphosphate (ATP), guanosine triphosphate (GTP), nicotinamide adenine

dinucleotide (NAD or NADH for the reduced form), or nicotinamide adenine dinucleotide phosphate (NADP or NADPH for the reduced form). CO₂ has a very low Gibbs free energy, requiring energy from an external source to facilitate reacting CO₂ into various products.

Single Enzyme Processes

Single enzyme processes for synthesis of products from CO₂ generally fall into one of two categories; oxidoreductases and lyases (synthases can also be used; however, their products are often not useful outside of the cellular setting).

Oxidoreductases are enzymes that assist in the transfer of electrons (oxidation-reduction, or redox reaction) between two molecules (a reductant to oxidant). The typical electron donors for these reactions are NAD and NADP. Oxidoreductases are found naturally in chloroplasts and mitochondria.

One of the products of oxidoreductases that has the most uses is formate. Formate has multiple industrial applications, including methanol and hydrogen production, fuel cells, and used in dyes. The reaction for conversion of CO₂ into formate is given in Equation (1).

The enzyme used for conversion of CO₂ to formate is Formate Dehydrogenase (F_{ate}DH) and utilizes NADH as a cofactor. The mechanisms for this reaction are shown in Figure 5. One of the issues with this process is the consumption of NADH; continually adding new NADH quickly forces this process to become financially unreasonable. To circumvent this problem, it is

necessary to regenerate the NADH used as the cofactor; the method commonly utilized is an artificial photosynthetic system that will be further discussed in the photo-enzymatic process section.

Figure 5: Reduction of CO₂ to formate by F₄₂₀H with cofactor of NADH [7]

The next product of oxidoreductases with multiple uses is CO. CO is used in processes ranging from methanol production, acetic acid production, as well as the Fischer-Tropsch process. The reaction for conversion of CO₂ into CO is given in Equation (2).

The enzyme used for conversion of CO₂ to CO is [NiFe] CO Dehydrogenase ([NiFe] CODH).

The mechanism for reduction of CO₂ to CO by [NiFe] CODH is shown in Figure 6.

Figure 7: Hydration of CO_2 to HCO_3^- by $[\text{Zn}]\text{CA}$ [8]

Enzyme Networks

Enzyme networks are much more common in natural processes and tend to be more effective than single enzyme processes, with more varied possible products; nearly all naturally occurring CO_2 utilization processes are enzyme networks. While enzyme networks have the benefit of being more flexible in desired product, they are more difficult to manage in an in vitro setting.

One of the most promising products of CO_2 conversion is methanol. Methanol is an effective fuel due to its relatively high energy content as well as its ease of transport/storage. The benefit of producing methanol from atmospheric CO_2 is two-fold; greenhouse gases

produced from combustion would be recycled by production of a renewable fuel source. The reaction pathway for reacting CO₂ into methanol is shown in Figure 8.

Figure 8: Reaction pathway of CO₂ to methanol [9]

Electro/photo-enzymatic Processes

An emerging field of CO₂ utilization, electro and photo-enzymatic processes generate free electrons to assist in the CO₂ reduction reaction.

Enzyme Immobilization

One of the largest impediments to using enzymes in an *in vitro* setting, is enzyme management. Enzyme immobilization is the method of fixing enzymes to a substrate, rather than having the enzymes suspended in the working fluid. The immobilization process removes the need for a complicated filtration in the product flow stream to separate enzymes from the desired product. Immobilizing the enzymes also reduces the need to continually add new enzymes as old enzymes are lost to the product stream. One of the major hurdles of enzyme immobilization is the reduction in activity of an enzyme after immobilization.

One method being investigated for separation of enzymes in lieu of immobilization, is encapsulation. Encapsulation has several advantages over immobilization. The biggest advantage of encapsulation is there is no reduction in enzyme activity (enzymes are not being

restricted, and thus retain full activity). The drawbacks to encapsulation include, increased complexity in manufacture (the process of encapsulating and controlling capsule size can be difficult), and an overall reduction in reaction rate due to the need for reactants and products to diffuse across the capsule membrane.

Microbial Fermentation

Utilizing microorganisms directly to convert CO₂ versus isolating and producing specific enzymes is a promising avenue of research. Performing CO₂ conversion to value added chemicals within selected microorganisms is desirable due to the fact that many of the more useful conversion pathways require a multitude of enzymes, along with various cofactors; these microorganisms already have systems in place to produce and regulate enzymes, as well as regenerate the necessary co-factor. Using microorganisms makes the conversion process simpler in some respects: enzymes are contained within cellular structures, therefore immobilization/encapsulation are no longer a concern, filtration of cells (with a size in the order of micrometers) is easier than filtration of enzymes (size in the order of nanometers), and production/regeneration of co-factor. There are some disadvantages to using microorganisms however: microorganisms typically require a more controlled environment to live/grow in (temperatures ranges that are acceptable for the enzymes used can kill the cell containing those enzymes), growth of cellular mass still requires some form of energy input (ultraviolet light if photosynthetic or some form of food source otherwise), genetic manipulation may be needed for

production of specific chemicals, and some method to regulate growth is necessary (introduction of growth factors).

One of the process being investigated utilizing microorganisms is the production of isobutyraldehyde by genetically modified *Synechococcus elongatus*. The reaction pathway is shown in Figure 9.

Figure 9: Synthesis of isobutyraldehyde from CO₂ by *Synechococcus elongatus*

Discussion

Actions need to be taken to help reduce CO₂ buildup in the atmosphere. Utilizing waste products (CO₂ in this case) to produce useful, valuable chemicals is an obviously desirable scenario. The question to ask is not “Is converting CO₂ to chemicals worth the effort?”, but rather “Is using enzymes to convert CO₂ favorable over utilizing inorganic catalysts?”.

Much more research needs be done before these CO₂ utilization technologies will be able to be implemented in any meaningful way. The process that has been studied to the greatest extent of the previously mentioned processes is most likely the methanol conversion process. The enzymatic conversion of CO₂ to methanol was first characterized in 1999.

The current annual methanol usage in the world is approximately 100 million tons (approximately 7.76×10^9 mol/day), as shown in Figure 11. Most of the methanol produced today is via syngas (CO and H₂ from methane) reacting over a catalyst.

Figure 10: Methanol USD value per metric ton ⁴⁴

Figure 11: Global methanol demand over five-year period 44

Currently, the maximum conversion rate of CO₂ to methanol from available studies is $20.96 \frac{\mu\text{mol}_{\text{CH}_3\text{OH}}}{\text{mg enzyme} \cdot \text{h}}$.⁴⁵ In order to meet current world demands of methanol, we would require 1.54×10^{10} grams of enzyme (17,000 tons). These calculations do not account for the need to make up enzyme lost due to filtration or denaturing, as well as NADH requirements for this process, which would further inflate the amount enzyme (and thus overall material) required.

Future Work

Using enzymes for CO₂ conversion is still very much in the fundamental science phase. Some of the major hurdles to be overcome include regeneration of co-factor, expense of enzyme production, and sensitivity of enzymes to environment. Identifying products that would be most likely to be profitable (such as methanol) is a prospective “next step”. Once a product has been identified, resources can be focused on optimizing enzymes for production of that specific chemical (likely involving genetic manipulation of a suitable existing enzyme) and reducing the cost of those enzymes.

Most of the enzymes being investigated for use in CO₂ conversion are naturally occurring. The isolation and use of naturally occurring enzymes allow researchers to mimic existing biological pathways. The issue arises when attempting to scale these processes up to an industrial level. These naturally occurring enzymes typically require strict pH and temperature controls and can denature otherwise. A potential solution to the fragility of naturally occurring enzymes is to use protein engineering to fabricate enzymes better suited to these tasks. Designing custom enzymes would enhance conversion rates and make enzymes that could operate at more diverse circumstances. Enzyme engineering, while showing promise, needs to be studied further (and for specific processes) to yield tangible results.

Conclusion

With growing concerns relating to rising atmospheric CO₂ levels, methods to reduce the amount of CO₂ released into the atmosphere are being widely investigated. Using waste CO₂ to produce valuable chemicals is an ideal solution. The reality of the situation, however, is that

more research is needed for these processes to advance from novelties to viable solutions. In addition, utilization of atmospheric CO₂ will never be the entirety of the solution; other methods (such as reduction of energy usage and converting to more renewable energy sources) will need to be incorporated to impart any meaningful change.

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