

The CO₂ Tree: The Potential for Carbon Dioxide Utilization Pathways

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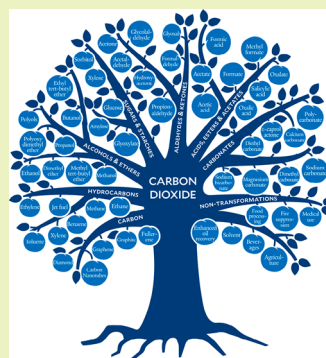
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ABSTRACT: Among the most active areas of chemistry research today is that of carbon dioxide utilization: an area of research that was viewed as futile and commercially impractical not so long ago due to the energetic stability of the CO₂ molecule. The breakthroughs that largely began in earnest in the 1990s have accelerated and now make up a diverse and plentiful portfolio of technological and scientific advances and commercialized technologies. Here, “The CO₂ Tree” is presented as a tool to illustrate the breadth of potential products from CO₂ utilization and to communicate the potential of these chemical breakthroughs to address the greatest challenge that society faces today: climate change. It is intended to be useful for scientists, engineers, legislators, advocates, industrial decision-makers, policy makers, and the general public to know what is already possible today and what may be in the near future.

KEYWORDS: CO₂ transformation, green chemistry, green innovation, climate change



The
CO₂ Utilization
Tree

1. INTRODUCTION

How can we reduce atmospheric CO₂? It may well be that decades into the future, one of the most positively impactful and highly regarded inventions of the current generation will be the conversion of carbon dioxide into valuable products.¹ Transforming what may be the biggest threat to many living things due to rapidly accelerating climate change^{2,3} into one of our greatest solutions could not only save future generations from the devastating impacts of climate change, but would be worthy of recognition.

Carbon capture, utilization, and storage (CCUS) has garnered increased interest across academia, industry, and government in recent decades due to the need to limit the global temperature increase to ensure climate stability. Despite this societal shift toward CCUS due to increased emissions, it remains absolutely vital to, first, avoid the generation of CO₂ from fossil sources. However, this is by no means a “war on carbon” as a whole, but rather the origin of that carbon, since the future of civilization will continue to rely heavily on carbon-based products and services. Reducing the increase of CO₂ levels from the use of fossil resources needs to be addressed simultaneously by three synergistic actions: avoiding CO₂ generation, implementing CO₂ mitigation, and utilizing CO₂ as carbon source. In this realm, CO₂ utilization presents a readily applicable and potentially cost-effective option.⁴ As

fossil-based carbon is phased out of the economy, as it ultimately must be, changing this gigantic and essential “value chain” of carbon across industries such as energy, pharmaceuticals, textiles, and manufacturing into a closed anthropogenic carbon cycle requires a drastic paradigm shift. Rather than accepting CO₂ as the inevitable waste once the carbon, even when originating from renewable sources, has fulfilled its function, it needs to be viewed as valuable feedstock. To put it succinctly, carbon dioxide can be the ultimate source of carbon, whether sourced as CO₂ or through renewable feedstocks, for humanity in the postfossil era.⁵

The intellectual and technological transition to realize this future state should not be underestimated. Analyzing CO₂-conversion within a framework that is largely identical to today’s petrochemical industry often results in challenges based on key aspects such as economic feasibility, large-scale potential, or long-term carbon sequestration.⁴ However, these criteria mainly arise from viewing CO₂ utilization

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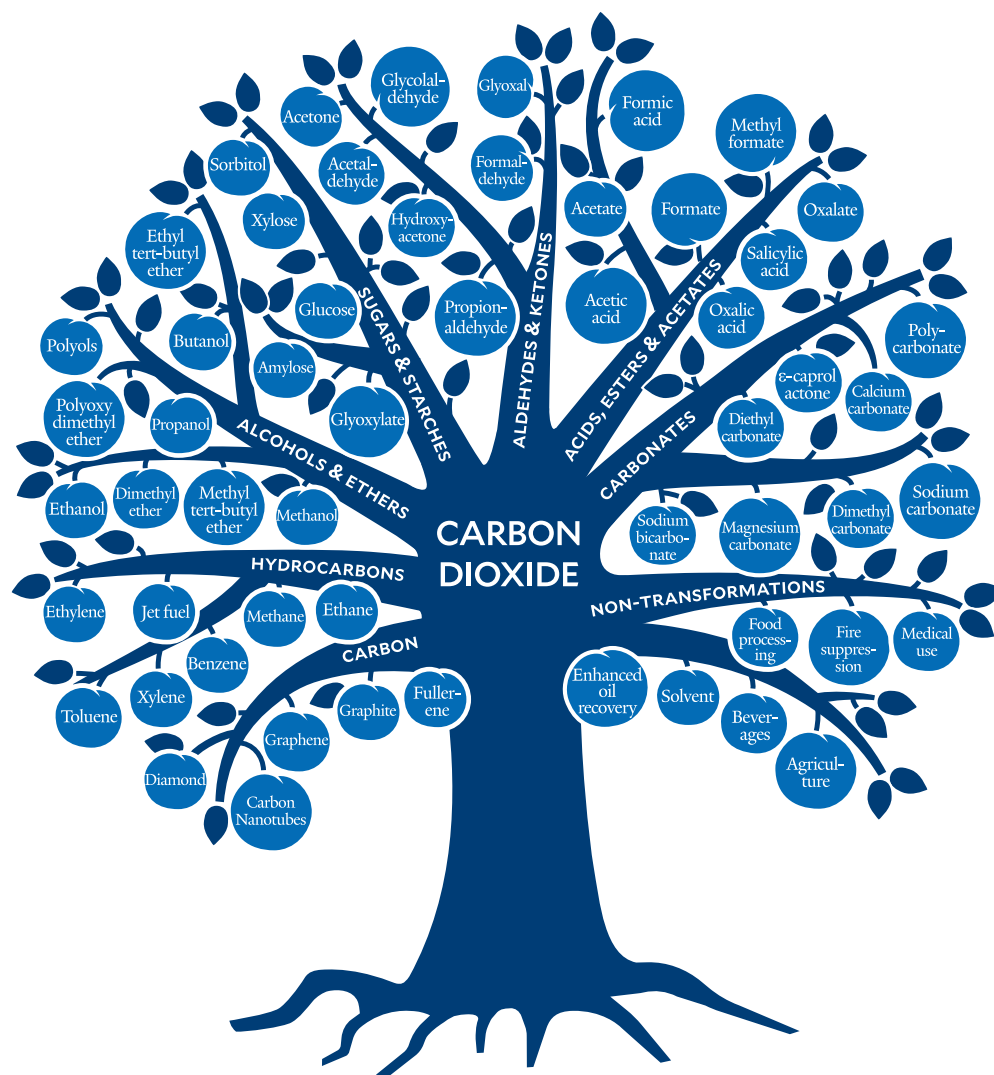


Figure 1. The CO₂ Tree highlighting the classes (branches) of compounds (fruits) that have been made from carbon dioxide from lab scale to commercial scale.

primarily as a method for carbon dioxide mitigation rather than the way forward toward “de-fossilization”. To a first approximation, the vast majority of people associated with developing the field of CO₂ utilization were trained at a time when it was virtually impossible, but certainly impractical, for a chemist to attempt to convert CO₂ at significant scale. As carbon dioxide has an enthalpy of formation (ΔH_f°) of -393.5 kJ/mol,⁶ it was understood to simply be at too low an energy state; too stable to even bother considering. After all, the reason it is able to persist in the atmosphere and contribute to global climate change is due to its inherent chemical stability.

It is important to distinguish the energetic balance of carbon dioxide-based processes from the need to “activate” the CO₂ molecule to engage in chemical transformations. While the energetic balance reflects the thermodynamic stability, the reactivity is governed by the kinetics of bond-breaking and bond-forming events. The energy input to render CO₂-based reactions thermodynamically feasible can be provided by energy-rich reactants such as H₂ or by means of electrical or photochemical driving forces, ultimately stemming from nonfossil primary sources to arrive at net zero or even carbon negative balances. The reactivity of CO₂, however, can be

steered largely by the use of catalysts that enable elementary steps that are kinetically hindered or even impossible. Notably, the role of the catalyst is in many cases to generate highly reactive intermediates from the coreagents rather than “activating” the CO₂ molecule itself.^{7,8} Thus, the catalyst opens the desired reaction channel, but its energetic balance is governed by the energy content of reagents and products. It is obvious that chemical transformations based on CO₂ will therefore require more primary energy input than reactions starting from fossil feedstocks. However, this simply reflects the stored sunlight embedded in the hydrocarbons over millions of years. In the context of climate change, a comparison of CO₂-based processes versus petrochemical processes is misleading if based on reaction energies only. In contrast, the carbon intensity or carbon dioxide emission of the overall process is the key performance indicator.⁹

While CO₂ transformations have typically been viewed as something only accomplished by plants and not replicable by humans, scientific advances have enabled synthetic CO₂ utilization chemistry. The early modern work of carbon dioxide conversion has resulted in detailed reviews and books that highlight this rich history that became accelerated in the

1990s.^{7,10–14} A partial treatment of this revolutionary work would be a disservice to the pioneers and so we refer the readers to these excellent comprehensive resources.^{7,10–18} The direct result of that momentum has allowed for green chemistry to emerge at the forefront of research efforts, specifically within carbon capture and utilization.

The impacts of this increased interest are consequential in the development of climate change solutions. 2023 was regarded as the warmest year since global records began in 1850 and 2024 is currently on track to top even 2023, measuring 1.35 and 1.54 °C above the preindustrial average, respectively.^{19,20} In addition, the petroleum company, BP projected in 2024 that the IPCC-defined “carbon budget” to remain within 2 °C global warming would be exceeded by the early 2040s on the current trajectory.²¹ Taken together, it is clear that the need for carbon utilization is dire. Without the ability to transform carbon dioxide into value-added materials, it would remain a waste with significant adverse environmental and social implications.^{22–25} But nearly more importantly, it would also be a costly economic loss. To reverse these environmental, social, and economic losses requires taking what was once viewed as science fiction and making it become science reality.

In chemistry, the tree as an illustrative metaphor has been used for at least a century, such as the “Petroleum Tree” diagram,²⁶ which was used to visualize the many products that could be derived from a barrel of crude oil at the time. It served to communicate how even then, petroleum touched almost all aspects of everyday life. The tree imagery was also used in “The Chlorine Tree” that communicated the utilization of chlorine in manufacturing processes as well as in many common chemical products. Most recently, the tree image was used as the “Green ChemisTREE”²⁷ to showcase all of the various scientific and technological breakthroughs realized or extended since the advent of green chemistry in 1998.

In this review, we again harness the tree metaphor and its compelling imagery to effectively represent the chemical breakthroughs and future potential of carbon dioxide utilization. As trees naturally undertake a significant portion of natural CO₂ transformation, the “CO₂ Tree” (Figure 1) is an appropriate way to illustrate the immense power of using carbon dioxide. While the topic of CO₂ capture is outside the scope of this review, one can imagine it derives from nonabatable emissions, biomass utilization, end-of-life of products, or the atmosphere. The implementation of CCUS from these sources, among others, will make CO₂ an economic driver to advance climate change solutions as it is available in appreciable quantity and purity.¹⁶ The breadth of the work that has been demonstrated is immense and will only be exceeded by further discoveries, inventions, innovations, enhancements, and scaling yet to be achieved. Meanwhile, this review focuses on the breadth of demonstrated chemical pathways of CO₂ utilization to highlight the state of knowledge and future implications toward defossilization of essential products and services, and hence reducing the impacts of climate change. Notably, we recognize the obvious power of biological methods to convert CO₂ as demonstrated by nature on a daily basis at scale, however, this review focuses exclusively on chemical pathways for CO₂ utilization and conversion to useful products.

Here, the branches of the CO₂ Tree represent the various chemical classes that can be directly accessed via CO₂ utilization from completely reduced carbon (Figure 2, left)

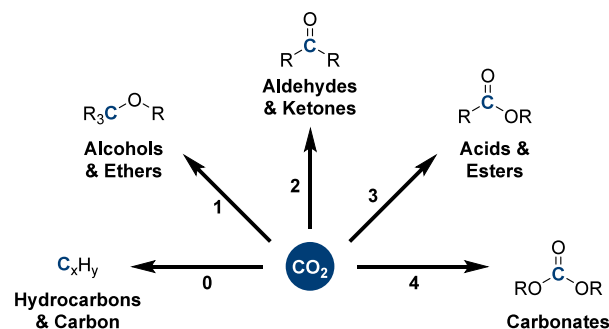


Figure 2. Graphical representation of the organization of the CO₂ tree from left to right based on the number of bonds between the primary carbon and electronegative oxygen (“reduction level”) for the variety of chemical classes included in this paper. Note: sugars and starches can be either 1 or 2.

all the way to fully oxidized carbonates (Figure 2, right). Each fruit then represents an important chemical product (e.g., methanol) or product category (e.g., polycarbonates), with an additional branch representing nontransformative CO₂ utilization including, for example, as a solvent or in food processing. Each branch will include a general chemical mechanism, how the transformations have been demonstrated, and what types of products can be generated. In Section 3, a discussion of the current technological state of the various pathways and their potential for reducing atmospheric CO₂ is included. In this endeavor, the reader will understand that due to the interconnectedness of molecules in their manufacturing, there will be unavoidable double-counting and so it would not be an appropriate analysis to simply add up the various contributions toward a reduction of CO₂ emissions. Nevertheless, a number of chemical utilization pathways have been evaluated thoroughly confirming their greenhouse gas reduction potential.⁹

While this review incorporates a large variety of chemical reactions that incorporate CO₂, it is impossible for this representation to be comprehensive. Rather, we seek to provide a useful overview of the status of CO₂ transformation science and the future potential of this critically important endeavor that is complementary to recent articles in this area.^{1,4,16,28–33} In this way, the mechanistic aspects governing the scientific advancements will be highlighted before a discussion of the technical implementation potential. It is the sincerest hope of the authors that this representation is soon out of date with new scientific and technological advances. However, we do believe that the CO₂ Tree represents a potentially important and lasting construct that will serve as a guide of what we can strive toward in the coming years.

Finally, it is an important admonition that while the range of science presented in this review identifies the many transformations of CO₂ that currently *can* be done, the decisions about what *should* be done must address more complex criteria. Many of these considerations, including the origins of the CO₂, types of catalysis employed, energy balance, and other life-cycle factors, have already been enumerated in a 2017 perspective paper.³⁴ Ignoring these important factors can result in “doing the right things wrong,” in other words, converting waste CO₂ into valuable products but simultaneously creating unintended consequences.

2. CO₂ UTILIZATION PATHWAYS

Among the various utilization pathways, the thermal (reverse water gas shift, RWGS³⁵) or electrochemical (coelectrolysis³⁶) conversion of CO₂ to carbon monoxide or carbon monoxide-hydrogen mixtures, also known as syngas, enables entry into existing petrochemical technologies. Some of the examples discussed in this review involve such transformations as an implicit part of the mechanism or as an explicit process step and their scientific and industrial implications are certainly relevant to the topic of climate change solutions. However, the important body of work regarding syngas and carbon monoxide catalysis in state-of-the-art technologies is not within the scope of this paper.

In addition to the applications described here that involve CO₂ as the single carbonaceous substrate, a large array of chemical reactions couple CO₂ with one or several coreagents. In this frame, CO₂ can be used as a building block to generate functional groups (e.g., in carboxylation reactions^{37–40}), but also as an oxidant (e.g., in oxidative dehydrogenations and couplings of alkanes^{41,42}). These transformations, while out of the direct scope of this review and surveyed elsewhere,^{37–42} represent notable utilizations of CO₂ as a sustainable feedstock in the chemical sector.

2.1. Carbon. Conversion of carbon dioxide to carbonaceous materials such as graphene, graphite, carbon nanotubes, or diamond requires the transfer of four electrons per carbon atom. To achieve the necessary transfer of electrons, commonly used reducing agents include alkali metals, alkaline earth metals,⁴³ or NaBH₄,^{43,44} often at increased temperature and pressure, which has the added benefit that a supercritical state of CO₂ can be reached. The primary pathways for CO₂ reduction involve metal reductants via combustion,⁴⁵ and electrolysis.^{46,47} Metal-based combustion methods commonly employ extreme temperatures (450–1000 °C) and pressures (80–1000 MPa), thereby resembling metallurgical processes.⁴⁵ Conversely, electrochemical processes commonly employ solid electrolyte oxidizers⁴⁸ or molten salt electrolytes^{45,49} to facilitate CO₂ reduction to carbonaceous materials. Such electrochemical methods are often more energy efficient than their thermal counterparts and can take advantage of renewable electricity sources; however, they are not flawless—solid carbon buildup can “coke” catalysts and hamper active sites,⁵⁰ and gas-to-solid kinetics are slow.⁵¹ While these processes usually yield a variety of solid products, reaction conditions and parameters can be tuned to drive selectivity of conversion from CO₂ to carbonaceous materials including graphite, graphene, carbon nanotubes, and even diamond, and reviews on the topic can be found in literature.^{45,52,53}

Graphene, first isolated by Novoselov and Geim in 2004 and honored with the Nobel Prize in Physics in 2010,⁵⁴ is a desirable target due to its high electron mobility coupled with high Young's modulus, rendering it an attractive material for electronic applications.^{55,56} Several 3D and near-2D graphene materials have been obtained from direct CO₂ reduction,⁵⁷ with numerous 3D graphene topologies achievable by tuning the specific synthetic methodology.⁵⁸ Reduction of CO₂ generally yields 3D graphene that falls into one of three loose classifications: coral-like,⁵⁹ flower/fungus-like,^{60–62} and honeycomb-like.⁶³ These reductions can be achieved both via combusive^{59–62} and electrocatalytic⁶³ pathways. Conversely, there have also been syntheses of near-2D graphene materials from CO₂. A two-step electrolytic process using a molten

electrolyte composed primarily of Li₂CO₃ at 770 °C generated carbon nanoplatelets of approximately 25–125 graphene layers from CO₂, which were then converted into graphene of 1–5 layers thickness via an electrochemical exfoliation process.⁶⁴ In another study, a combustion process at 750 °C was reported to generate near-2D graphene *in situ* in molten magnesium metal following ultrasonication of the reaction melt and H₂SO₄ etching of residual Mg. The obtained graphene material was then shown to exhibit good capacity cycling performance.⁶⁵

Graphite is composed of stacked layers of graphene and is a sought-after synthetic target as it is the primary anode material in commercial lithium-ion batteries.⁶⁶ A recent one-step reaction between carbon dioxide and lithium aluminum hydride at subcritical temperatures (126 °C) and pressures (10 MPa) directly yielded pure graphite at 99.988 wt % purity in the form of submicroflakes, the performance of which rivaled commercial materials and purity (99.996%).⁶⁷ Graphite has also been generated from flue gas, a blend of CO₂ and SO₂, through a molten electrolytic process in Li₂CO₃–Na₂CO₃–K₂CO₃–Li₂SO₄ when above 775 °C.⁶⁸ The authors demonstrated that at temperatures >775 °C, very little sulfur could be found in the produced graphite material, but graphite purity was not reported.

Carbon nanotubes (CNT) are cylinders made from “rolled” graphene sheets and can be single- or multiwalled. CNTs are highly sought-after due to their high tensile strength, thermal conductivity, and potential for carrying currents.^{58,69} Combustive methods include the use of metallic Li, Na, Mg, and Ca alongside either dry ice in an autoclave, or flowing gaseous CO₂ through a tube furnace at temperatures ranging from 550–1000 °C, followed by an acidic workup that usually includes the removal of formed metal carbonates before isolation of CNT byproducts.^{52,70–72} Examples for the electrocatalytic pathway include the synthesis of linear or tangled CNTs from CO₂ in molten Li₂CO₃ or Li₂CO₃–Li₂O at 750 °C.⁷³ Both materials were shown to be useful as electrode materials in battery applications, with the tangled CNTs demonstrating an increasing capacity over time.⁷³ Other studies have explored the effect of using mixed carbonate electrolytes for converting CO₂ to CNTs and found that partially substituting Li₂CO₃ with the alkali carbonate Na₂CO₃ does yield CNTs at 770 °C, but not K₂CO₃,⁷⁴ and that molten Li₂CO₃–MCO₃ (M = Ca, Sr, Ba) electrochemical systems at 750 °C yielded CNTs with increased thickness.⁷⁵ When graphene sheets are “imperfectly” arranged, carbon nanofibers (CNF) can be produced in a similar electrochemical system from CO₂ using molten carbonates.⁷⁶ Finally, there also exist reports of generating CNTs from CO₂ using a hybrid reactor of dielectric barrier discharge and solid oxide electrolyzer.⁷⁷

Other carbonaceous materials generated directly from CO₂ include the formation of C₆₀ fullerene and diamond using dry ice and metallic Li or K in an autoclave system at high temperature and pressure. One study reported isolating C₆₀ fullerene using metallic Li at a temperature of 700 °C and sufficient amounts of dry ice to reach pressures of ~100 MPa for 10h.⁷⁸ Another study reported isolating diamonds of 4–450 μm in size using metallic K or Li at 460 °C and sufficient dry ice to reach a pressure of approximately 83 MPa for 10h.⁷⁹

2.2. Hydrocarbons. Hydrocarbons including methane, ethane, ethylene, and aromatics (benzene, toluene, xylene) contain carbon in its most reduced state. The direct use of CO₂ as a feedstock for hydrocarbon production has gained interest due to their high demand and compatibility with

modern fossil fuel-based energy infrastructure.⁸⁰ The conversion of CO₂ to hydrocarbons has been demonstrated electrochemically,⁸¹ photocatalytically,⁸² and via plasmonic catalysis.⁸³ To achieve the necessary electron transfer, platinum group and transition metals such as palladium, copper, and iron have been employed. To ensure the reduction will occur, hydrogen gas is required for thermocatalytic conversion and is frequently generated *in situ* during electrocatalytic reduction.^{84,85} As mentioned in Section 3.1, electrochemical methods combine the use of renewable electricity with a high potential for energy efficiency in the reduction of carbon dioxide.

Methane is the shortest (C₁) hydrocarbon constituting >90% of natural gas,⁸⁶ which in turn provides more than 20% of the world's primary energy.⁸⁷ The gas and liquid fuel infrastructure have been a strong driver for the Sabatier reaction or CO₂ methanation, which is the catalytic conversion of CO₂ and hydrogen to methane. A plethora of catalysts, reactor designs, and conditions have already been proposed in this concept, termed "Power-to-Gas".⁸⁸ For example, a commonly reported CO₂ reduction reaction to methane features a high temperature solid oxide electrolysis cell (SOEC) with (multi)-metallic heterogeneous catalysts (Figure 3, top).^{89–91} On the other hand, electrochemical pathways

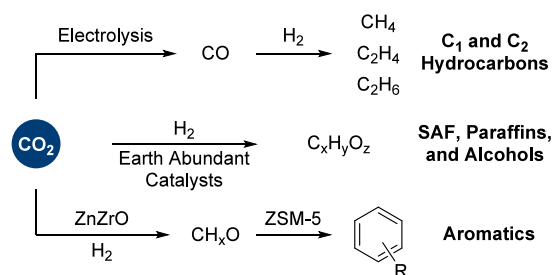


Figure 3. Adapted reaction pathways diagram highlighting mechanisms from CO₂ to (top) methane, ethane, and ethylene; (middle) SAF, paraffins, and alcohols; and (bottom) aromatics. Figure adapted with permission from ref 90 (Copyright 2014 American Chemical Society), ref 104 (Copyright 2018 Elsevier Inc.), and ref 105 (Copyright 2022 American Chemical Society). ZSM-5—zeolite socony mobil-5.

have utilized Ni_xGa_y-based catalysts to reduce CO₂ to a mixture of methane, ethane, and ethene with 0.1 M Na₂CO₃ acidified to a pH of 6.8 with 1 atm CO₂.⁹²

The saturated C₂ building block ethane can be obtained electrochemically from CO₂ using nanostructured Pd-doped Cu-catalysts,⁸¹ as well as more recently, using Fe₂O₃-catalysts with 42% Faradaic efficiency (FE).⁹³ The use of Cu₂O as the working electrode has been shown to produce ethylene and ethanol at FE of 32.1% and 16.4%, respectively.⁸¹ The addition of PdCl₂ to the system shifted the reaction toward ethane (30.1% FE), significantly reducing the production of ethylene to 3.4% FE.⁸¹ However, ethylene makes up over 200 million metric tons (MMT) of polymer precursor in today's society.⁹⁴ Endeavors to convert CO₂ directly to ethylene usually employ electrocatalytic methods, wherein Cu-based materials are almost exclusively employed.⁹⁵ Research efforts are increasingly moving toward optimizing the (nano)structuration of the catalyst, better understanding the microenvironment of the electrode and more generally, toward optimizing the design of the electrolyzer.^{96,97} These endeavors have led to the

development of lab-scale devices reaching faradaic efficiencies >60% and current densities >200 mA/cm²,^{98,99} which are important thresholds for industrial production. However, to achieve economic viability, further improvements such as an increase in energy efficiency by abating operating cell voltage and CO₂ loss are important to reach a target price of \$1000 per ton of ethylene. Another recent example of CO₂ to ethylene conversion is a reaction cascade, linking the CO₂-to-CO conversion in an electrochemical cell with a membrane electrode assembly for the CO-to-ethylene transformation.¹⁰⁰ Many other approaches to produce ethylene from CO₂-containing feeds have been reviewed in detail¹⁰¹ and private actors have expressed interest in electrolytic CO₂-to-ethylene technology.¹⁰² Coupling a multireactor setup with a cascade of electrocatalytically generated H₂O₂ resulted in the oxidation of ethylene to ethylene glycol, opening up another avenue for CO₂ utilization.¹⁰³

A particularly impactful area of CO₂ conversion lies in the production of Sustainable Aviation Fuel (SAF), as it accounts for roughly 2.5% of global greenhouse gas (GHG) emissions.¹⁰⁶ SAF is a mixture of varying chain length hydrocarbons alongside important additives to ensure compatibility with current turbines. To utilize SAF in jet engines, the fuel must pass stringent standards including combustion efficiency, stability, energy capacity, and deposition rate standards.¹⁰⁷ SAF preparation from CO₂ generally employs transition metal catalysts, hydrogen as a reductant, and renewable energy sources. Two distinct approaches are currently under commercial development:

- (1) The electrochemical reduction of CO₂ to CO followed by a biological fermentation and subsequent thermochemical upgrading step has been explored by national laboratories across the U.S.¹⁰⁸ While this process has been shown to achieve olefin selectivity up to 81%, this pathway will not be further discussed due to its syngas intermediate.¹⁰⁸ Not surprisingly, the vast majority of CO₂-to-SAF pathways involve the Fischer–Tropsch process¹⁰⁹ or RWGS.^{105,110,111}
- (2) A more direct approach, developed by Air Company, utilizes fixed bed reactors in a single-step process for the production of alcohols and paraffins from CO₂ (Figure 3, middle).¹⁰⁵ As this process has been developed commercially, specific details are confidential. In general, this process combines CO₂ with H₂ gas in a catalytic fixed-bed reactor to convert >90% of inlet CO₂ to a suite of paraffinic products.¹⁰⁵ The thermocatalytic processes typically involve earth-abundant metal catalysts, like Fe or Co, that bypass the CO intermediate by combining H₂ and CO₂ at elevated pressure (~10 MPa) and increased temperature (275–350 °C) to produce a suite of C₉ – C₂₄ hydrocarbons with >90% conversion.^{105,112} Both methodologies are based on groundbreaking studies describing the synthesis of alcohols or simple hydrocarbons from CO₂, which were eventually refined to allow for the preparation of SAF.^{113,114}

The direct conversion of CO₂ to benzene, toluene, and other aromatic compounds has been achieved through catalyst development. For example, a system containing Zn/ZrO-zeolite tandem catalysts (Figure 3, bottom) proved to generate hydrocarbon fractions with up to 73% aromatic content.¹⁰⁴ A related catalyst featuring Zn/AlO_x and zeolites was optimized for the generation of fractions particularly rich in xylenes.¹¹⁵

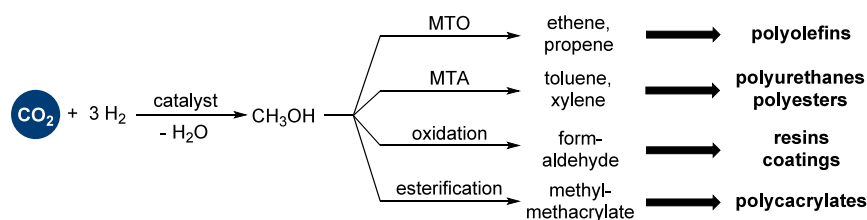


Figure 4. Overview of the reaction pathways utilizing methanol as a central CO₂-based intermediate for applications in the polymer industry across chemical classes. MTO = methanol-to-olefins; MTA = methanol-to-aromatics.

Newer catalyst systems featuring Fe and Cu in combination with zeolites resulted in lighter aromatic fractions including benzene (<5% selectivity), xylene (≤72% selectivity), and toluene (≤40% selectivity) due to mass transfer limitations of heavy aromatics (C₅₊) out of the zeolite.¹¹⁶

Ongoing research on direct CO₂-hydrocarbon transformations is of particular interest, since sidestepping reaction pathways involving CO as an intermediate represents great potential in terms of process efficiency.¹¹⁷ The direct light-driven conversion of CO₂ to hydrocarbons is of particularly high interest, as light-driven transformations only minimally depend on electrical grids and battery storage systems, and can take full advantage of sunlight, water, and CO₂, thereby emulating nature's photosynthesis.¹¹⁸

2.3. Alcohols and Ethers. Alcohols and ethers can serve as versatile fuel additives or replacements and can act as chemical intermediates for producing polycarbonates as well as other chemicals.^{119–124} Alcohols including methanol,¹²⁵ ethanol,^{126,127} butanol,^{121,122} and propanol^{122,128} as well as ethers (dimethyl ether^{120,129,130} (DME), methyl *tert*-butyl ether,¹³¹ ethyl *tert*-butyl-ether,¹³¹ and polyoxy dimethyl ethers (OME_{*n*})^{132–134}) are formed from the reduction of CO₂ with sufficient H₂ equivalents. The primary pathways for CO₂ conversion to alcohols and ethers are electrocatalytic,^{135–139} photocatalytic,^{137,140–142} and thermocatalytic reduction.^{143–148}

Green production of methanol is extensively studied due to its versatility as a fundamental precursor for olefins used to make polymers, jet fuel, gasoline, aromatics, formaldehyde, acetic acid, and even ethers. Its central role in existing and future applications, such as in the polymer industry is highlighted in Figure 4. Apart from its wide application potential, methanol is a C₁ alcohol and known as one of the easiest alcohols to produce.^{121,124,125,146} While photocatalytic and electrocatalytic processes hold promise for the future, they currently face selectivity and catalyst degradation challenges complicating technology upscaling, whereas thermocatalytic reduction currently offers higher energy density, more efficient mass transfer, and more effective catalytic efficiency.¹²⁴ Traditional methanol production utilizes syngas and the RWGS reaction,¹⁴⁴ however, this has been defined as outside the scope of this review. Instead, Figure 5 highlights the direct hydrogenation of CO₂ to methanol with the addition of H₂. Additionally, ethanol can effectively be produced as an intermediate after direct hydrogenation to methanol in the ultimate synthesis of butanol (Figure 5).^{124,149,150} The figure illustrates the conversion of CO₂ to butanol via methanol, DME, and ethanol, which are desirable products in their own right. Catalysis research has been pivotal in enhancing the yield and selectivity of direct CO₂ hydrogenation with reduced energy consumption. Catalysis research in the area is ongoing, resulting in a wide range of uniquely designed catalyst materials spanning Al, Co, Cu, In, Cr, La, Rh, Si, Ti, Zr, Pd,

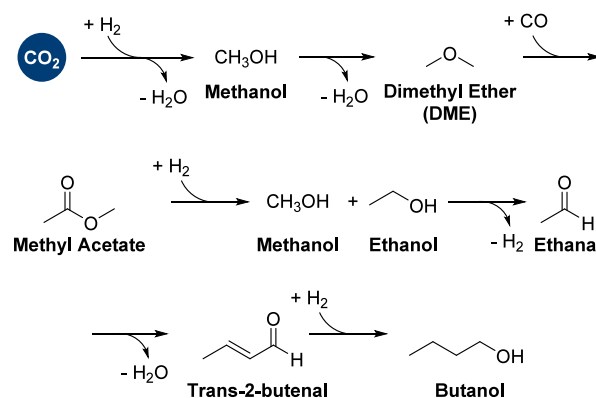


Figure 5. Reaction scheme for the multistep conversion of CO₂ to butanol. Figure partially adapted with permission from ref 122. Copyright 2018 Elsevier Ltd.

and Zn.^{151–155} Despite these heterogeneously catalyzed processes, significant progress has been made using homogeneous liquid-phase molecular catalysts, such as alkali bases, to hydrogenate CO₂ to methanol, targeting high selectivity and activity at lower temperatures,^{156,157} the avoidance of precious metals,^{158,159} and integrated carbon capture with utilization.^{160,161}

The first pilot plant aiming to produce methanol through direct hydrogenation was constructed in 1994 by German company LurgiAG,^{162,163} which found high pressure (6 MPa) and low temperatures (260–270 °C) to favor methanol formation over CO at 35%–45% yield using a commercial copper–zinc–alumina (CZA) catalyst. Merely two years later, the National Institute for Resources and Environment (NIRE) and the Research Institute of Innovative Technology for the Earth (RITE) demonstrated conversion of CO₂ to methanol through direct hydrogenation with 99.7% selectivity at the slightly milder conditions of 250 °C and 5 MPa.¹⁶⁴ While additional pilot scale CO₂ hydrogenation plants have been developed since the turn of the 21st century,^{165–169} all operate off the same basic principles with modification in catalyst material or hydrogen source. With a capacity of 4000 tons per year (t/yr), Carbon Recycling International based in Grindavik, Iceland operates the current largest-scale plant utilizing flue gas from a geothermal plant at the mildest conditions of 225 °C and 5 MPa.^{170,171} Most recently, Air Company has demonstrated single-step production of alcohols and paraffins utilizing captured CO₂ and H₂ obtained via water electrolysis.¹¹⁴ While this process is currently optimized for ethanol production, its product streams include high-purity ethanol (13 t/yr), methanol (10 t/yr), and n-propanol (9 t/yr).^{105,114,172} This implicates that Air Company's technology has the potential to produce a range of short chain alcohols with slight modifications in operating conditions or catalyst.

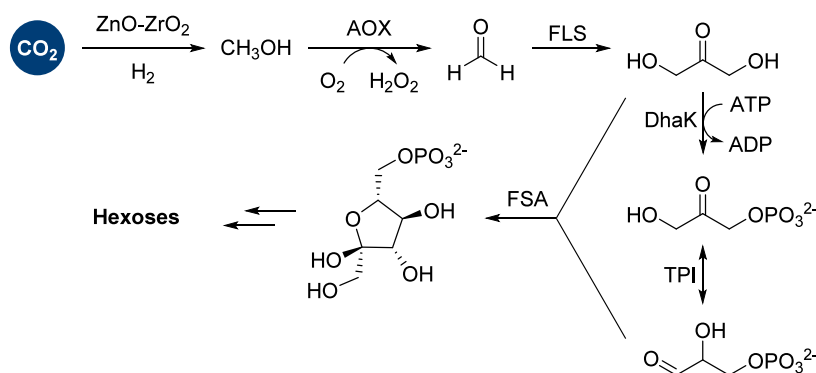


Figure 6. Example of an enzymatic pathway from CO₂ to carbohydrates (here: hexoses). Figure modified with permission from ref 190. Copyright 2023 Science China Press. AOX = alcohol oxidase; FLS = formolase; DhaK = dihydroxyacetone kinase; FSA = fructose 6-phosphate aldolase.

Dimethyl ether (DME) is also known to be among the most valuable and adaptable chemicals that can be produced from CO₂. Apart from serving as a crucial precursor for methylation agents, DME is attractive as a fuel substitute for diesel engines and gas turbines, with production primarily via methanol dehydration, which is currently considered state-of-the-art for renewable DME production.^{119,120,130,173,174} Recently, the one-step direct synthesis of DME has gained attention due to its versatility. This process relies on hybrid/bifunctional catalysts that incorporate metal sites for CO₂ hydrogenation to methanol and Brønsted acid sites for subsequent methanol dehydration to produce DME. While Cu–Zn sites have shown high activity for CO₂ hydrogenation, conventional Cu/ZnO catalysts have been shown to also catalyze the RWGS reaction.¹²⁰ Instead, the addition of zeolitic and other modifiers, such as HZSM-5, have been found to increase DME selectivity up to 75% compared to catalysts without HZSM-5 (0% DME selectivity).¹²⁹ Additional ethers, including oxymethylene dimethyl ether (OME₁), currently derived from the reaction of methanol with formaldehyde, can also be produced from CO₂ hydrogenation with H₂ in the presence of methanol.^{175–177} This homogeneously catalyzed reaction shows favorable economic potential with applications for OME₁, for example, as a fuel additive.¹⁷⁸

2.4. Sugars and Starches. Sugars and starches are an often overlooked class of molecules used, for example, across the textile, surfactant, and plastic industries.¹⁷⁹ The use of carbon dioxide in the formation of sugar and starch molecules has been studied since the identification of photosynthesis in the 1600s.^{180,181} The discovery of the formose reaction to convert formaldehyde to sugars in 1861¹⁸² has motivated the recent transition toward abiotic synthesis of glucose, xylose, and sorbitol with carbon dioxide.^{183–186} Pathways from CO₂ toward molecules larger than three carbons face unique multistep, high-energy challenges.¹⁸⁴ For this reason, the majority of CO₂ to sugar pathways involve CO, formaldehyde, or methanol intermediates before continued thermal or electrochemical transformation to sugars.^{184,185} Further work has also taken this reaction beyond simple sugars to produce amylose, amylopectin, and glyoxylate as larger sugar polymers.¹⁸⁷ The use of chemical methodologies can accelerate reaction rates from days (biologically) to hours (chemically).^{184,187}

Developing abiotic methods for direct conversion of CO₂ to sugars is generally considered challenging due to the need for sequential reactions to form the specific arrangement of carbon–carbon and carbon–oxygen bonds of saccha-

rides.^{184,188} For that reason, studies have focused on the development of efficient reaction cascades in which CO₂ is first converted to formaldehyde to then undergo the formose reaction to various sugars.¹⁸⁸ The formose reaction converts formaldehyde (“form-”) to a mixture of sugars (“-ose”) by using a divalent cation (typically calcium) as a catalyst.^{182,189} Conversion of CO₂ to formaldehyde has been extensively reported in the literature; however, this process suffers from low yields, which limits scalability.^{184,188} Formaldehyde production is further discussed in Section 3.5. Moreover, studies have shown that using glycolaldehyde as an organic initiator is required to achieve substantial sugar-generation rates.^{184,189}

A recent study compared CO₂ to formaldehyde and glycolaldehyde experimental methods to determine key parameters in the subsequent conversion to sugars.¹⁸⁴ The key finding was that electrochemical CO₂ conversion with a B-doped diamond electrode resulted in insufficient formaldehyde productivity levels to sustain the formose reaction.¹⁸⁴ The use of Cu-nanoparticles, on the other hand, resulted in peak glycolaldehyde production of 12 μg/h at –0.80 V versus RHE.¹⁸⁴ Interestingly, the authors found that increasing negative potential coupled with a Cu-nanoparticle catalyst over-reduced the resultant aldehydes after C–C coupling.¹⁸⁴ While there have been significant advancements in the conversion of CO₂ to sugars,¹²⁶ the maturity of abiotic CO₂-to-sugars technology is still in the early phase of development, barring significant challenges with reaction yield and selectivity.¹³⁰

Another particular challenge is the potential formation of non-natural formose sugars, which have been shown to cause death in rats due, in part, to their branched structures not found in nature.^{188,189,191} To address this, significant research effort has been placed in determining suitable formose reaction conditions targeting digestible sugars including glucose, fructose, and sucrose.¹⁸⁸ Achieving high stereoselectivity is also an important factor for the commercial viability of the cascade from CO₂ to sugars. Research on the use of stereospecific ligands to increase the yield of D-glucose in the formose reaction has been reported.^{188,190} In addition, few studies have explored the conversion of CO₂ to methanol followed by cell-free enzymatic pathways to synthesize D-glucose or starch (Figure 6).^{187,190} Recently, a hybrid electrochemical/biotic reaction platform was developed to convert CO₂ to acetic acid followed by reaction with engineered *S. cerevisiae* to glucose at 8.9 μmol/g yeast per hour.¹⁹²

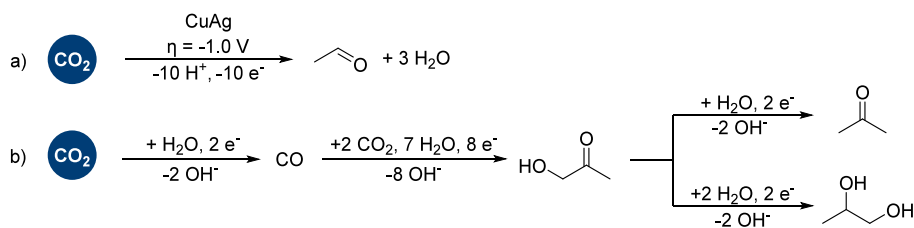


Figure 7. Reaction scheme for (a) the electrochemical production of acetaldehyde from CO_2 and (b) the production of acetone and 1,2-propanediol from carbon dioxide. Figure adapted with permission from ref 214 (Copyright 2023 American Chemical Society) and ref 213 (Copyright 2023 American Chemical Society).

2.5. Aldehydes and Ketones. Ketones and aldehydes have applications across the industrial landscape due to the ubiquity of the carbonyl ($\text{C} = \text{O}$) group among product classes. Research on CO_2 conversion to aldehydes and ketones has focused on thermal hydrogenation,¹⁹³ photocatalysis,¹ biochemical transformations,¹⁹⁴ and electrocatalysis.¹⁹⁵ Seminal studies on electrochemical CO_2 reduction have suggested that Cu is the only monometallic electrode material that can convert CO_2 into hydrocarbons and multicarbon oxygenates, an assertion that still holds true three decades later.^{196–198} CO_2 to aldehyde/ketone pathways continue to be plagued by unwanted cascading reactions due to $\text{C} = \text{O}$ reactivity.¹⁹⁵ This results in wide product distributions and low selectivity.¹⁹⁵ To combat this challenge, research is focused on the development of novel alternative materials that can exclusively produce the desired carbonyl-containing compound, such as formaldehyde,¹⁹⁹ acetone, or glycolaldehyde.²⁰⁰

Formaldehyde is the smallest aldehyde and serves as both a preservative and a precursor for resins in plastic production.¹⁹⁹ As the only C_1 aldehyde or ketone in existence, formaldehyde does not involve the challenging $\text{C}-\text{C}$ coupling reactions that are required to produce larger aldehydes and ketones, resulting in its prevalence in literature. Early research on electrochemical formaldehyde production from CO_2 found boron-doped diamond (BDD) electrodes effective, capable of achieving a Faradaic efficiency (FE) of 62% in a 0.1 M NaCl electrolyte solution, and an FE of 74% in CO_2 -saturated methanol.²⁰¹ However, BDD electrodes are expensive and made under extreme conditions.²⁰⁰ More recently, researchers have leveraged the known reduction abilities of Cu²⁰² as well as its relative accessibility to integrate into photoelectrochemical (PEC) regimes to selectively target products requiring more than two electron transfers.²⁰³ The use of a Cu electrode has been shown to improve formaldehyde FE to 85.1% in a system equipped with a (040)-faceted BiVO_4 photoanode and -0.9 V overpotential.²⁰⁴ Unique technical combinations can enable drastic enhancements in performance, so different PEC configurations may soon be pivotal in tackling deficiencies in current CO_2 reduction methods.

While much scholarship on formaldehyde production from CO_2 utilizes electrochemistry, novel research pathways have explored the use of unique thermo-, biochemical, and catalytic systems. Rather, these processes take inspiration from biological systems and photosynthetic transformations to create high-value chemicals. Photochemical reduction of CO_2 to formaldehyde tends to incorporate cobalt nanomaterial-based semiconductor cocatalysts on photoactive titania supports due to the relatively small band gap of Co as well as its ability to efficiently absorb visible light.^{205–207} In particular, 90.8% selectivity toward formaldehyde from CO_2 was found to result from the use of 1 wt % Co-oxide embedded

within tunnel-structured potassium titanates ($\text{K}_2\text{Ti}_6\text{O}_{13}$) exposed to 40 W broadband visible light irradiation (290–900 nm) at ambient temperature and pressure.²⁰⁵ Furthermore, the use of immobilized enzymes²⁰⁸ and microbes²⁰⁹ on metallic surfaces have been explored, finding that formate dehydrogenase and formaldehyde dehydrogenase in tandem with mercaptopropyl-functionalized mesostructured cellular foams produced $24 \mu\text{mol/g}_{\text{cat}}$ of formaldehyde in 1 h (37 °C, 0.5 MPa).²⁰⁸ These nonelectrochemical pathways serve as proposed low-energy alternatives to sustainable aldehyde and ketone production.

Simpler strategies are modeled after current industrial reactor setups that use heat and metal catalysts for C_1 production. The direct hydrogenation of CO_2 in liquid methanol was found to selectively produce formaldehyde with Pt–Ni bimetallic catalyst at room temperature with 7 MPa of 16:1 $\text{H}_2:\text{CO}_2$ gas.¹⁹³ While 100% selectivity toward formaldehyde remains a noble goal, overall product yields remain low ($1.8 \text{ mM/g}_{\text{cat}}$) for this reaction.¹⁹³ More recently, a Ru-nanostructured catalyst (0.5 wt %) anchored on reduced layered double hydroxide was reported to increase CO_2 reduction activity to formaldehyde 200-fold.²¹⁰ This process utilized a 1:1 $\text{H}_2:\text{CO}_2$ mixture (2 MPa) at 30 °C in DI water to produce formaldehyde with a maximum yield of 58.7%.²¹⁰

As the size of the desired aldehyde increases, the process necessitates more electrons and CO_2 molecules. In addition to benefits of Cu to electrochemically produce formaldehyde, the need for additional electron transfer, the more energetically taxing $\text{C}-\text{C}$ bond formation required for acetaldehyde production,²¹¹ and the unregulated oxophilicity of Cu all contribute to decreased acetaldehyde FEs.²¹² To attempt to mitigate this effect, researchers developed a bimetallic CuAg electrode which showed a maximum acetaldehyde FE of $\sim 14\%$ at 20% Ag concentration (Figure 7a).²¹³ This electrode also increased the FE for the production of other aldehydes, including glyoxal and propionaldehyde, bringing the total FE for this functional group to 20%, a 4-fold increase compared to monometallic Cu.²¹³

Furthermore, glyoxal represents an interesting C_2 dialdehyde product often consumed as an intermediate²¹⁵ with a high energy storage capacity of 143 kJ/C.¹⁹⁵ Unfortunately, due to its consumption as an intermediate, reported FEs are typically less than 1%.¹⁹⁵ Despite low glyoxal yields, Cu-based catalysts have proven to be effective in suppressing the parasitic hydrogen evolution reaction (HER) and increasing selectivity toward C_2 products.¹⁹⁵

To convert CO_2 into ketones such as acetone, more energetically costly $\text{C}-\text{C}$ bond couplings must occur (Figure 7b). Mechanistic investigations have determined that acetone and hydroxyacetone formation over Cu surfaces is most likely dependent on CO-glycolaldehyde/glyoxal coupling.²¹⁴ Re-

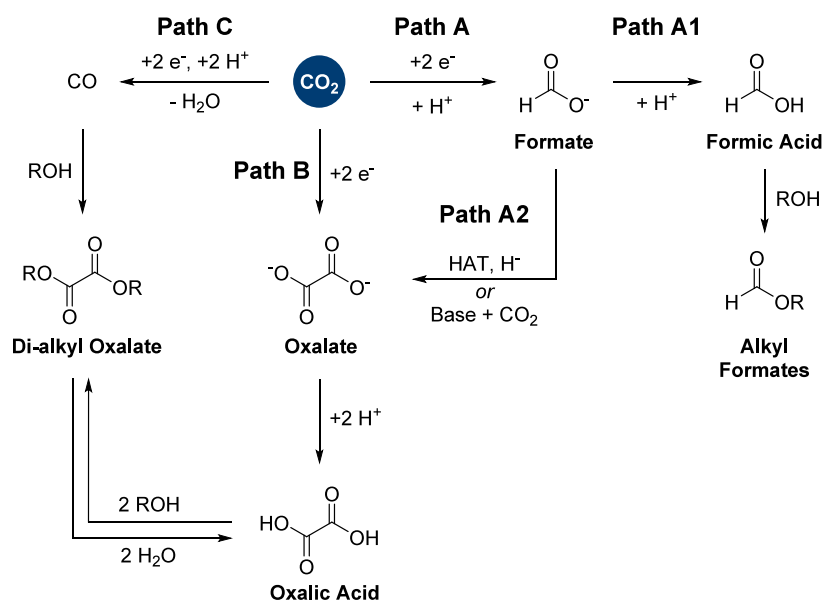


Figure 8. Complementary pathways to formic acid (Path A1) and oxalic acid from direct (Path B) and indirect (Paths C and A2) CO₂ conversion. HAT – hydrogen atom transfer.

searchers employed a Cu mesh electrode alongside a 0.1 M KHCO₃ electrolyte to tune the reduction activity, finding hydroxyacetone as a minor product (<0.1% FE), that increased to ~2.2 μmol per Coulomb with the addition of CO to the reaction, indicating CO–CO coupling limitations.²¹⁴ Further advancements utilizing single-atom Cu catalysts dispersed on N-doped carbon substrates resulted in acetone as the major product, boasting a 36.7% FE.²¹¹ This result was attributed to stabilizing effects induced by Cu-pyrrolic metal–support active sites.²¹¹ The broad array of uses for aldehydes and ketones necessitates further research to refine the electrocatalytic reduction of CO₂ to acetone and other, larger ketones, particularly methyl ethyl ketone and multiple pentanedione isomers recently detected in electrochemical flow cells.²¹⁶

2.6. Acids, Esters, and Acetates. The reduction of CO₂ to acids and esters is one of the widest studied CO₂ transformations.²¹⁷ While there are a plethora of methods that incorporate CO₂ into larger organic molecules,^{39,217,218} especially salicylic acid,²¹⁹ there are also several acids and esters that can be formed exclusively from CO₂ including acetate,²²⁰ acetic acid,^{221,222} and formate.^{223,224} The most ubiquitous of these is formic acid, wherein the reversible reaction of 1 equiv of CO₂ + 2e⁻ + 2H⁺ also serves to make formic acid a suitable carbon-neutral hydrogen storage and production source.²²⁵ The key pathway to formic acid and its alkyl esters (Figure 8, Path A1) first involves the reduction of CO₂ to formate, which is most often realized electrochemically,^{224,226–228} but thermal²²⁹ and photochemical^{230,231} methods have also been reported. Formate ions can then be further protonated to formic acid and esterified to alkyl formates. Recently, formic acid production from CO₂ in flue gas has been demonstrated in a pilot plant at 82% yield and 92 wt % purity at a scale of 10 kg per day.²³² In the study, the authors found that production costs could be reduced by 37% and the global warming potential reduced by 42% when compared to conventional formic acid (\$\$) production.²³²

Oxalic acid (overall: 2 equiv of CO₂ + 2e⁻ + 2H⁺) is an important chemical in cleaning applications but there is growing interest for its use as a C₂ building block.²³³ There are

3 potential pathways from CO₂ to oxalic acid; a direct route via direct reduction of CO₂ (Figure 8, Path B), most often achieved electrochemically, which proceeds via the coupling of 2 equiv of the CO₂^{•-} radical anion,^{234,235} or by two indirect routes via formate²³⁶ or oxidative carbonylation of CO²³⁷ (Figure 8, Path A2 or C, respectively). The transformation of formate to oxalate dates back to 1882 and often requires elevated temperatures and anaerobic conditions. More recently, focus has switched to the use of carbonite dianions (generated via hydride²³⁸ or a base^{233,239}) as strong nucleophiles which can then react with formate or CO₂ to yield the desired oxalate which is subsequently acidified to oxalic acid.

2.7. Carbonates. Carbonates, both inorganic and organic, serve as valuable building blocks for industrial applications and as a key component of carbon sequestration strategies. Inorganic carbonates including CaCO₃,²⁴⁰ MgCO₃,²⁴¹ and Na₂CO₃²⁴² are traditionally synthesized through thermochemical mineral carbonation, precipitation, or injection into geologic formations with the use of metal oxides or hydroxides.^{243–246} Mineral carbonation is a common industrial route that reacts CO₂ with a metal hydroxide such as Ca(OH)₂ or Mg(OH)₂, resulting in precipitation of metal carbonates.²⁴⁷ The most well-known example of this are cement based materials (CBM).²⁴⁸ Sodium carbonate (Na₂CO₃), also known as soda ash, is an important glass and detergent precursor produced through the Solvay process, wherein CO₂ is reacted with sodium chloride and ammonia in the presence of limestone, resulting in the precipitation of Na₂CO₃.^{249,250} Sodium bicarbonate (NaHCO₃), on the other hand, can be synthesized through the reaction of sodium carbonate with additional CO₂ for use as an antacid, as baking soda, and for water treatment purposes.²⁴³ Carbonates of potassium,²⁵¹ lithium,²⁵² and barium^{253,254} are produced through similar processes that involve the reaction of CO₂ with their respective metal hydroxides or oxides, and find use as fertilizers, drying agents, batteries, pharmaceuticals (mood stabilizers), and other applications.^{243,252,255,256}

Organic carbonates are typically produced through oxidative carbonylation processes both thermochemically²⁵⁷ and electrochemically.^{258–261} Two organic carbonates that have been demonstrated from transformation of CO₂ are dimethyl- and diethyl carbonate (DMC, DEC), which represent economically valuable and versatile molecules for use as solvents or methylation agents to replace highly toxic phosgene.^{259,262} Both DMC and DEC have been synthesized from CO₂ with the respective alcohols in a range of different ways that include alkali metal alkoxides or catalytic organic bases.²⁶³ One of the most promising pathways is the nonreductive transformation with the respective alcohol in the presence of a metal oxide catalyst, such as CeO₂ (Figure 9).²⁶⁴ These thermochemical

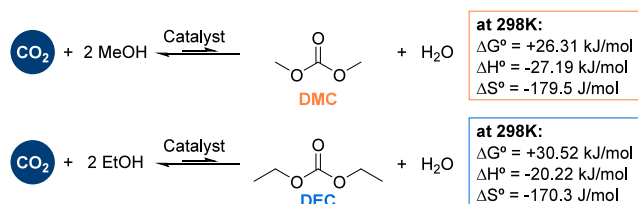


Figure 9. Reaction schemes for the conversion of CO₂ to (a) dimethyl carbonate (DMC) and (b) diethyl carbonate (DEC). Figure adapted with permission from ref 257. Copyright 2022 American Chemical Society.

reactions typically require temperatures between 80–160 °C and 5–20 MPa pressure.²⁶⁴ CeO₂-based catalysts have been reported to reach up to 92.4% methanol conversion with 99% DMC selectivity,²⁶⁴ whereas the use of choline hydroxide as a base catalyst resulted in only 0.6% methanol conversion, despite a high (95.2%) selectivity toward DMC.²⁶⁵ One limitation of these reactions is that the reaction equilibrium lies in favor of the starting alcohol and CO₂, as the water produced as a byproduct reacts in the presence of a catalyst to decompose the dialkyl carbonate. Often to facilitate a high conversion, such as seen with CeO₂, the addition of a dehydrating agent is required to shift the equilibrium in the favor of desired dialkyl carbonate.^{257,261,264} Although in the early stages, DMC and DEC can also be synthesized through redox-neutral electrochemical conversion,²⁶¹ where DMC can be produced from CO₂ and MeOH with up to 60% FE utilizing a Pd/C catalyst, gold cathode, and NaBr supporting electrolyte.²⁶¹

Cyclic carbonates are the thermodynamic products of the cycloaddition of epoxides (usually not CO₂-derived) with CO₂ in the presence of a catalyst, such as metal complexes or organic bases.^{266,267} ϵ -caprolactone is a cyclic carbonate with biomedical applications that has been demonstrated to undergo rapid polymerization to poly(carbonate-block-ester) in the presence of CO₂ and cyclohexene oxide as an epoxide with a Zn-based catalyst.²⁶⁸ Diaryl carbonates have also been synthesized through the oxidative carbonylation of phenols with CO or CO₂,^{269,270} and the resulting diphenyl carbonates can be employed as monomers for polycarbonate synthesis, as demonstrated in the Asahi Kasei process.^{269,271} More recently, a novel method was reported to synthesize polycarbonates directly from CO₂ and diols, using a CeO₂ catalyst and a sacrificial dehydrating agent (i.e., 2-furonitrile).²⁷²

The reaction of epoxides with CO₂ can also lead to polymeric carbonate products in a reaction typically involving the rate-limiting ring-opening of the epoxide with the addition

of a metal catalyst before CO₂ is inserted into the metal-alkoxy bond.^{273–275} While industrial developments have primarily focused on propylene and ethylene oxide as epoxide sources due to their prevalence in plastic manufacturing,²⁷⁶ natural epoxides, such as limonene oxide (Figure 10), can also be

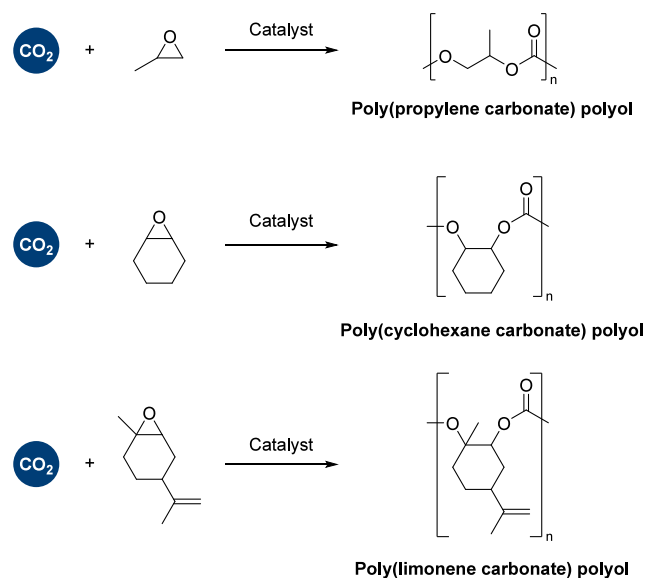


Figure 10. Representative synthesis pathways of polycarbonates (a) poly(propylene carbonate), (b) poly(cyclohexane carbonate), and (c) poly(limonene carbonate) from CO₂ and epoxides.

effectively polymerized.²⁷⁷ Research into polyethercarbonates from CO₂ has revealed double metal cyanides and dinuclear Zn-complexes as effective catalysts, resulting in maximum CO₂ incorporation at 43 wt %.²⁷⁶ Technologies for CO₂-based polyols have been developed at the kiloton scale by Novomer (later sold to Saudi Aramco),²⁷⁸ Covestro,²⁷⁹ and Eonic Technologies. A life cycle assessment (LCA), completed by Covestro, reported that a 19% reduction in greenhouse emissions can be achieved through the substitution of petroleum-based polyols with CO₂-based polyols.²⁸⁰

2.8. Nontransformative Utilization. While CO₂ transformations via chemical reactions offer an alternative to sequestration, nontransformative use of CO₂ (Figure 11) has the potential to realize chemical and economic benefits on its

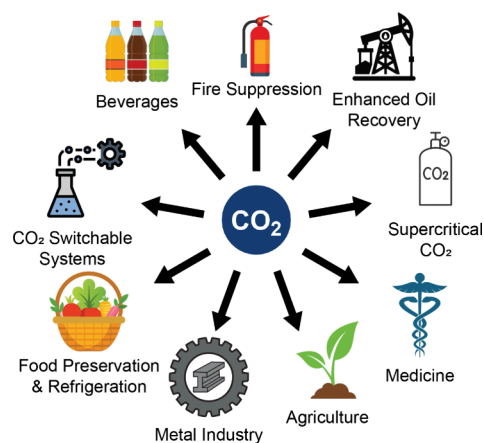


Figure 11. Schematic highlighting the breadth of uses for non-transformative use of carbon dioxide. Copyright Adobe Stock.

own across sectors. The climate change benefits of non-transformative use are reduced compared to transformative pathways, especially in the case of fossil-based CO₂, however, nonfossil CO₂ can still have a positive impact when used in the following ways. The International Energy Agency (IEA) reports ~230 million tonnes (Mt) of CO₂ as gas, liquid, dry ice, and even in its supercritical form,²⁸¹ are already used every year across industries,²⁸² such as beverage and food processing, fire suppression, urea manufacturing, enhanced oil recovery (EOR), metal fabrication, and in agriculture for stimulation of plant growth or pest control.^{33,281–284} Further, CO₂ is utilized in medicine,^{285–287} electricity-generating turbines,²⁸⁸ and in its supercritical form as an efficient and versatile green solvent.²⁸⁹

Carbon dioxide's accessible critical point (31 °C, 7.4 MPa) and significant physical property (temperature, density) tunability around the critical point make it advantageous to deploy as a supercritical fluid, both as a solvent and as a working fluid for power generation.^{290–293} Supercritical fluid extraction (SFE) technology utilizes CO₂ as a nontoxic solvent for extracting flavors and essential oils or decaffeinating coffee, that offers additional benefits including improved permeability, tunable extraction capabilities, and reusability.²⁸⁹ By altering the temperature and pressure of CO₂, the density and subsequent solvent polarity varies drastically, which can result in enhanced selectivity. This key feature of SFE has been applied in biorefineries, including the sequential extraction of triglycerides at lower density and polarity (642 mg/mL) followed by xanthophyll at higher density and polarity (971 mg/mL).²⁹⁴ The application of supercritical CO₂ as solvent for chemical reactions under continuous-flow operation is receiving significant interest²⁹⁵ and its practical implementation has been demonstrated on a technical scale.²⁹⁶ Supercritical CO₂ is beneficial for use in power generation turbines due to its density, which is nearly twice as dense as steam.²⁸⁸ This, in turn, leads to thermal efficiency improvements greater than 10% and a 10x reduction in the required physical footprint of CO₂ turbines compared to steam turbines.²⁹⁷

The food and beverage industry utilizes 11 Mt/yr²⁸³ of food-grade CO₂ (99.9% v/v purity) to produce carbonated drinks, deoxygenated water, and milk products, as well as in food preservation.²⁸³ To enhance product longevity, CO₂ acts as a highly efficient inert shield during food production, capable of displacing air in the canning process to enhance product longevity.²⁹⁸ CO₂ is also used as dry ice to keep food items cool during transportation²¹⁷ as well as to facilitate rapid freezing.^{33,281}

In medicine, medical-grade CO₂ (>99.5% v/v purity²⁹⁹) has been employed as a therapeutic treatment for more than a century, owing to its antioxidative and anti-inflammatory attributes, as well as its broad-spectrum virucidal and antimicrobial efficacy.²⁸⁷ A recent study even discussed the potential for moist, warm CO₂ around the temperature and humidity of human lungs, as an effective viral inactivation treatment for the SARS-CoV-2 virus.²⁸⁷ CO₂ has also been used in carboxytherapy as a direct injection or bolus injection into differing layers of the skin to address skin irregularities by reacting with intracellular water to form carbonic acid and release oxygen.²⁸⁵ Additionally, it has been shown effective as a contrast agent in diagnostic procedures such as cavography, arteriography, and venography due to its lack of renal toxicity and anaphylactic response.²⁸⁶

Enhanced oil recovery is a process that injects CO₂ as a miscible flooding agent to increase crude oil recovery from

depleted conventional or shale oil wells by decreasing the viscosity of the oil for easier extraction and as a displacement agent.²⁸⁴ This technology has been used for decades for improving oil recovery and estimates suggest that up to 5% of total US crude oil is produced using the CO₂-EOR process.²⁸⁴ While traditionally, maximum oil and CO₂ recovery has been the goal, "EOR+" is emerging as a coexploitation method to further increase oil recovery while sequestering CO₂ underground.^{284,300} However, without direct CO₂ capture and with the advance of other carbon conversion and storage solutions, its benefits are dubious at best and can lead to a net increase in CO₂ emissions.²⁸⁴

In chemical process applications, CO₂ can also be used to tune the properties of appropriately designed solvents and materials to facilitate separation and purification processes.^{291,301} For example, CO₂ reacts reversibly with amine-functionalized solvents to form carbonate and bicarbonate salts, which can be phase-separated by sharply switching polarity.³⁰² In catalysis, the reversible hydrogenation of CO₂ to formic acid and formate species has been exploited to develop adaptive catalytic systems³⁰³ which reactivity can be controlled in a reversible, rapid, and robust manner simply by switching the feed gas composition from pure H₂ to a mixture of H₂ and CO₂. For example, Ru nanoparticles immobilized on amine- and guanidine-functionalized support materials catalyzed the full hydrogenation of furanic ketones and bicyclic heteroaromatics under H₂, and their partial hydrogenation under H₂+CO₂.^{304–306} For CO₂-responsive materials and catalysts, CO₂ is not converted into value-added chemicals but serves as an environmentally benign molecular trigger to control physicochemical properties and catalytic performance in a reversible manner, and is thus released at the end of the process. However, such approaches using recycled greenhouse gas have the potential to provide significant benefits in terms of energy and process efficiency, thereby decreasing greenhouse gas emissions.

3. OUTLOOK AND CONCLUSIONS

The CO₂ Tree is a representation of current approaches and future potential to exploit carbon dioxide as a raw material for valuable products and molecular building blocks or for other chemical functions. This is often discussed in the context of the necessary phase-out of fossil-based feedstocks that are the current basis of the chemical industry. By virtue of being a thermodynamically stable molecule, there will always be a cheap and plentiful supply of carbon dioxide to use as the basis of a future chemical industry to serve the needs of an ever-growing human population. Knowing how to use and transform this molecule both efficiently from a chemical perspective, and effectively from a broader systems perspective will be essential to the sustainability and resiliency of a closed anthropogenic carbon cycle. In other words, CO₂ utilization offers the potential to "harvest" renewable energy into the material world.

The various branches and products found on the CO₂ Tree vary widely in terms of when and how they can be expected to be commercially relevant at scale.^{246,307–310} The multitude of relevant factors that impact the pace and magnitude of the commercialization process go far beyond the chemistry and engineering processes and include matters of government policy, geopolitics, investment trends, business environment, and industrial inertia.

The classical technology readiness levels (TRLs) of a process are used to assess the maturity of a particular technology on a nine point scale based on certain parameters.³¹¹ At the early stage, a TRL of 1 indicates that scientific research is just beginning, whereas a TRL of 9 corresponds to a process that has been “proven” through successful large-scale operation.^{310,311} While technology readiness levels are of greatest use for individual companies and of more limited utility accounting for all of the circumstances that influence the scaling of technology on an economy-wide application, it is useful as a snapshot of the current situation. In this way, Figure 12 highlights the range of TRLs reported for

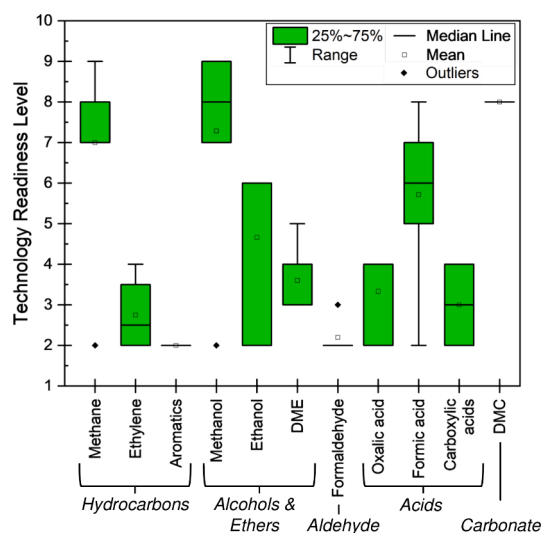


Figure 12. Technology readiness level (TRL) ranges and averages for the conversion of CO₂ to select products across chemical classes. Figure adapted with permission from ref 246 (Copyright 2020 Wiley-VCH GmbH), ref 307 [Copyright 2023 American Chemical Society], ref 308 (2020 Elsevier B.V.), ref 309 (Copyright 2020 Royal Society of Chemistry), and ref 310 (Copyright 2024 Elsevier B.V.).

varying CO₂ conversion technologies for 11 chemicals or chemical classes included in the CO₂ Tree.^{246,307–310} Technologies for methane, methanol, and DMC production from CO₂ all result in an average TRL > 7. On the other hand, some chemicals, such as DME, remain at low TRL (~4) due to the prevalence of the methanol dehydration pathway over the direct CO₂ hydrogenation route.^{312,313} Poly(oxyethylene) ethers (OME_n) similar to DME result in TRLs at or below 4,^{132–134} indicating the need for further scale-up and optimization—and/or enabling social, political, and economic conditions—to realize commercialization. In general, polymer production processes using CO₂ as building blocks have also reached TRL levels >7. Within the chemical classes, alcohols and ethers, followed by acids, esters, and acetates have the highest average technology readiness levels.

It is imperative that proposed CO₂ utilization pathways balance potential CO₂ offsets with the energy and chemical requirements necessary for its transformation. For example, the conversion of CO₂ to carbon materials (e.g., graphene) currently requires extreme temperatures and pressures, possibly leading to more CO₂ emitted than utilized as feedstock. And while methane from CO₂ boasts an average TRL of 7, this process is currently based on the use of solid oxide electrolysis cells operating at around 800 °C using rare metal catalysts such as iridium (Earth crustal abundance =

0.000037 ppm).³¹⁴ Here, methanation converts CO₂ and H₂ into natural gas at lower exergy and economic value. While it may help to temporarily store renewable electricity in a practical energy carrier, the hydrogenation of CO₂ to lower reduction levels (i.e., further to the right on the CO₂ tree, Figure 1) such as methanol, formaldehyde, or syngas would seem more attractive for subsequent chemical use of CO₂. To truly embody the principles of green chemistry, future research in this area must prioritize transformation pathways with low energy inputs, the use of abundant, low-cost reagents and catalysts, and those that achieve high atom economy to prevent additional waste generation.

As important as it is to reflect on those current transformations that can be realized in the near term, it remains critically important to develop new approaches to scaling the emerging transformations discussed throughout this review. This will require a diversity of approaches and may include a mix of process-intensified systems, modular systems, flow systems, distributed processes, or integrated systems. As *in silico* screening of catalysts becomes more powerful and algorithm-based mining of experimental and computational data shows its potential, moving from analytical to predictive for the design of fully catalytic systems may come into reach. The linear scale of the TRL concept is not fully capable of mapping out such intertwined innovation cycles and “out-of-the-box” leapfrog innovations. Therefore, its application as a framework for public funding in research and development should be critically challenged to avoid lock-in effects in mainstream developments. The innovation in the thinking required to exploit the necessary discoveries covered in this paper goes beyond the fundamental chemistry to include not only engineering design and plant operation, but also the relevant enabling policies and economic environments to make this necessary transformation viable.

While a review of any scientific or technological advance will, of necessity, be a snapshot in time, in the case of CO₂ utilization this is even more exaggerated due to the extremely dynamic nature of the field. This review explicitly focused on the direct products and applications of CO₂ itself; however, as we imagine the future importance of CO₂ as a feedstock it will necessarily include derivative products where CO₂ further reacts with products obtained from CO₂ transformations. This includes explicitly building blocks from biomass where nature has already upgraded CO₂ with the help of renewable energy. This cascade multiplies as we envision the array of products from the “air refinery” where products from nitrogen and water vapor combine with the products of CO₂ to realize the vast majority of current organic products as well as many yet to be conceived. What the CO₂ Tree portrays is an image of what is possible and has been demonstrated today that was often viewed as impractical or impossible by many people in the past. The difference between possible versus impossible is infinite while the progression up the optimization ladder is incremental. In addition to meeting the imperative of phasing out of fossil carbon, the work of CO₂ utilization is essentially a driver of innovation to create new molecules, new transformations, new functionality, and new performance for the future. Like all wise innovation, it is not simply about improving on the flaws of the old but creating the excellence of the new. While recognizing that challenges are real, Nelson Mandela observed, “It always seems impossible until it is done.”

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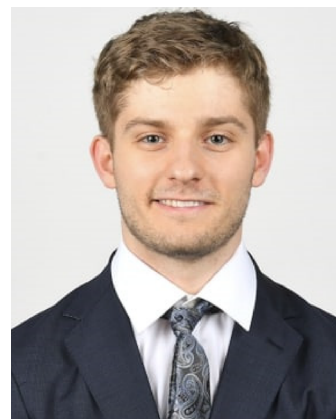


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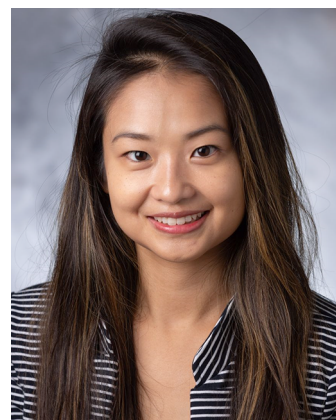
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