Challenges and Opportunities in Converting CO_2 to Carbohydrates

Casey P. O'Brien,* Madelynn J. Watson, Alexander W. Dowling

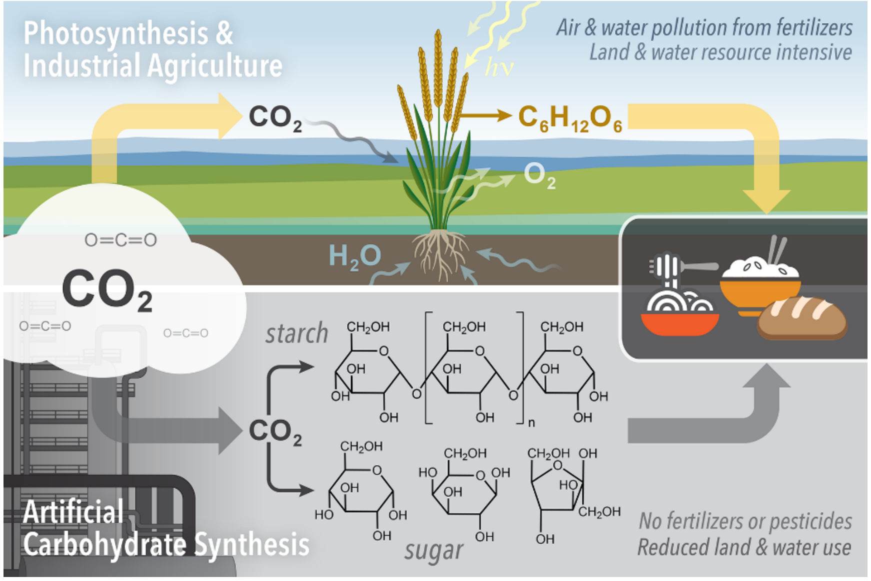
Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA

*Corresponding Author Email Address: cobrie23@nd.edu

Abstract

The agriculture industry relies on biogenic photosynthesis to meet world demands for carbohydrates that are used for food and consumer products. However, this biogenic approach requires extensive land and water resources, produces significant greenhouse gas (GHG) emissions, and pollutes freshwater sources with excess nitrogen fertilizers. As the global population increases, the demand for carbohydrates will surpass what biogenic photosynthesis can supply, and negative environmental impacts will be exacerbated. In principle, edible carbohydrates could be synthesized artificially from CO_2. Compared to the current biogenic approach, artificial carbohydrate synthesis from CO_2 has significantly lower GHG emissions, reduced freshwater requirements, a smaller physical footprint, and no need for fertilizers or pesticides. Converting CO_2 to edible carbohydrates is a significant challenge, however, because of the high thermodynamic stability of CO_2, the high complexity of carbohydrates, and the required scale of such a process. This Perspective examines these challenges, and identifies opportunities for scientific innovation to enable commercially-viable artificial carbohydrate synthesis from CO_2 at gigaton-per-year scales.

TOC Graphic


Photosynthesis & Industrial Agriculture
Air & water pollution from fertilizers
Land & water resource intensive
hv
CO2
C6H12O6
O2
H2O
O=C=O
CO2
O=C=O
O=C=O
starch
CH2OH
O
OH
OH
OH
n
CO2
sugar
HO
CH2OH
No fertilizers or pesticides
Reduced land & water use
Artificial Carbohydrate Synthesis

The emission of anthropogenic greenhouse gases (GHGs) has increased steadily since the Industrial Revolution, primarily from the excessive extraction and use of fossil fuels, increasing the concentration of CO_2 in the atmosphere from the pre-industrial value of ~280 ppm to the current value of ~420 ppm.[1] Consequently, the global surface temperature has increased by at least 1.1 °C compared to pre-industrial levels.[2] The Paris Agreement set a goal to limit the global temperature increase to well below 2 °C and preferably below 1.5 °C compared to pre-industrial temperatures.[3] Utilizing renewable energy sources is probably the best route to solving the GHG emissions problem in the long term. However, achieving 100% renewable energy is not feasible in the near term and fossil fuels will continue to be a significant energy carrier for decades.[4] Limiting global warming to less than 2 °C will therefore require the development of carbon capture, utilization, and storage technologies that remove tens of gigatons of CO_2 per year ($GtCO_2$/y) from the air and either utilize it or store it permanently.[5,6]

While carbon capture and storage (CCS) in geological formations or in oceans will likely be required to prevent greater than 2 °C global warming,[6] there are significant concerns regarding the feasibility of CCS,[7] the possibility of leakage,[8] increasing ocean acidity,[9] and the high cost (greater than $1 trillion annually[9]). Utilizing the captured CO_2 to create a revenue stream may be a better alternative to CCS. CO_2 can be used directly for a variety of applications (drink carbonation, enhanced oil recovery), or used as a renewable feedstock to produce valuable products such as fuels, chemicals, and even potentially food (carbohydrates).[10-12] The main challenge of carbon capture and utilization (CCU) is the sheer magnitude of the task in both the physical capacity and cost. For example, it is estimated that ~10 Gt of CO_2 must be removed from the air *every year* to prevent 2 °C global warming (by 2050),[5] yet there are few products with a global market at the Gt/y level. In fact, liquid fuels (~2 Gt/y currently[13]) and cereal grains (~3 to 4

Gt/y of corn, wheat, and rice[14,15]) are the only carbon-based products that are currently produced at the Gt/y levels. In other words, the only two applications of CCU that could scale to the necessary Gt/y levels are liquid fuels production and artificial food production.

This Perspective focuses on artificial synthesis of carbohydrates from CO_2 to supplement or replace industrial agriculture for starch and sugar production *at Gt/y scales*. Artificial carbohydrate synthesis from CO_2 could mitigate the substantial environmental impacts associated with industrial agriculture and simultaneously mitigate water and food scarcity in underdeveloped nations. It could also be used as a food and life support system in isolated bunkers to reduce existential risk in the event of a global agricultural catastrophe, such as super volcanic eruptions, climate change, or nuclear winter.[16]

The Environmental Impacts of Industrial Agriculture. The industrialization of food production over the past century has enabled the world population to grow from ~1.6 billion in 1900 to nearly 8 billion currently.[17] Much of the increase in the food productivity over the past century is attributed to the excessive use of fertilizers, which are responsible for ~10 to 37% of global GHG emissions (~5 to 20 $GtCO_2eq/y$),[15,18-21] depending on where boundaries are drawn, and ~78% of water pollution from eutrophication.[19] Industrial agriculture is also resource intensive, using ~38 to 43% of global habitable land (~1.5 billion hectares for cropland and ~3.4 billion hectares for grazing land)[19,22] and ~70% of global freshwater supplies.[19] A 2015 report[23] by the Food and Agriculture Organization of the United Nations estimated that the environmental costs (natural capital) of industrialized crop production are currently ~$1.15 trillion per year, which is 170% of the production value of the crops. Furthermore, there is a gross inequality in the access to food across the globe with nearly one billion people underfed in developing countries.[22,24,25]

The global demand for food is expected to increase by 50 to 100% by the end of the century due to combination of the increase in the global population to 10 to 12 billion by the end of the century, and the increase in per-capita food consumption.[26] At the same time, climate change will reduce crop yields, which will exacerbate food insecurity and lead to more malnutrition globally.[27] As most uncultivated land plays important ecological roles, there are few prospects to expand the 1.5 billion hectares of cropland currently under cultivation. Thus, another crisis in addition to managing GHG emissions is feeding the growing population without further destroying the environment. This will require radically different approaches to how we produce food, including potentially artificial food production.[28]

ARTIFICIAL CARBOHYDRATE SYNTHESIS: PRACTICAL ASPECTS

Carbohydrates (starch and sugar) are the main energy source for humans, making up ~50 to 70% of human caloric needs.[29] Currently, humans get carbohydrates from staple foods such as wheat, corn, rice, potatoes, fruits and vegetables, which synthesize starch and sugar using CO_2, water, and sunlight (photosynthesis). Because of the high complexity of photosynthesis, which involves over 60 steps,[12] the energy efficiency of photosynthesis is very low. The *theoretical maximum* energy efficiency (solar energy to carbohydrates) of photosynthesis is only 4.6% for C3 plants (e.g. wheat, rice) or 6.0% for C4 plants (e.g. corn, sugarcane).[30] However, the global average efficiency of biogenic photosynthesis is actually much lower (less than 1%[31]) because the conditions (sunlight, water, and temperature) that are optimal for photosynthesis are rarely satisfied. Consequently, vast land areas, as well as large amounts of fertilizers and water, are required to produce the Gt/y of carbohydrates that are necessary to feed the global population.

In principle, starch and sugar could be produced artificially from CO_2 with greater efficiency and with much lower environmental impacts than industrial agriculture.[10-12] For example, Cai et al.[12] estimated that the theoretical maximum solar-to-starch efficiency for artificial synthesis of starch from CO_2 (~9%) is ~1.5 to 2 times greater than the maximum theoretical efficiency of biogenic photosynthesis (~4.6 to 6.0%[30]). Dinger and Platt[10] also estimated that the theoretical solar-to-food efficiency of artificial sugar production from CO_2 (6 to 15%) is significantly greater than that of photosynthesis, and Garcia Martinez et al.[11] also concluded that a food production system based on glycerol is viable using existing technologies with efficiencies (electricity-to-food) of ~10 to 21%.

In addition to higher theoretical efficiency, artificial carbohydrate synthesis also does not require nitrogen fertilizers (or herbicides or pesticides), and therefore could mitigate tens of $GtCO_2eq/y$ of GHG emissions as well as mitigate water pollution from nitrogen fertilizers. Artificial carbohydrate synthesis also has a substantially reduced physical footprint compared to agriculture and thus could free up billions of hectares of land that is currently used for agriculture, and use that land for renewable energy generation (wind and solar farms) or for carbon capture (reforestation) to further mitigate GHG emissions. Most (~77%) of the land that is currently used for agriculture is used for livestock feed, including grazing land and land used for animal feed production, with the remaining ~23% used for crop production.[32] Artificial carbohydrate synthesis could be used for animal food production, but it would not eliminate the need for grazing land, a major drive of land usage. Artificial carbohydrate synthesis also has drastically reduced freshwater requirements compared to agriculture. While crop production requires about 1,300 to 1,600 Gt of water per Gt of crop produced for irrigation (Table 1),[31,33] artificial carbohydrate synthesis would in theory require less than 1 kg of water per kg of carbohydrate, although practical water requirements may be significantly greater than 1 kg in a mature artificial carbohydrate synthesis industry.[10]

Artificial carbohydrate synthesis could also address global food insecurity, which currently affects nearly one billion people worldwide[22,24,25] and "diminishes global economic productivity by 2% – 3% annually (USD 1.4 – 2.1 trillion), with individual country costs estimated at up to 10% of country GDP".[27] There are many different drivers of global food insecurity,[25] including fossil fuel prices, rising demand for food, climate change, natural resource (i.e. water, land) availability and degradation, trade markets, investments in agriculture (which have been declining for decades), and increasing biofuel production. Artificial carbohydrate synthesis would address most—but not all—of these drivers to potentially create a more secure global food system. For example, food prices (and hence food security) are currently tied to fossil fuel prices, but artificial carbohydrate synthesis powered by renewable electricity would require little, if any, fossil fuel inputs. Artificial carbohydrate synthesis also has reduced freshwater and land requirements, and is less sensitive to changes in global temperatures and CO_2 levels, than industrial agriculture. Artificial carbohydrate synthesis would also address the rising demand for food by increasing the food production capacity of the planet beyond what is possible by crop production. In developing countries that rely heavily on imported food, which is sensitive to global trade markets, artificial carbohydrate synthesis could potentially stabilize food prices and food security (depending on the stability of renewable electricity prices). A key driver of food insecurity, which artificial carbohydrate synthesis would not address, is the declining investments in agriculture over the past few decades. Substantial increases in funding for research and development will be required over the next several decades to deploy artificial carbohydrate synthesis industries at Gt/y scales.

Direct Comparison of Industrial Agriculture and Artificial Carbohydrate Synthesis. Table 1 summarizes several key metrics associated with industrial agriculture and artificial carbohydrate synthesis side-by-side for comparison: technology readiness level (TRL), energy intensity, GHG emissions intensity, water intensity, and land-use intensity. All of the metrics listed in Table 1, except the TRL, are given with the basis of producing 1 Gt of carbohydrate. The TRL of artificial carbohydrate synthesis is approximately 3 to 4, which represents characteristic proof-of-concept (TRL 3) or system validation in laboratory environment (TRL 4). Industrial agriculture, on the other hand, is at the highest TRL level of 9. Sample calculations for the values in Table 1 can be found in the Supporting Information (SI). For artificial carbohydrate synthesis, Table 1 reports the nominal case and **Figure 1** and **Figure S1** (in the SI) reports ranges computed via multivariable sensitivity analyses.

Table 1. Key metrics associated with industrial agriculture and artificial carbohydrate synthesis.

	Industrial Agriculture	**Artificial Carbohydrate Synthesis**
Technology Readiness Level (TRL)	9	3 to 4
Energy Intensity (TWh/Gt carbohydrate)	300 to 2,000	14,000
GHG Emissions Intensity (GtCO$_2$eq/Gt carb.)	2	-1.3
Land-use Intensity (million hectares/Gt carb.)	400	0.7
Water Intensity (GtH$_2$O/Gt carb.)	1,300 to 1,600	1

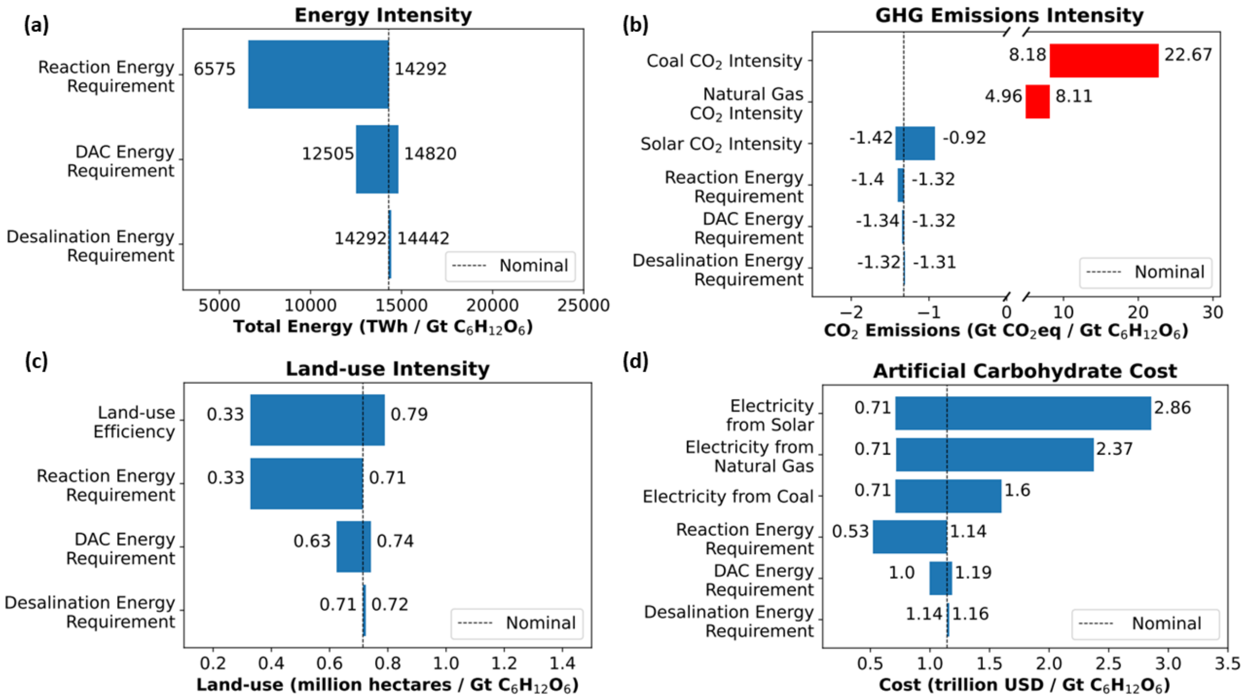


Figure 1. Tornado diagrams visualize the sensitivity of four system performance metrics – (a) energy intensity, (b) GHG emissions intensity, (c) land-use intensity, and (d) cost – with respect to single dimension perturbations of key input parameters: direct air capture (DAC) energy requirement (kJ/mol_{CO_2}), CO_2 intensity (gCO_2eq/kWh), land-use efficiency (m^2/GWh), reaction energy requirement (kJ/mol_{hexose}), desalination energy requirement (kJ/mol_{H_2O}), and electricity cost ($/MWh). For panels (b) and (d), CO_2 intensity and electricity cost are analyzed for three technologies: coal, natural gas, and solar. In each tornado diagram, the dashed line shows the nominal value (reported in Table 1, 1.15 trillion USD/Gt glucose of artificial carbohydrate cost). Each row shows how varying each input parameter between low and high values impacts the calculated metrics. In panel (b), the blue and red shading corresponds to net negative and net positive GHG emissions, respectively.

The energy intensity of industrial agriculture (~300-2,000 TWh/Gt) is derived from the energy used to produce crops in the United Kingdom, which was estimated by Woods et al.[34] to be ~1 to 6 GJ/t. This estimate includes both direct energy use (e.g., fuel for machinery) and indirect energy use for fertilizers, pesticides and machinery production. We estimate the energy intensity of artificial carbohydrate synthesis to be ~14,000 TWh/Gt using an extension of the analysis by Dinger and Platt[10] (see SI for sample calculations) that only considers direct energy use for water desalination, direct air capture (DAC), and total reaction chemistry. We did not account for indirect energy use for fertilizers or pesticides production because artificial carbohydrate synthesis does not require fertilizers or pesticides. We also did not account for indirect energy use for machinery production because we argue that it is insignificant compared to the direct energy use for water desalination, DAC, and the total reaction chemistry. Machinery production is a relatively minor contributor (~10-20%[34]) to overall energy use in industrial agriculture, and industrial agriculture requires a wide range of different machinery that would not be required in an artificial carbohydrate synthesis plant, such as machinery for planting, fertilization, pest management, irrigation, harvesting, and post-harvest storage. These calculations suggest artificial carbohydrate requires 7 to 50 times more human-input energy than industrial agriculture. This is because the energy intensity of industrial agriculture does not include the energy collected via photosynthesis, whereas the artificial carbohydrate synthesis analysis includes electrical energy inputs, which would likely come from photovoltaic (PV) solar. For reference, the total global energy consumption in 2019 was about 170,000 TWh,[35] so producing 1 Gt/y of artificial carbohydrates from CO_2 would consume ~8% of the global energy use.

Figure 1(a) shows the sensitivity of the artificial carbohydrate energy intensity to three key input parameters: direct air capture (DAC) energy requirement for CO_2 feedstock, desalination energy requirement for water feedstock, and the reaction energy requirement. A wide range of DAC energy intensities are reported in literature. For example, Lackner[36] reported a DAC energy requirement of 50 kJ/mol_{CO_2} (300 kJ/mol_{hexose}) for their DAC design, Dinger and Platt[10] use a nominal value of 243 kJ/mol_{CO_2} (1458 kJ/mol_{hexose}) and state current DAC technologies are ~300 kJ/mol_{CO_2} (1800 kJ/mol_{hexose}), and Hong,[37] in their comparative analysis of DAC to other CO_2 removal technologies, report 254 kJ/mol_{CO_2} (1524 kJ/mol_{hexose}) for a DAC energy requirement. Based on this literature, we consider 50 kJ/mol_{CO_2} (300 kJ/mol_{hexose}) to 300 kJ/mol_{CO_2} (1800 kJ/mol$_{hexose}$). For water desalination energy input, we consider the optimistic case of stochiometric water consumption with a nominal energy requirement of 0.4 kJ/mol$_{H_2O}$ (2.4 kJ/mol$_{hexose}$).[10] To account for needing excess water or less efficient desalination, we consider an order of magnitude (10 times) increase in water desalination energy input. We choose such a wide range to illustrate the computed performance metrics are insensitive to water desalination energy. Dinger and Platt[10] estimate the nominal reaction energy requirement for the total chemistry (conversion to syngas, syngas to methanol, methanol to formaldehyde, and formaldehyde to hexose) to be 7863 kJ/mol$_{hexose}$ corresponding to a synthesis efficiency of 0.36 which accounts for reaction and energy inefficiencies of a "quasi-mature" technology. The total theoretical reaction energy required for hexose synthesis from CO_2 is calculated as the thermodynamic reaction energy, 2800 kJ/mol$_{hexose}$, representing the case of 1.0 synthesis efficiency. Based on these values from Dinger and Platt[10] we consider a range from 2800 kJ/mol$_{hexose}$ to 7863 kJ/mol$_{hexose}$. **Figure 1(a)** shows the reaction energy requirement has the greatest effect on the total energy suggesting reaction energy is the largest contributor to the overall energy consumed. This is not surprising given that carbohydrate synthesis from CO_2 is a highly endothermic process.[38] **Figure S1(a)** in the SI shows a two-dimensional sensitivity with respect to the reaction energy requirement and DAC energy requirement input parameters. Based on these results, we estimate that the electricity-to-carbohydrates efficiency, defined here as the efficiency of converting electrical energy to carbohydrate energy, is about 0.31 (see Supporting Information for calculations).

The total GHG emissions associated with crop production is estimated to be ~2 $GtCO_2eq$ per Gt of crop produced. This estimate is derived from the work of Xu et al.,[15] and includes GHG emissions associated with land-use change from cropland, GHG emissions from cropland (CO_2, CH_4, N_2O), and GHG emissions associated with manufacturing and transporting fertilizers and pesticides, but excludes GHG emissions associated with livestock and grazing land. The GHG emissions associated with artificial carbohydrate synthesis have not been evaluated to our knowledge. To first approximation, we estimate that the GHG emissions of artificial carbohydrate synthesis are about -1.3 GtCO_2eq per Gt of carbohydrate produced. This estimate is based on the stoichiometry of the reaction $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ (i.e., 6 moles of CO_2 are consumed to produce 1 mol of carbohydrate) and the amount of GHG emissions associated with generating ~14,000 TWh of renewable electricity (i.e., the estimated energy required to produce 1 Gt of carbohydrate), which was estimated to be 3.5 to 12 gCO_2eq/kWh by Pehl et al.[39] This estimate does not account for other indirect GHG emissions associated with, for example, the manufacture of machinery or transportation of carbohydrate product. As discussed earlier, we argue that the energy use, and hence the GHG emissions associated with, the manufacture of machinery and transportation of carbohydrate product are insignificant compared to that of DAC, water desalination, and the overall reaction energy.

Figure 1(b) shows the sensitivity of GHG emissions to four input parameters: electricity CO_2 intensity, reaction energy requirement, DAC energy requirement, and desalination energy requirement. For the latter three parameters, the ranges previously reported for **Figure 1(a)** were used in this analysis. For CO_2 intensity, three sources of electrical energy are analyzed: coal, natural gas, and solar. Solar was estimated to be as low as 3.5 gCO_2eq/kWh by Pehl et al.[39] and as high as 38 gCO_2eq/kWh by Burkhardt et al.[40] Natural gas and coal reported much higher values of 450 to 670 gCO_2eq/kWh[41] and 675 to 1689 gCO_2eq/kWh[42] respectively. **Figure 1(b)** shows that electricity from solar results in CO_2 capture with a GHG emissions intensity of -1.42 to -0.92 Gt CO_2eq per Gt carbohydrate whereas electricity from natural gas or coal results in higher GHG emissions than industrial agriculture. Moreover, using the analysis procedure outlined in the SI, we compute an electricity CO_2 intensity of 102.5 g CO_2eq/kWh results in GHG emissions of 0.0 Gt CO_2eq per Gt carbohydrate (assuming the nominal case values for all other input parameters). For context, the average emissions from electricity generation in California in 2019 were 202.3 g CO_2eq/kWh with 42.5% natural gas, 19% hydroelectric, 14% solar, 8% nuclear, 6.8% wind, 5.4% geothermal, 0.1% coal, and 4.1% other.[43-45] Moreover, **Figure S1(b)** shows the sensitivity of GHG emissions with respect to the two most important input parameters – reaction energy requirement and CO_2 intensity – and includes a contour for 0 Gt CO_2eq per Gt carbohydrate emissions. This analysis suggests that artificial carbohydrate synthesis can provide net negative GHG emissions even when integrated with an only partially decarbonized electric grid.

The land-use intensity of industrial agriculture (~400 million hectares/Gt) was estimated from the total land area used for crop land (~1.5 billion hectares)[15,19,22] and the total amount of crops produced worldwide (~3 to 4 Gt).[14,15] As a first order approximation to the land-use intensity of artificial carbohydrate synthesis, we assumed that solar fields for electricity generation would be the dominant land-use factor. The land-use efficiency for a 13% capacity factor PV solar field was reported in literature as 500 m^2/GWh.[46] Using the total energy previously estimated as ~14,000 TWh/Gt glucose the land-use intensity was estimated as 0.7 million hectares/Gt glucose. **Figure 1(c)** shows the sensitivity of the land-use by varying the solar field land-use efficiency between 229 m^2/GWh and 551 m^2/GWh.[46] DAC energy requirement, reaction energy requirement, and desalination energy requirement input parameters were also varied over the previously defined ranges. Land-use efficiency and reaction energy requirement had the largest effects on total land-use intensity because the reaction energy requirement is the most important factor for total energy intensity, and total land-use computed as land-use efficiency times total energy intensity. **Figure S1(c)** shows sensitivity of land-use intensity to these two most important input parameters.

Estimated Costs of Artificial Carbohydrate Synthesis. Artificial carbohydrate synthesis has not been viewed as competitive with biogenic carbohydrate production because industrial agriculture is heavily subsidized[28] and the external environmental costs associated with industrial agriculture (~$1.15 trillion per year[23]) are not reflected in the market price for the carbohydrates. However, if one considers these external costs, and the potential environmental and societal benefits of artificial carbohydrates production, then artificial carbohydrate synthesis may be competitive with biogenic carbohydrate production.

Dinger and Platt[10] recently evaluated the economics of artificial sugar synthesis from atmospheric CO_2 and water. They concluded that, if the environmental costs associated with industrial agriculture are accounted for in the price of sugar, then artificial sugar production is already competitive with the biogenic approach. They showed that the cost of the artificial process would decrease as renewable energy becomes cheaper, and as the efficiency of the process improves.[10] However, their calculations were based on several assumptions that may not be valid in reality even for a mature artificial carbohydrate synthesis industry. For example, they assumed that the production costs of hexoses from formaldehyde are less than or equal to the production costs of formaldehyde from syngas (on a per-carbon-atom basis). This assumption is based on the design of the formose reactor reported by Deng et al.,[47] which Dinger and Platt[10] argue is similar in complexity, and thus similar in cost, to the formaldehyde synthesis reactor chain. Dinger and Platt[10] also assumed that robust and sufficiently cheap catalysts will be available in the mid-term for targeted stereoisomer production (i.e. D-glucose), which is uncertain.

The cost of artificial carbohydrates, neglecting indirect and capital costs, was estimated using the total energy consumed in artificial carbohydrate synthesis multiplied by the cost of electricity. For the nominal case, with a total energy intensity of ~14,000 TWh/Gt glucose and solar electricity cost of 80 \$/MWh,[48] we estimate a cost of 1.15 trillion \$/Gt glucose which is equivalent to 1.15 \$/kg glucose. We can compare this to the traditional agriculture cost reported by Dinger and Platt.[10] They report the spot market value of sugar to be 0.34 \$/kg and they estimate total costs, including external (i.e., natural capital) costs, to be approximately 1 \$/kg in humid regions and 2.24 \$/kg in semi-arid regions. To estimate the indirect costs associated with CO_2 emissions, we consider the cost of removing generated CO_2 with DAC. In conventional agriculture we estimate ~2 kg CO_2 produced for 1 kg glucose produced, and for artificial synthesis 1.3 kg CO_2 are consumed for 1 kg of glucose produced. The cost of DAC is estimated in literature as ~0.3 \$/kg.[37] Using this value we can estimate an indirect cost of ~0.6 \$/kg glucose with conventional agriculture and an indirect benefit of ~0.4 \$/kg glucose with artificial synthesis. This is a net difference of 1.0 \$/kg. **Figure 1(d)** considers a sensitivity analysis which includes the total cost using electricity from solar, natural gas, and coal with cost ranges between 50 to 200 \$/MWh,[48] 50 to 166 \$/MWh,[43-45] and 50 to 112 \$/MWh,[2-4] respectively. **Figure 1(d)** shows that the cost of producing artificial carbohydrates is heavily impacted by the cost of solar electricity, further strengthening the argument that future reductions in renewable energy costs will allow artificial carbohydrate synthesis to be economically feasible. **Figure S1(d)** shows the two-dimensional sensitivity of artificial carbohydrate cost to reaction energy requirement and the cost of electricity.

CO_2 CONVERSION TO CARBOHYDRATES: TECHNICAL ASPECTS

Historical Perspective and State of the Art. In 1861, Alexander Butlerov discovered that formaldehyde could be converted into a sugar-like substance (characterized by the smell and taste of the solution) by heating with a base.[49] Since Butlerov's discovery, the conversion of formaldehyde to sugars—the formose reaction—has been studied extensively.[11,50-59] Much progress has been made in identifying the formose reaction products,[22,51-53,57,60] identifying suitable catalysts and reaction conditions,[11,54,55,58,59] and characterizing the kinetics of the reaction.[56] The formose product distribution is highly sensitive to the reaction conditions,[50] but the reaction generally produces dozens of different products, including straight-chain and branched-chain carbohydrates ranging from four to seven carbon atoms, with a majority of hexose (C6) sugars,[53] but also saccharinic acids, polyols, methanol, and formic acid.[50,51,57] The formose sugars are typically not digestible and can even cause death in rats at 50% of their diet level.[53,61] The exact reason for the toxicity of formose sugars is not clear, but it has been postulated[60] that the toxicity is related to the formation of branched-chain sugars and L-sugars, which do not occur in nature. Likholobov, Weiss and Sakharov[62] demonstrated that a high selectivity to glucose (75%) could be achieved without producing branched-chain sugars by operating at elevated temperature (98 °C) and at low formaldehyde conversion (18%).[55] However, the glucose was likely a racemic mixture with ~50% L-glucose, which is not digestible.

In a recent patent application,[63] Air Company reported a multi-step cascade process for converting CO_2 into sugars that utilized chiral ligands to enhance the stereoselectivity in the final product. Their three-step process initially converts CO_2 with H_2 into methanol using a copper-based heterogeneous catalyst. The methanol produced in the first reactor is then fed to a second reactor that dehydrogenates methanol to formaldehyde using an iron-based catalyst. In the final step, formaldehyde is converted to sugar by the formose reaction using coordination complexes of $Ca(OH)_2$ and chiral ligands (e.g., L-proline) to catalyze the transformation. They reported a D-glucose yield of 23% along with galactose and/or fructose (2% yield), ribose (3% yield), and other unidentified sugars.

Recently, there has been several significant advancements in hybrid chemo-enzymatic[12] and electro-biocatalytic[64,65] processes that convert CO_2 to starch, glucose, and other foods with a high degree of control over the product stereochemistry. These hybrid processes use temporally and spatially separated reactors to first convert CO_2 to carbohydrate intermediates (e.g. formaldehyde, acetic acid, acetate) using chemical or electrochemical processes and then biocatalytic processes (e.g. enzymes, yeast fermentation) to convert these intermediates into starch, glucose, or other carbohydrates. Cai et al.[12] developed a cell-free chemo-enzymatic process (**Figure 2(a)**) for converting CO_2 to starch. The modular process, called the artificial starch anabolic pathway (ASAP), consisted of 11 core reactions divided into four modules: (1) a C1 module to convert CO_2 to formaldehyde via methanol; (2) a C3 module for converting formaldehyde to D-glyceraldehyde 3-phosphate (GAP); (3) a C6 module to convert GAP to D-glucose-6-phosphate (G-6-P); and (4) a Cn module for starch synthesis. The pathway was designed computationally and optimized to synthesize starch from CO_2 at an overall rate ~8.5 times greater than starch photosynthesis in maize. It is not clear if the artificially synthesized starch is edible, but the structure of the synthetic starch was similar to standards, determined from their NMR and UV-vis spectra. Zheng et al.[64] developed a hybrid electro-biocatalytic system (**Figure 2(b)**) for converting CO_2 to glucose with high yield. The electro-biocatalytic process first converted CO_2 to pure acetic acid through a two-step electrolysis. Acetic acid was then converted to glucose by microorganism fermentation in a bioreactor using a genetically engineered *Saccharomyces cerevisiae* yeast.

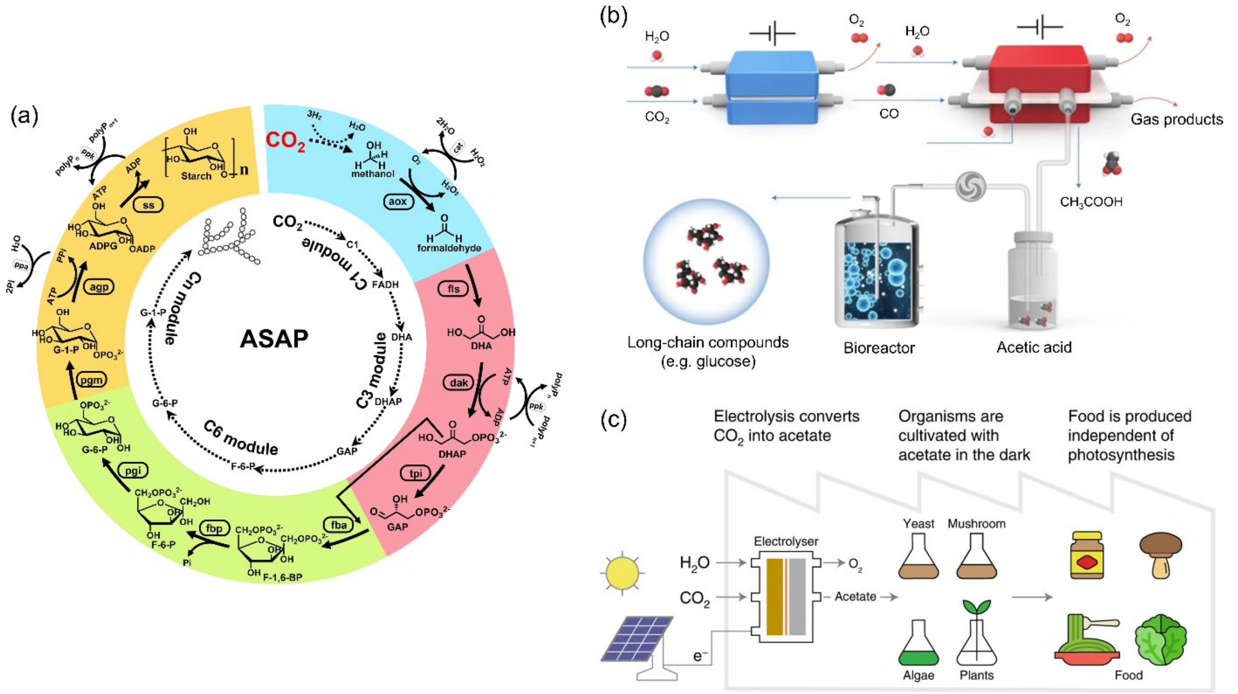


Figure 2. (a) Artificial starch anabolic pathway (ASAP) modular process for starch synthesis from CO_2, from Cai et al,[12] reprinted with permission from AAAS. (b) Hybrid electro-biosystem for glucose synthesis from CO_2, by Zheng et al.,[64] reprinted by permission from Springer Nature. (c) Hybrid electro-biological system for CO_2 conversion to food via acetate, by Hann et al.,[65] reprinted by permission from Springer Nature.

Hann et al.[65] recently demonstrated a hybrid inorganic-biological process (**Figure 2(c)**) that first electrochemically reduced CO_2 to acetate, which could then support the growth of food-producing organisms such as algae, fungi and crop plants independent of photosynthesis with a solar-to-food energy conversion efficiency about 4 to 18 times greater than biological photosynthesis. The acetate effectively serves as the carbon and energy source for the food-producing organisms. One advantage of this approach, using food-producing organisms to convert reduced CO_2 intermediates into food-grade products, is that it can produce protein and lipids in addition to carbohydrates.

These cascade processes[12,63-65] demonstrate the feasibility of converting CO_2 to carbohydrates with a high degree of control over the product stereochemistry, which is critical for synthesis of safe and digestible carbohydrates. Moreover, these processes establish a blueprint for developing modular reaction systems tunable for CO_2 conversion to a variety of carbohydrates, as well as proteins. Dividing the cascade reaction into individual modules avoids undesirable interactions between different enzymes/catalysts and allows for optimization of each module independent from the others. However, all of these technologies are currently at a relatively low TRL (~3 to 4, as discussed previously), and there are still significant challenges that will need to be overcome to enable commercially-viable artificial carbohydrate synthesis from CO_2 at the required Gt/y scale.

In the following sections we discuss the challenges and opportunities associated with CO_2 conversion to edible carbohydrates. **Figure 3** summarizes the main pathways from CO_2 to carbohydrates. The technology readiness level (TRL) of each step is indicated by the thickness of arrow: TRL 2 to 4 (proof-of-concept), TRL 5 to 7 (demonstration under realistic operating conditions up to pilot-scale), and TRL 8 to 9 (deployment at commercial scale).[66] We first discuss the challenges and opportunities of converting CO_2 to formaldehyde, which is a key intermediate in many of the pathways from CO_2 to carbohydrates (see **Figure 3**). We then discuss the challenges and opportunities for converting formaldehyde into carbohydrates. Finally, carbohydrate conversion to protein is discussed.

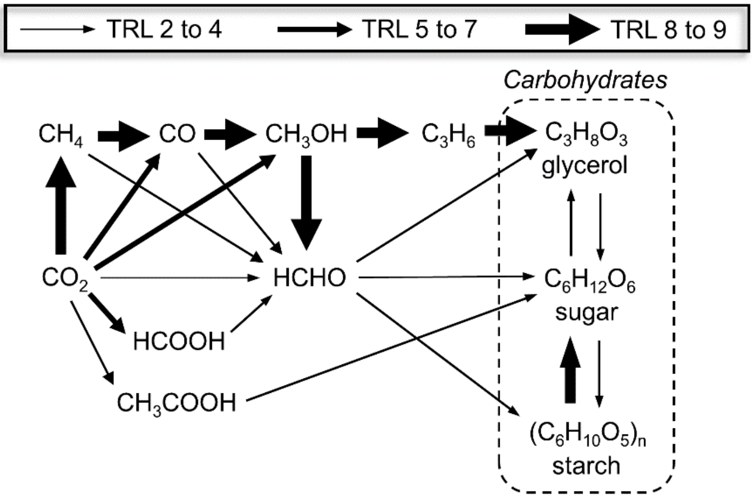


Figure 3. Possible pathways for CO_2 conversion to carbohydrates (sugar, starch, and glycerol). The thickness of the arrows represents the technology readiness level (TRL) of each conversion step, defined in the legend.

CO_2 Conversion to Formaldehyde. The most direct route to carbohydrate synthesis from CO_2 involves direct conversion of CO_2 to formaldehyde, followed by conversion of formaldehyde to carbohydrates such as sugar, starch, or glycerol (see **Figure 3**). However, direct conversion of CO_2 to formaldehyde is not favorable thermodynamically and, as such, has been rarely reported in the literature.[67,68] Thus, the main challenge of converting CO_2 to formaldehyde is overcoming thermodynamic limitations to achieve high conversion and selectivity to formaldehyde. There are several different approaches to circumvent thermodynamic limitations of direct CO_2 conversion to formaldehyde, including: (*i*) converting CO_2 to formaldehyde *indirectly* via CH_4, CO, CH_3OH, or HCOOH (**Figure 3**);[12,69,70] (*ii*) using photocatalytic,[62,71,72] electrocatalytic,[72,73] or plasma-catalytic[74-76] approaches to drive the reaction; and (*iii*) trapping/stabilizing formaldehyde as formaldehyde derivatives (e.g. acetals).[68,77,78]

Industrially, formaldehyde is produced from methane via multiple energy-intensive processes including steam reforming of methane to CO, methanol synthesis from CO, and methanol partial oxidation and/or dehydrogenation to formaldehyde (see **Figure 3**).[79,80] The most technologically-advanced (i.e. highest TRL) pathway from CO_2 to formaldehyde may be to convert CO_2 to methane using the established Sabatier Process (TRL 8 to 9)[81,82] and then use the existing formaldehyde production infrastructure to convert CO_2-derived methane to formaldehyde via CO and methanol. All steps in this indirect pathway from CO_2 to formaldehyde are currently at a TRL of 8 or 9. The main advantage of this indirect approach is that it is well-established and leverages existing infrastructure.

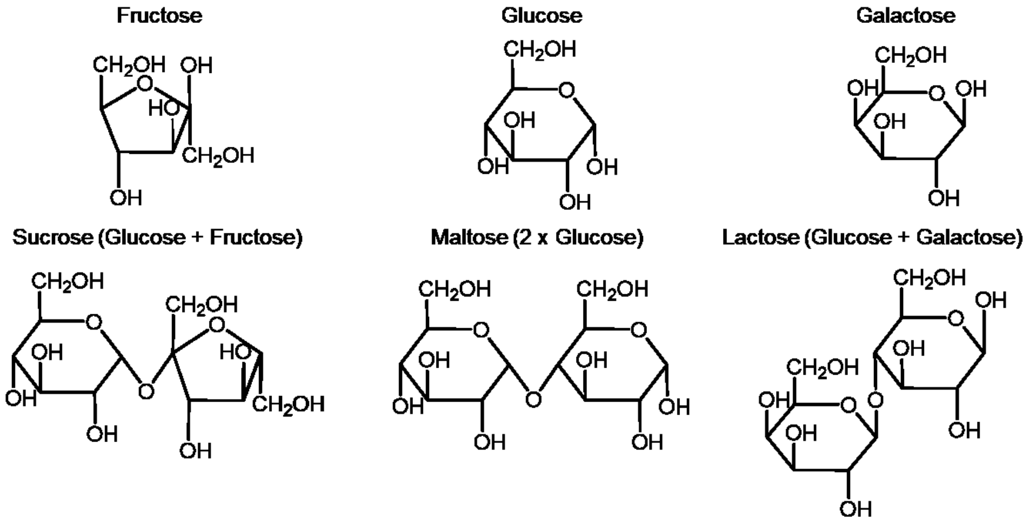
The main drawback of this indirect approach is that it involves multiple steps. However, there are many opportunities to reduce the energy intensity of indirect formaldehyde production by developing more efficient catalysts and processes, and by bypassing steps in the reaction (see **Figure 3**). For example, CO_2 could be converted to methanol directly,[12,83-85] bypassing two reaction steps for methane and CO intermediate production. Methanol is one of the most readily derived chemicals from CO_2 with existing processes at an intermediate TRL of 6 to 7.[82,86] CO_2 could also be converted directly to CO via the reverse water-gas shift reaction (TRL 6[82]),[87] bypassing the Sabatier process. Other shortcuts include direct conversion of methane to formaldehyde[88,89] and CO conversion to formaldehyde;[90,91] both of these processes are currently at a low TRL of 2 to 3, however.[66] Other possible indirect routes to formaldehyde include CO_2 reduction to formic acid (TRL 3 to 5),[82] followed by dehydration-hydrogenation into formaldehyde (TRL 3 to 4).[69,70,92]

While indirect approaches to formaldehyde are the most technologically mature and are likely the most feasible in the near term, there are many opportunities to develop electrochemical, photochemical, and/or plasma-catalytic approaches to directly convert CO_2 to formaldehyde. The main challenge of photo/electro/plasma-catalytic reduction of CO_2 to formaldehyde is achieving high conversion and selectivity to formaldehyde over the many other products that are usually formed. Typically, the products of electro/photo/plasma-catalytic reduction of CO_2 include CO, CH_3OH, HCOOH, or CH_4, and formaldehyde. The product distribution can be controlled to some extent by tuning the reaction conditions and catalyst. For example, Nakata et al.[73] showed that a boron-doped diamond (BDD) electrode achieved a high yield of formaldehyde during electrochemical reduction of CO_2 in methanol electrolyte with a high Faradaic efficiency of 74%. Kim et al.[72] used a photoelectrochemical approach using a $BiVO_4$ photoanode and a Cu cathode in NaCl electrolyte to achieve 85% Faradaic efficiency to formaldehyde. How exactly to tune the reaction conditions and catalyst to achieve high selectivity and yield to formaldehyde are not well-understood. Thus, there is a significant need and opportunity for fundamental science that will enable the development of new catalysts and processes to directly convert CO_2 to formaldehyde with high selectivity and yield.

Another approach to circumventing thermodynamic limitations of CO_2 conversion to formaldehyde involves trapping or stabilizing formaldehyde through the formation of derivatives such as acetals.[68,77,78] The drawback of this approach, which will likely prevent its application for CO_2 conversion to carbohydrates at Gt/y scales, is that it requires a stoichiometric amount of additives to stabilize formaldehyde, and it requires a method (e.g. treatment with CsF[78]) to liberate the formaldehyde product.

Formaldehyde Conversion to Carbohydrates. While there are high-TRL pathways for converting CO_2 to formaldehyde, as discussed above, processes for converting formaldehyde to sugar or starch for human consumption are currently at a low TRL of 3 to 4 in our estimation (see **Figure 3**). Unlike the energetically uphill CO_2 conversion to formaldehyde, the conversion of formaldehyde to carbohydrates is thermodynamically favorable.[56] The main challenge of converting formaldehyde (or acetic acid/acetate) to carbohydrates is controlling product stereochemistry to achieve high selectivity and high yield to edible carbohydrates with nutritional value. This is a significant challenge because: (*i*) carbohydrates are structurally complex with multiple stereocenters and a wide range of possible enantiomers, diastereomers, epimers, and glycosidic linkages (for oligo- and polysaccharides); and (*ii*) the physiological and health effects of carbohydrates are highly sensitive to the carbohydrate stereochemistry. Many carbohydrates do not have nutritional value and some may even cause serious health problems. It is therefore critical to control the stereochemistry of the carbohydrate product through catalyst/enzyme design and reaction engineering, which is a significant challenge.

Formaldehyde Conversion to Sugar. Sugars are mono- or disaccharides composed of one or two simple sugar units, respectively. The three most important sugars in human nutrition are glucose, fructose, and galactose (**Figure 4**), which are monosaccharides (simple sugars). During digestion, all carbohydrates are broken down into these monosaccharides, which are absorbed into the bloodstream. Other important sugars include sucrose, maltose, and lactose (**Figure 4**), which are all disaccharides that consist of two simple sugar units connected by a glycosidic bond. Sucrose is formed from glucose and fructose units connected by an α(1→4) glycosidic bond; maltose consists of two glucose units connected by an α(1→4) glycosidic bond; and lactose consists of galactose and glucose units connected by a β(1→4) glycosidic bond. Except for galactose, which is only found in nature bound to glucose in the form of lactose, all of these sugars are found in nature in milk (lactose), malt grains (maltose), fruit (maltose, sucrose, fructose), vegetables (maltose, fructose), honey (fructose, glucose), sugar cane (sucrose), and sugar beet (sucrose, fructose), for example. While there may be other sugars that are digestible and have nutritional value, these six sugars can be incorporated into the human diet without adverse side effects and therefore these sugars should be targeted for artificial sugar synthesis.



Fructose

Glucose

Galactose

Sucrose (Glucose + Fructose)

Maltose (2 x Glucose)

Lactose (Glucose + Galactose)

Figure 4. Chemical structures of the most important natural sugars in human nutrition: fructose, glucose, galactose, sucrose, maltose, and lactose.

The formose reaction is the traditional method for producing sugars from formaldehyde. However, the formose reaction is typically catalyzed by inorganic (e.g. $Ca(OH)_2$) and organic (e.g. tertiary amines) catalysts[50] that are not stereospecific and produce a wide range of straight-chain and branched-chain sugars, as well as other compounds such as polyols, saccharinic acids, and methanol, that are not digestible and can even be toxic. Thus, there is a significant opportunity for the development of stereospecific catalysts that can convert formaldehyde to digestible sugars with control over product stereochemistry. As discussed above, Air Company has recently developed a $Ca(OH)_2$ catalyst modified with chiral L-proline ligands that is capable of converting formaldehyde to D-glucose with a 23% yield.[63] Zheng et al.[64] also developed a genetically engineered yeast to produce glucose from acetic acid with high yield. It is not clear from their work whether the glucose produced was pure D-glucose, L-glucose, or a racemic mixture, however. The main challenge of this approach is scaling it to Gt/y levels, which will require the development of new catalysts with high activity, high stereoselectivity, high stability, and low cost.

Formaldehyde Conversion to Starch. Starch is a polysaccharide (complex carbohydrate) that is composed of ~20 to 30% amylose and ~70 to 80% amylopectin (**Figure 5**).[12,93] Amylose is a linear polymer composed of α-D-glucose sub-units connected by α(1→4) glycosidic bonds. Amylopectin is also a polymer that is composed of α-D-glucose sub-units connected by α(1→4) linkages, but amylopectin has a branched structure resulting from additional α(1→6) glycosidic bonds. During digestion, enzymes in the body break the glycosidic bonds of starch and break it down into individual α-D-glucose units, which are absorbed into the bloodstream and used as an energy source.

The physiological properties of carbohydrates are highly sensitive to the stereochemistry of the sugar sub-units. For example, cellulose is a polysaccharide that is composed of β-D-glucose sub-units connected by β(1→4) glycosidic bonds (**Figure 5**). The human body contains enzymes that are capable of breaking the α(1→4) glycosidic bonds of starch but not the β(1→4) glycosidic bonds of cellulose, and therefore humans can digest starch but not cellulose. Some animals such as cows, horses, and sheep have enzymes that can digest cellulose. Therefore, artificial cellulose could be used for animal feed, which accounts for ~35% of global crop production.[22] Cellulose could also be used for paper manufacturing, which could mitigate up to ~200 million tons of GHG emissions that are currently associated with paper manufacturing.[94] For all of these different potential applications, a high degree of control over the stereochemistry is required.

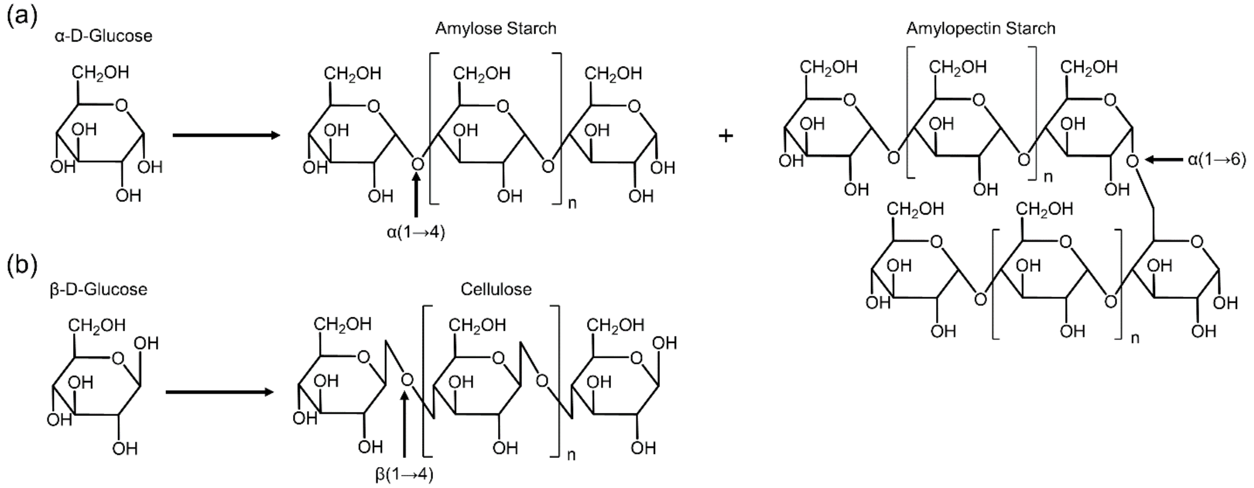


Figure 5. (a) Starch is composed of amylose and amylopectin, which are both polymers consisting of α-D-glucose sub-units connected by α(1→4) glycosidic bonds, and α(1→6) glycosidic bonds for amylopectin. (b) Cellulose consists of β-D-glucose sub-units connected by β(1→4) glycosidic bonds.

Cai et al.[12] developed the ASAP process for selectively converting CO_2 to starch with high selectivity and yield to starch. They achieved this by using an inorganic ZnO-ZrO_2 catalyst to convert CO_2 with H_2 to methanol, and then an enzymatic cascade of 10 reactions to convert methanol to amylose starch using separated modules. These modules could be modified to steer the products towards other carbohydrates. For example, Cai et al.[12] demonstrated that the product distribution could be tuned from the straight-chain amylose starch to the branched-chain amylopectin starch by introducing a starch branching enzyme. In principle, this approach could be used to synthesize other carbohydrates such as cellulose or sugar by substituting different enzymes and modules.

While the ASAP process, and other hybrid electro-biocatalytic processes,[64] have demonstrated the feasibility of artificial starch and glucose synthesis from CO_2, there is still much work that is required to translate the laboratory scale process (~410 $mg \cdot L^{-1}h^{-1}$)[12] to Gt/y levels.

This will require the development of new enzymes/catalysts and modules with high activity, high stability, and low cost.

CO_2 Conversion to Glycerol. One alternate solution to the stereoselectivity challenge of sugar and starch synthesis is to convert formaldehyde, methanol, or non-edible sugars from the formose reaction, to glycerol (see **Figure 3**). Glycerol (**Figure 6**) is chemically a sugar alcohol (polyol), but is categorized by the U.S. Food and Drug Administration as a carbohydrate in terms of nutrition. Glycerol is considered safe for human consumption at high dosages equivalent to ~70% of the average daily caloric needs.[95] It has a sweet taste similar to sugar, a high gross energy density of 4,310 kcal/kg,[96] and enters similar metabolic pathways as that of carbohydrates.[97] It can be oxidized to CO_2 and water via glycolysis, releasing 4,310 kcal/kg of energy, or converted to glucose via gluconeogenesis, depending on the physiological conditions.[97-100] Glycerol is also a safe feed for cows and poultry.[99,101] A key advantage of glycerol over other carbohydrates is its lack of chiral centers, which eliminates the need for enantiospecific catalysts to drive the reaction towards a particular enantiomer. Glycerol can also be converted to carbohydrates (see **Figure 3**) using enzymatic approaches.[102-104]

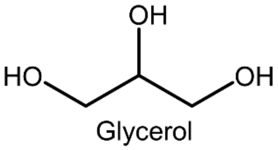


Figure 6. Chemical structure of glycerol.

Industrially, glycerol is currently produced as a by-product of biodiesel production,[105] but there are several other routes to glycerol production from different feedstocks that are relevant to the artificial carbohydrate synthesis reaction network (**Figure 3**). Non-edible sugars from the formose reaction can be converted to glycerol by hydrogenation or fermentation of formose sugars.[106-108] Formaldehyde could also be converted to glycerol by self-condensation via dihydroxyacetone (**Figure 3**).[109-111] These are both low-TRL processes with many opportunities to advance the technology through catalyst and process development.

Alternatively, there is a higher-TRL pathway to glycerol production through methanol (see **Figure 3**). Methanol can be converted to propylene using Lurgi's Methanol to Propylene (MTP®) process or UOP/Hydro's Methanol to Olefins (MTO) process, both of which have been successfully commercialized.[112-115] Propylene can then be converted to allyl chloride via a commercialized high-temperature chlorination process,[116,117] which can be converted to glycerol by hydrolysis.[105,118] All steps in this pathway from methanol to glycerol are at a high TRL of 8 to 9, and thus glycerol production from CO_2, via methanol, is the pathway with the highest TRL and lowest barrier to commercialization. A drawback of this route is that it requires chlorine for allyl chloride synthesis, and it involves multiple process steps. Another drawback of glycerol is that it is not currently used in the human diet in significant amounts and there will likely be significant hesitance, or resistance, to incorporate it into the diet, whereas starch and sugar can be readily converted to staple foods. Glycerol synthesized from CO_2 could be used for animal feed, decreasing the environmental impacts of animal feed production, while technologies for CO_2 conversion to sugar and starch for human consumption are developed.

FOOD, FEED, AND FUEL

Carbohydrate Conversion to Protein. While carbohydrates are the main energy source for the human body, and constitute the majority (~50-70%) of the calories in the human diet,[29] proteins supply the body with essential amino acids. Humans get most of their protein from animal protein (meat and dairy) and plant-based protein (e.g., nuts, legumes, beans). The demand for protein is increasing and global demand is expected to exceed 1 Gt/y by 2030. [119] However, increasing animal production to meet growing demand is not sustainable, and the environmental impacts of protein production, particularly animal protein,[120] are substantial. Furthermore, millions of children in developing countries are currently suffering from stunted growth as a result of protein malnutrition.[121] Single cell protein (SCP) is a potential solution to address the increasing demand for protein and simultaneously mitigate the environmental impacts and social injustices of protein production.

SCP is protein synthesized in a ferementer using bacteria, fungi (filamentous fungi, yeast), or algae cultures, which is suitable for human consumption or animal feed. The technology for SCP production has been developed over the past 100 years and has been commercialized since the 1970's.[122] Yeast SCP was produced and used at large-scale to feed soldiers during World Wars 1 and 2. Bacteria-based Pruteen was the first SCP commercialized for animal feed.[123,124] Quorn™ is a filamentous fungi-based SCP that was commercialized in 1985 to produce food protein for human consumption. Quorn has a texture that resembles meat and is used as a meat substitute (quorn.com).

SCP production requires a carbon source and a nitrogen source. Commercialized processes use starch-derived glucose (Quorn™ and Marmite®), sugar from paper pulp (Pekilo), methanol (Pruteen), and methane from natural gas (UniProtein® and FeedKind®) as the carbon substrate for SCP growth.[122] Other carbon substrates used for SCP growth include acetic acid and glycerol.[125] Nitrogen sources typically used for SCP production include ammonia, ammonium salts, urea, and nitrate, but wastewater containing nitrogen has also receive significant attention.[126]

Protein Production from CO_2-derived Artificial Carbohydrates. Many of the carbon sources used in SCP processes (e.g. glucose, starch, methanol, methane) are also intermediates in the reaction network for artificial carbohydrate synthesis from CO_2 (see **Figure 3**). Thus, there is a significant opportunity to integrate artificial carbohydrate synthesis from CO_2, using the approaches described earlier, with protein production for human consumption and animal feed using the commercialized approaches described above (see **Figure 7**).

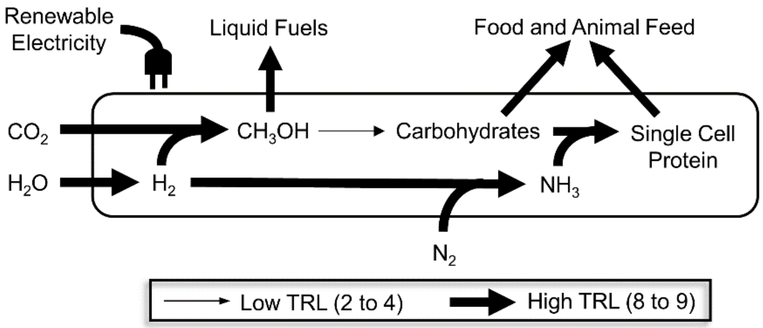


Figure 7. Process for synthesizing liquid fuels and artificial food/feed CO_2, H_2O, N_2, and renewable electricity. The thickness of the arrows represents the technology readiness level (TRL) of each conversion step, defined in the legend. Conversion of methanol, or other intermediates such as formaldehyde, to carbohydrates is a critical bottleneck (i.e. low TRL) in the production of artificial food/feed from CO_2.

Glucose is the only carbon source that has been used to produce commercial SCPs for human consumption (Quorn and Marmite), to our knowledge.[122] This glucose is currently derived from starch in biomass,[102] but it could in principle be derived from CO_2 via methanol or formaldehyde intermediates (see **Figure 3**). This CO_2-derived glucose could then be converted to SCP (e.g. Quorn^{TM}) for human consumption. The key bottleneck in this pathway, in terms of the maturity of the technologies involved in such a process, is methanol (or formaldehyde) conversion to glucose, which is currently at a low TRL of 3 to 4 (see **Figure 7**). All other steps in the reaction network from CO_2 to protein are at a high TRL of 8 to 9.

Alternatively, other intermediates in the reaction pathway from CO_2 to carbohydrates (**Figure 3**), such as methanol and methane, could be converted to SCPs for *animal feed* using commercialized processes (e.g., Pruteen, UniProtein, FeedKind®). All of the technology required for CO_2 conversion to animal feed, via methane or methanol, is already at a high TRL of 8 or 9. There are also lower-TRL pathways from CO_2 to SCPs that involve other intermediates in CO_2 conversion to carbohydrates, such as acetate/acetic acid. Molitor et al.[127] recently developed a two-stage bioprocessing system consisting of a bioreactor to first convert CO_2 to acetate using a pure culture of *Clostridium ljungdahlii*, and then another bioreactor to convert acetate with oxygen and ammonia into SCP. Glycerol can also be used as carbon source for SCP growth, and there are higher-TRL pathways from CO_2 to glycerol (see Figure 3), but lipids are typically produced, not protein.[128-130]

Combining SCP production with artificial carbohydrate synthesis from CO_2 would reduce the GHG emissions, water pollution, and land and water use for food production even further than for artificial carbohydrate synthesis from CO_2 alone.[131] It would also address protein and general malnutrition in developing countries. Although nitrogen is required for SCP production, nitrogen could be used much more efficiently in an SCP process than in industrial agriculture. Animals are inefficient at converting plant protein to animal protein, and thus large amounts of plant protein are required to produce animal protein, and about 50-70% of the nitrogen in fertilizer is lost in runoff, leaching volatilization, and denitrification.[126] Water contaminated by nitrogen fertilizers could also be used as the nitrogen source for SCP production,[126] further mitigating the environmental impacts of industrial agriculture. Most of the cost of SCPs is in the carbon substrate,[132] so combining SCP production with artificial carbohydrate synthesis from CO_2 would not add a large cost to the overall process.

Liquid fuels production could also be integrated with artificial carbohydrate synthesis and SCP production from CO_2 in the process shown in **Figure 7**. Methanol, a key intermediate in carbohydrate and SCP production, can also be used directly as a liquid fuel, or processed further into liquid fuels using Mobil's Methanol to Gasoline (MTG) process,[133-135] for example. If the technology associated with the process is capable of being scaled up sufficiently, such an integrated process could meet global demands for food, animal feed, and liquid fuels while utilizing up to ~10 Gt of CO_2 per year. This would re-balance the global carbon and nitrogen cycles and mitigate global food and water scarcity. Such a process would certainly be energy-intensive and costly, but it may be a better alternative to geological storage of CO_2, and given the high environmental and societal costs of current approaches to food and fuel productions, the costs may be outweighed by the benefits. Much work is required to understand these cost-benefit relationships, and to develop and scale-up the technology.

Other Challenges and Opportunities. In addition to the technical challenges discussed above related to conversion of CO_2 to edible carbohydrates, there are several other challenges that will need to be overcome to enable commercially-viable artificial carbohydrate synthesis from CO_2 at Gt/y scales. First and foremost, the deployment of artificial carbohydrate synthesis at Gt/y scales will require a successful global energy decarbonization with inexpensive and plentiful renewable energy. Based on our energy intensity estimates summarized in **Figure 1(a)**, producing 1 Gt/y of artificial carbohydrates will require ~14,000 TWh of electricity. In 2020, the amount of renewable electricity generated by solar PV was ~800 TWh,[136] and that of wind power was ~1,500 TWh.[137] Thus, the renewable energy capacity of the planet will need to increase by a factor of at least 6× to enable artificial carbohydrate synthesis at Gt/y scales. Recently, through Executive Order 14057,[138] the US government has set a goal of "100 percent carbon pollution-free electricity by 2030." As discussed previously, net negative GHG emissions with artificial carbohydrate synthesis are expected with a partially decarbonized electric grid (less than ~100g CO_2eq/kWh electricity carbon intensity). The simple systems and sensitivity analysis presented here shows the promise of artificial carbohydrate synthesis to result in net negative GHG emissions at the 1 Gt/y scale. This work strongly motivates future research to develop catalytic materials and processes and to conduct more rigorous technoeconomic analysis considering lifecycle emissions, capital costs, and additional costs to accommodate the non-dispatchable nature of renewable energy (e.g., energy storage for wind or solar).

More broadly, replacing industrial agriculture with artificial carbohydrate synthesis will have far-reaching environmental and social consequences that are difficult to predict. The long-term physiological and health effects of consuming unnatural carbohydrates are unknown and will need to be thoroughly investigated. Social life cycle analyses are needed to determine the direct and indirect environmental and economic consequences of artificial carbohydrate synthesis. For example, it is important to understand how potentially disruptive technology such as artificial carbohydrate synthesis would impact agriculture and related sectors of the global economy and labor markets.

CONCLUSIONS

Artificial synthesis of edible carbohydrates from CO_2 is a promising approach to mitigate climate change from GHG emissions, reduce water pollution from nitrogen fertilizers, increase the food production capacity of the planet, and reduce water and food scarcity in developing countries, relative to the current biogenic approach to food production. However, synthesis of artificial carbohydrates from CO_2 is a significant challenge due to thermodynamics and the high stereospecificity required in the final carbohydrate product. There are many opportunities for scientific innovation to overcome these challenges and potentially enable viable artificial carbohydrate synthesis. Achieving this ultimate goal at the necessary Gt/y scales will require worldwide collaboration between chemists, biologists, chemical engineers, and food engineers, among other disciplines. It will also require an energy transition to inexpensive, widespread renewable energy.

Supporting Information: Analysis data, sample calculations, and supplement Figure S1 (PDF), Python computer code for analysis and visualization (https://github.com/dowlinglab/CO2-to-carbs-analysis)

Biographies

Casey P. O'Brien is an assistant professor in the Department of Chemical and Biomolecular Engineering at the University of Notre Dame. His main research interests are in CO_2 capture and utilization, and in the development of advanced operando spectroscopy techniques for probing catalytic interfaces under realistic operating conditions.

Madelynn J. Watson is a 2nd year PhD student in the Department of Chemical and Biomolecular Engineering at the University of Notre Dame. Her research interests center around computational multiscale optimization methods for sustainable fuels and hydrocarbon conversion.

Alexander W. Dowling is an assistant professor in the Department of Chemical and Biomolecular Engineering at the University of Notre Dame. His research team develops process systems engineering, data science, and computational optimization methods to analyze sustainable energy systems including CO_2 capture, membranes, and decarbonized co-production of H_2 and electricity.

Acknowledgments: This work was funded through U.S. National Science Foundation CAREER award (CBET-2144362). M.J. Watson received support from a Graduate Assistance in Areas of National Need fellowship from the Department of Education via grant number P200A210048 and the Arthur J. Schmitt Presidential Leadership Fellowship administered by the University of Notre Dame.

References

(1) NASA Jet Propulsion Laboratory, accessed January 27, 2022, https://climate.nasa.gov/vital-signs/carbon-dioxide/.

(2) Hansen, J.; Ruedy, R.; Sato, M.; Lo, K. Global Surface Temperature Change. *Rev. Geophys.* **2010,** *48* (4). https://doi.org/10.1029/2010RG000345.

(3) Horowitz, C. A. Paris Agreement. *Int. Legal Mater.* **2017,** *55* (4), 740.

(4) IEA **2016**, *World Energy Outlook 2016*. IEA, Paris. https://www.iea.org/reports/world-energy-outlook-2016. Accessed 1 Sept. 2022.

(5) UNEP **2017**. The Emissions Gap Report 2017. United Nations Environment Programme (UNEP), Nairobi.

(6) Kelemen, P.; Benson, S. M.; Pilorgé, H.; Psarras, P.; Wilcox, J. An Overview of the Status and Challenges of CO_2 Storage in Minerals and Geological Formations. *Frontiers Clim.* **2019,** *1*. doi: 10.3389/fclim.2019.00009.

(7) Ehlig-Economides, C.; Economides, M. J. Sequestering carbon dioxide in a closed underground volume. *J. Petrol. Sci. Eng.* **2010,** *70* (1), 123.

(8) Newmark, R. L.; Friedmann, S. J.; Carroll, S. A. Water Challenges for Geologic Carbon Capture and Sequestration. *Envir. Man.* **2010,** *45* (4), 651.

(9) Gulzar, A.; Gulzar, A.; Ansari, M. B.; He, F.; Gai, S.; Yang, P. Carbon dioxide utilization: A paradigm shift with CO_2 economy. *Chem. Eng. J. Adv.* **2020,** *3*, 100013.

(10) Dinger, F.; Platt, U. Towards an Artificial Carbohydrates Supply on Earth. *Frontiers Sus. Food Sys.* **2020,** *4* (90). doi: 10.3389/fsufs.2020.00090.

(11) García Martínez, J. B.; Alvarado, K. A.; Christodoulou, X.; Denkenberger, D. C. Chemical synthesis of food from CO2 for space missions and food resilience. *J. CO_2 Util.* **2021,** *53*, 101726.

(12) Cai, T.; Sun, H.; Qiao, J.; Zhu, L.; Zhang, F.; Zhang, J.; Tang, Z.; Wei, X.; Yang, J.; Yuan, Q.et al. Cell-free chemoenzymatic starch synthesis from carbon dioxide. *Science* **2021,** *373* (6562), 1523.

(13) U.S. Energy Information Administration. **2022**. *Short-Term Energy Outlook January 2022*.

(14) FAO. **2021**. *Food Outlook: Biannual Report on Global Food Markets*. Food Outlook, November, 2021. Rome. https://doi.org/10.4060/cb7491en.

(15) Xu, X.; Sharma, P.; Shu, S.; Lin, T.-S.; Ciais, P.; Tubiello, F. N.; Smith, P.; Campbell, N.; Jain, A. K. Global greenhouse gas emissions from animal-based foods are twice those of plant-based foods. *Nature Food* **2021,** *2* (9), 724.

(16) Denkenberger, D. C.; Pearce, J. M. Feeding everyone: Solving the food crisis in event of global catastrophes that kill crops or obscure the sun. *Futures* **2015,** *72*, 57.

(17) Horton, P.; Horton, B. P. Re-defining Sustainability: Living in Harmony with Life on Earth. *One Earth* **2019,** *1* (1), 86.

(18) US EPA. **2021**. *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2019*. https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks. Accessed 1 Sept. 2022.

(19) Poore, J.; Nemecek, T. Reducing food's environmental impacts through producers and consumers. *Science* **2018,** *360* (6392), 987.

(20) Rosenzweig, C.; Mbow, C.; Barioni, L. G.; Benton, T. G.; Herrero, M.; Krishnapillai, M.; Liwenga, E. T.; Pradhan, P.; Rivera-Ferre, M. G.; Sapkota, T.et al. Climate change responses benefit from a global food system approach. *Nature Food* **2020,** *1* (2), 94.

(21) Crippa, M.; Solazzo, E.; Guizzardi, D.; Monforti-Ferrario, F.; Tubiello, F. N.; Leip, A. Food systems are responsible for a third of global anthropogenic GHG emissions. *Nature Food* **2021,** *2* (3), 198.

(22) Foley, J. A.; Ramankutty, N.; Brauman, K. A.; Cassidy, E. S.; Gerber, J. S.; Johnston, M.; Mueller, N. D.; O'Connell, C.; Ray, D. K.; West, P. C.; Balzer, C.; Bennett, E. M.; Carpenter, S. R.; Hill, J.; Monfreda, C.; Polasky, S.; Rockström, J.; Sheehan, J.; Siebert, S.; Tilman, D.; Zaks, D. P. M., Solutions for a cultivated planet. *Nature* **2011,** *478* (7369), 337.

(23) FAO. **2015**. *Natural Capital Impacts in Agriculture: Supporting Better Business Decision-Making*. Food and Agriculture Organization of the United Nations.

(24) FAO, IFAD, UNICEP, WFP, and WHO. **2020**. *The State of Food Security and Nutrition in the World 2020. Transforming Food Systems for Affordable Healthy Diets*.

(25) Fyles, H.; Madramootoo, C. **2016**. Key Drivers of Food Insecurity in *Emerging Technologies for Promoting Food Security* (pp. 1-17). Oxford: Woodhead Publishing.

(26) Godfray, H. C. J.; Beddington, J. R.; Crute, I. R.; Haddad, L.; Lawrence, D.; Muir, J. F.; Pretty, J.; Robinson, S.; Thomas, S. M.; Toulmin, C. Food Security: The Challenge of Feeding 9 Billion People. *Science* **2010,** *327* (5967), 812.

(27) Brown, M. E.; Antle, J.M.; Backlund, P.; Carr, E.R.; Easterling, W.E.; Walsh, M.K.; Ammann, C.; Attavanich, W.; Barrett, C.B.; Bellemare, M.F.; Dancheck, V.; Funk, C.; Grace, K.; Ingram, J.S.I.; Jiang, H.; Maletta, H.; Mata, T.; Murray, A.; Ngugi, M.; Ojima, D.; O'Beill, B.; Tebaldi, C. **2015** *Climate Change, Global Food Security, and the U.S. Food System*. http://www.usda.gov/oce/climate_change/FoodSecurity2015Assessment/FullAssessment.pdf. Accessed 1 Sept. 2022.

(28) Horton, P. We need radical change in how we produce and consume food. *Food Secur.* **2017,** *9* (6), 1323.

(29) Chen, H.-G.; Zhang, Y. H. P. New biorefineries and sustainable agriculture: Increased food, biofuels, and ecosystem security. *Renew. Sustain. Energy Rev.* **2015,** *47*, 117.

(30) Zhu, X.-G.; Long, S. P.; Ort, D. R. What is the maximum efficiency with which photosynthesis can convert solar energy into biomass? *Curr. Opin. Biotech.* **2008,** *19* (2), 153.

(31) Zhang, Y.-H. P. Next generation biorefineries will solve the food, biofuels, and environmental trilemma in the energy–food–water nexus. *Energy Sci. Eng.* **2013,** *1* (1), 27.

(32) Food and Agriculture Organization of the United Nations. FAOSTAT Statistical Database.

(33) Mekonnen, M. M.; Hoekstra, A. Y. The green, blue and grey water footprint of crops and derived crop products. *Hydrol. Earth Sys. Sci.* **2011,** *15* (5), 1577.

(34) Woods, J.; Williams, A.; Hughes, J. K.; Black, M.; Murphy, R. Energy and the food system. *Philosoph. Trans. Royal Soc, B: Biolog, Sci,* **2010,** *365* (1554), 2991.

(35) bp Statistial Review of World Energy **2021**. https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2021-full-report.pdf. Accessed 1 Sept. 2022.

(36) Lackner, K. S. Capture of carbon dioxide from ambient air. *Eur. Phys. J. Special Top.* **2009,** *176* (1), 93.

(37) Hong, W. Y. A techno-economic review on carbon capture, utilisation and storage systems for achieving a net-zero CO_2 emissions future. *Carbon Capture Sci. Tech.* **2022,** *3*, 100044.

(38) Petela, R. An approach to the exergy analysis of photosynthesis. *Solar Energy* **2008,** *82* (4), 311.

(39) Pehl, M.; Arvesen, A.; Humpenöder, F.; Popp, A.; Hertwich, E. G.; Luderer, G. Understanding future emissions from low-carbon power systems by integration of life-cycle assessment and integrated energy modelling. *Nature Energy* **2017,** *2* (12), 939.

(40) Burkhardt III, J. J.; Heath, G.; Cohen, E. Life Cycle Greenhouse Gas Emissions of Trough and Tower Concentrating Solar Power Electricity Generation. *J. Ind. Ecol.* **2012,** *16* (s1), S93.

(41) O'Donoughue, P. R.; Heath, G. A.; Dolan, S. L.; Vorum, M. Life Cycle Greenhouse Gas Emissions of Electricity Generated from Conventionally Produced Natural Gas. *J. Indust. Ecol.* **2014,** *18* (1), 125.

(42) Whitaker, M.; Heath, G. A.; O'Donoughue, P.; Vorum, M. Life Cycle Greenhouse Gas Emissions of Coal-Fired Electricity Generation. *J. Indust. Ecol.* **2012,** *16* (s1), S53.

(43) U.S. Energy Information Administration. **2022**. Form EIA-860, Annual Electric Generator Report.

(44) U.S. Energy Information Administration. **2022**. Form EIA-861, Annual Electric Power Industry Report.

(45) U.S. Energy Information Administration. **2022**. Form EIA-923, Power Plant Operations Report.

(46) Hernandez, R. R.; Hoffacker, M. K.; Field, C. B. Land-Use Efficiency of Big Solar. *Envi. Sci. Tech.* **2014,** *48* (2), 1315.

(47) Deng, J.; Pan, T.; Xu, Q.; Chen, M.-Y.; Zhang, Y.; Guo, Q.-X.; Fu, Y. Linked strategy for the production of fuels via formose reaction. *Sci. Reports* **2013,** *3* (1), 1244.

(48) Xiao, M.; Junne, T.; Haas, J.; Klein, M. Plummeting costs of renewables - Are energy scenarios lagging? *Energy Strategy Rev.* **2021,** *35*, 100636.

(49) Butlerow, A. Bildung einer zuckerartigen Substanz durch Synthese. *Justus Liebigs Annalen der Chemie* **1861,** *120* (3), 295.

(50) Delidovich, I. V.; Simonov, A. N.; Taran, O. P.; Parmon, V. N. Catalytic Formation of Monosaccharides: From the Formose Reaction towards Selective Synthesis. *ChemSusChem* **2014,** *7* (7), 1833.

(51) Kopetzki, D.; Antonietti, M. Hydrothermal formose reaction. *New J. Chem.* **2011,** *35* (9), 1787.

(52) Weiss, A.H.; Krylov, O.V.; Sakharov, M.M.; Ghorochovatskii, Y.B. Synthetic Carbohydrates from Formaldehyde. *J. Food Proc. Preserv.* **1978,** *2* (1), 63.

(53) Weiss, A. H.; Socha, R. F.; Likholobov, V. A.; Sakharov, M. M. Formose sugars from formaldehyde. *Appl. Catal.* **1981,** *1* (5), 237.

(54) Khomenko, T.; Golovina, O.; Sakharov, M.; Krylov, O.; Partridge, R.; Weiss, A. Homogeneously catalyzed formaldehyde condensation to carbohydrates: IV. Alkaline earth hydroxide catalysts used with glycolaldehyde co-catalyst. *J. Catal.***1976,** *45* (3), 356.

(55) Likholobov, V. A.; Weiss, A. H.; Sakharov, M. M. The use of temperature to simplify formose sugar composition. *React. Kinetics Catal. Lett.* **1978,** *8*, 155.

(56) Socha, R. F.; Weiss, A. H.; Sakharov, M. M. Homogeneously catalyzed condensation of formaldehyde to carbohydrates: VII. An overall formose reaction model. *J. Catal.* **1981,** *67* (1), 207.

(57) Omran, A.; Menor-Salvan, C.; Springsteen, G.; Pasek, M. The Messy Alkaline Formose Reaction and Its Link to Metabolism. *Life* **2020,** *10* (8), 125.

(58) Yamashita, K.; Wakao, N.; Nango, M.; Tsuda, K. Formose reaction by polymer-supported thiazolium salts. *J. Polym. Sci. A: Polym. Chem.* **1992,** *30* (10), 2247.

(59) Matsumoto, T.; Yamamoto, H.; Inoue, S. Selective formation of triose from formaldehyde catalyzed by thiazolium salt. *J. Amer. Chem. Soc.* **1984,** *106* (17), 4829.

(60) Partridge, R. D.; Weiss, A. H.; Todd, D. Branched-chain carbohydrate structures resulting from formaldehyde condensation. *Carbohydrate Res.* **1972,** *24* (1), 29.

(61) Chermside, H.; Furst, A.; Graudenz, J.; Shapira, J. Some aspects of the toxicity of formose sugars. *Western Pharmacol. Soc. Proc.*, **1970**, 13, 57.

(62) Lobanov, A. V.; Kholuiskaya, S. N.; Komissarov, G. G. Photocatalytic Synthesis of Formaldehyde from CO_2 and H_2O_2. *Doklady Phys. Chem.* **2004,** *399* (1), 266.

(63) Sheehan, S. W.; Chen, C. Apparatus and method for conversion carbon dioxide to sugars. International Patent Application Number WO 2022/133033 A1, **2022**.

(64) Zheng, T.; Zhang, M.; Wu, L.; Guo, S.; Liu, X.; Zhao, J.; Xue, W.; Li, J.; Liu, C.; Li, X.et al. Upcycling CO_2 into energy-rich long-chain compounds via electrochemical and metabolic engineering. *Nature Catal.* **2022,** *5* (5), 388.

(65) Hann, E. C.; Overa, S.; Harland-Dunaway, M.; Narvaez, A. F.; Le, D. N.; Orozco-Cárdenas, M. L.; Jiao, F.; Jinkerson, R. E. A hybrid inorganic–biological artificial photosynthesis system for energy-efficient food production. *Nature Food* **2022,** *3* (6), 461.

(66) Buchner, G. A.; Stepputat, K. J.; Zimmermann, A. W.; Schomäcker, R. Specifying Technology Readiness Levels for the Chemical Industry. *Ind. Eng. Chem. Res.* **2019,** *58* (17), 6957.

(67) Chan, F. L.; Altinkaya, G.; Fung, N.; Tanksale, A. Low temperature hydrogenation of carbon dioxide into formaldehyde in liquid media. *Catal. Today* **2018,** *309*, 242.

(68) Bontemps, S.; Sabo-Etienne, S. Trapping Formaldehyde in the Homogeneous Catalytic Reduction of Carbon Dioxide. *Angew. Chemie Int. Ed.* **2013,** *52* (39), 10253.

(69) Liu, W.; Hou, Y.; Hou, B.; Zhao, Z. Enzyme-catalyzed Sequential Reduction of Carbon Dioxide to Formaldehyde. *Chinese J. Chem. Eng.* **2014,** *22* (11), 1328.

(70) Nabavi Zadeh, P. S.; Zezzi do Valle Gomes, M.; Åkerman, B.; Palmqvist, A. E. C. Förster Resonance Energy Transfer Study of the Improved Biocatalytic Conversion of CO_2 to Formaldehyde by Coimmobilization of Enzymes in Siliceous Mesostructured Cellular Foams. *ACS Catal.* **2018,** *8* (8), 7251.

(71) Kumar, A.; Ananthakrishnan, R. Visible light-assisted reduction of CO_2 into formaldehyde by heteroleptic ruthenium metal complex–TiO_2 hybrids in an aqueous medium. *Green Chem.* **2020,** *22* (5), 1650.

(72) Kim, C. W.; Kang, M. J.; Ji, S.; Kang, Y. S. Artificial Photosynthesis for Formaldehyde Production with 85% of Faradaic Efficiency by Tuning the Reduction Potential. *ACS Catal.* **2018,** *8* (2), 968.

(73) Nakata, K.; Ozaki, T.; Terashima, C.; Fujishima, A.; Einaga, Y. High-Yield Electrochemical Production of Formaldehyde from CO_2 and Seawater. *Angew. Chemie Int. Ed.* **2014,** *53* (3), 871.

(74) Gómez-Ramírez, A.; Rico, V. J.; Cotrino, J.; González-Elipe, A. R.; Lambert, R. M. Low Temperature Production of Formaldehyde from Carbon Dioxide and Ethane by Plasma-Assisted Catalysis in a Ferroelectrically Moderated Dielectric Barrier Discharge Reactor. *ACS Catal.* **2014,** *4* (2), 402.

(75) Wang, L.; Yi, Y.; Wu, C.; Guo, H.; Tu, X. One-Step Reforming of CO_2 and CH_4 into High-Value Liquid Chemicals and Fuels at Room Temperature by Plasma-Driven Catalysis. *Angew. Chemie Int. Ed.* **2017,** *56* (44), 13679.

(76) Lee, G.; Go, D. B.; O'Brien, C. P. Direct Observation of Plasma-Stimulated Activation of Surface Species using Multi-Modal In-Situ/Operando Spectroscopy Combining Polarization-Modulation Infrared Reflection-Absorption Spectroscopy, Optical Emission Spectroscopy, and Mass Spectrometry. *ACS Appl. Mater. Interf.* **2021**, *13* (47), 56242.

(77) Siebert, M.; Seibicke, M.; Siegle, A. F.; Kräh, S.; Trapp, O. Selective Ruthenium-Catalyzed Transformation of Carbon Dioxide: An Alternative Approach toward Formaldehyde. *J. Amer. Chem. Soc.* **2019,** *141* (1), 334.

(78) Rauch, M.; Strater, Z.; Parkin, G. Selective Conversion of Carbon Dioxide to Formaldehyde via a Bis(silyl)acetal: Incorporation of Isotopically Labeled C1 Moieties Derived from Carbon Dioxide into Organic Molecules. *J. Amer. Chem. Soc.* **2019,** *141* (44), 17754.

(79) Millar, G. J.; Collins, M. Industrial Production of Formaldehyde Using Polycrystalline Silver Catalyst. *Ind. Eng. Chem. Res.* **2017,** *56* (33), 9247.

(80) Heim, L. E.; Konnerth, H.; Prechtl, M. H. G. Future perspectives for formaldehyde: pathways for reductive synthesis and energy storage. *Green Chem.* **2017,** *19* (10), 2347.

(81) Vogt, C.; Monai, M.; Kramer, G. J.; Weckhuysen, B. M. The renaissance of the Sabatier reaction and its applications on Earth and in space. *Nature Catal.* **2019,** *2* (3), 188.

(82) Jarvis, S. M.; Samsatli, S. Technologies and infrastructures underpinning future CO_2 value chains: A comprehensive review and comparative analysis. *Renew. Sus. Energy Rev.* **2018,** *85*, 46.

(83) Cherevotan, A.; Raj, J.; Dheer, L.; Roy, S.; Sarkar, S.; Das, R.; Vinod, C. P.; Xu, S.; Wells, P.; Waghmare, U. V.et al. Operando Generated Ordered Heterogeneous Catalyst for the Selective Conversion of CO_2 to Methanol. *ACS Energy Lett.* **2021,** *6* (2), 509.

(84) Xie, S.; Zhang, W.; Lan, X.; Lin, H. CO_2 Reduction to Methanol in the Liquid Phase: A Review. *ChemSusChem* **2020,** *13* (23), 6141.

(85) Behrens, M. Heterogeneous Catalysis of CO_2 Conversion to Methanol on Copper Surfaces. *Angew. Chemie Int. Ed.* **2014,** *53* (45), 12022.

(86) Pérez-Fortes, M.; Schöneberger, J. C.; Boulamanti, A.; Tzimas, E. Methanol synthesis using captured CO_2 as raw material: Techno-economic and environmental assessment. *Appl. Energy* **2016,** *161*, 718.

(87) Jin, R.; Easa, J.; O'Brien, C. P. Highly Active CuO_x/SiO_2 Dot Core/Rod Shell Catalysts with Enhanced Stability for the Reverse Water Gas Shift Reaction. *ACS Appl. Mater. Interf.* **2021,** *13* (32), 38213.

(88) Tian, J.; Tan, J.; Zhang, Z.; Han, P.; Yin, M.; Wan, S.; Lin, J.; Wang, S.; Wang, Y. Direct conversion of methane to formaldehyde and CO on B_2O_3 catalysts. *Nature Comm.* **2020,** *11* (1), 5693.

(89) Zhao, Y.-X.; Li, Z.-Y.; Yuan, Z.; Li, X.-N.; He, S.-G. Thermal Methane Conversion to Formaldehyde Promoted by Single Platinum Atoms in $PtAl_2O_4^-$ Cluster Anions. *Angew. Chemie Int. Ed.* **2014,** *53* (36), 9482.

(90) Bahmanpour, A. M.; Hoadley, A.; Mushrif, S. H.; Tanksale, A. Hydrogenation of Carbon Monoxide into Formaldehyde in Liquid Media. *ACS Sus. Chem. Eng.* **2016,** *4* (7), 3970.

(91) Bahmanpour, A. M.; Hoadley, A.; Tanksale, A. Formaldehyde production via hydrogenation of carbon monoxide in the aqueous phase. *Green Chem.* **2015,** *17* (6), 3500.

(92) Masel, R. I.; Ni, Z. R.; Chen, Q.; Rosen, B. A. Hydrogenation of Formic Acid to Formaldehyde. United States Patent No. US 9,193,593 B2, **2015**.

(93) Tester, R. F.; Karkalas, J.; Qi, X. Starch—composition, fine structure and architecture. *J. Cereal Sci.* **2004,** *39* (2), 151.

(94) Tomberlin, K. E.; Venditti, R.; Yao, Y. Life cycle carbon footprint analysis of pulp and paper grades in the united states using production-line-based data and integration. *BioResources* **2020,** *15* (2), 3899.

(95) Patlar, S.; Yalçin, H.; Boyali, E. The effect of glycerol supplements on aerobic and anaerobic performance of athletes and sedentary subjects. *J. human kinetics* **2012,** *34*, 69.

(96) Greenfield, H.; Southgate, D. A. T. **2003**. *Food Composition Data: Production, Management and Use, Second Edition*; Food and Agriculture Organization of the United Nations.

(97) Tao, R. C.; Kelley, R. E.; Yoshimura, N. N.; Benjamin, F. Glycerol: Its Metabolism and Use as an Intravenous Energy Source. *J. Parenteral Enteral Nutrition* **1983,** *7* (5), 479.

(98) Brisson, D.; Vohl, M.-C.; St-Pierre, J.; Hudson, T. J.; Gaudet, D. Glycerol: a neglected variable in metabolic processes? *BioEssays* **2001,** *23* (6), 534.

(99) Min, Y.; Yan, F.; Liu, F.; Coto, C.; Waldroup, P. Glycerin-a new energy source for poultry. *Int. J. Poultry Sci.* **2010,** *9* (1), 1.

(100) Lin, E. C. C. Glycerol Utilization and its Regulation in Mammals. *Ann. Rev. Biochem.* **1977,** *46* (1), 765.

(101) Kholif, A. E. Glycerol use in dairy diets: A systemic review. *Animal Nutrition* **2019,** *5* (3), 209.

(102) Schoevaart, R.; van Rantwijk, F.; Sheldon, R. A. A Four-Step Enzymatic Cascade for the One-Pot Synthesis of Non-natural Carbohydrates from Glycerol. *J. Org. Chem.* **2000,** *65* (21), 6940.

(103) Babich, L.; van Hemert, L. J. C.; Bury, A.; Hartog, A. F.; Falcicchio, P.; van der Oost, J.; van Herk, T.; Wever, R.; Rutjes, F. P. J. T. Synthesis of non-natural carbohydrates from glycerol and aldehydes in a one-pot four-enzyme cascade reaction. *Green Chem.* **2011,** *13* (10), 2895.

(104) Schoevaart, R.; van Rantwijk, F.; Sheldon, R. A. Carbohydrates from glycerol: an enzymatic four-step, one-pot synthesis. *Chem. Commun.* **1999,** (24), 2465.

(105) Bagnato, G.; Iulianelli, A.; Sanna, A.; Basile, A. Glycerol Production and Transformation: A Critical Review with Particular Emphasis on Glycerol Reforming Reaction for Producing Hydrogen in Conventional and Membrane Reactors. *Membranes* **2017,** *7* (2).

(106) Eoff, J. R.; Linder, W. V.; Beyer, G. F. Production of Glycerin from Sugar by Fermentation. *J. Ind. Eng. Chem.* **1919,** *11* (9), 842.

(107) Taherzadeh, M. J.; Adler, L.; Lidén, G. Strategies for enhancing fermentative production of glycerol—a review. *Enzyme Microbial Tech.* **2002,** *31* (1), 53.

(108) Wang, Z.; Zhuge, J.; Fang, H.; Prior, B. A. Glycerol production by microbial fermentation: A review. *Biotech. Adv.* **2001,** *19* (3), 201.

(109) Wright, L. W. **1972**. *Tungsten oxide promoted and supported nickel catalyst* (U.S. Patent No. 3,691,100). U.S. Patent and Trademark Office.

(110) Chao, J. C.; Huibers, D. T. **1982**. *Catalytic hydrogenolysis of alditols to produce glycerol and polyols* (U.S. Patent No. 4, 366,332). U.S. Patent and Trademark Office.

(111) Gracey, B. P.; Hudson, B.; Williams, P. S. **1992**. *Sunthesis of glycerol from formaldehyde* (U.S. Patent No. 5,097,089). U.S. Patent and Trademark Office.

(112) Koempel, H.; Liebner, W. Lurgi's Methanol to Propylene (MTP®) Report on a Successful Commercialisation. *Studies Surf. Sci. Catal.* **2007**, *167*, 261.

(113) Jasper, S.; El-Halwagi, M. M. A Techno-Economic Comparison between Two Methanol-to-Propylene Processes. *Processes* **2015,** *3* (3), 684.

(114) Tian, P.; Wei, Y.; Ye, M.; Liu, Z. Methanol to Olefins (MTO): From Fundamentals to Commercialization. *ACS Catal.* **2015,** *5* (3), 1922.

(115) Gogate, M. R. Methanol-to-olefins process technology: current status and future prospects. *Petrol. Sci. Tech.* **2019,** *37* (5), 559.

(116) Kneupper, C.; Saathoff, L. Allyl Chloride. In *Kirk-Othmer Encyclopedia of Chemical Technology*, https://doi.org/10.1002/0471238961.0112122511140521.a01.Accessed 1 Sept. 2022.

(117) Piccinini, N.; Anatra, U.; Malandrino, G.; Barone, D. Safety analysis for an allyl chloride plant. *Plant/Operations Progr.* **1982,** *1* (1), 69.

(118) Tymstra, F. T.; Office, U. S. P., Ed. USA, 1952.

(119) Boland, M. J.; Rae, A. N.; Vereijken, J. M.; Meuwissen, M. P. M.; Fischer, A. R. H.; van Boekel, M. A. J. S.; Rutherfurd, S. M.; Gruppen, H.; Moughan, P. J.; Hendriks, W. H. The future supply of animal-derived protein for human consumption. *Trends Food Sci. Tech.* **2013,** *29* (1), 62.

(120) Reijnders, L.; Soret, S. Quantification of the environmental impact of different dietary protein choices. *Amer. J. Clin. Nutr.* **2003,** *78* (3), 664S.

(121) Semba, R. D. The rise and fall of protein malnutrition in global health. *Annals Nutr. Metab.* **2016,** *69* (2), 79.

(122) Ritala, A.; Häkkinen, S. T.; Toivari, M.; Wiebe, M. G. Single cell protein—state-of-the-art, industrial landscape and patents 2001–2016. *Frontiers Microbiol.* **2017,** *8*, 2009.

(123) ICI to scale up single cell protein process. *Chem. Eng. News Arch.* **1976,** *54* (42), 25.

(124) Westlake, R. Large-scale Continuous Production of Single Cell Protein. *Chemie Ingenieur Technik* **1986,** *58* (12), 934.

(125) Spalvins, K.; Zihare, L.; Blumberga, D. Single cell protein production from waste biomass: comparison of various industrial by-products. *Energy Procedia* **2018,** *147*, 409.

(126) Matassa, S.; Batstone, D. J.; Hülsen, T.; Schnoor, J.; Verstraete, W. Can Direct Conversion of Used Nitrogen to New Feed and Protein Help Feed the World? *Envir. Sci. Tech.* **2015,** *49* (9), 5247.

(127) Molitor, B.; Mishra, A.; Angenent, L. T. Power-to-protein: converting renewable electric power and carbon dioxide into single cell protein with a two-stage bioprocess. *Energy Envir. Sci.* **2019,** *12* (12), 3515.

(128) Papanikolaou, S.; Aggelis, G. Lipid production by Yarrowia lipolytica growing on industrial glycerol in a single-stage continuous culture. *Bioresource Tech.* **2002,** *82* (1), 43.

(129) Gajdoš, P.; Nicaud, J.-M.; Čertík, M. Glycerol conversion into a single cell oil by engineered Yarrowia lipolytica. *Eng. Life Sci.* **2017,** *17* (3), 325.

(130) Meesters, P. A. E. P.; Huijberts, G. N. M.; Eggink, G. High-cell-density cultivation of the lipid accumulating yeast Cryptococcus curvatus using glycerol as a carbon source. *Appl. Microbiol. Biotech.* **1996,** *45* (5), 575.

(131) Sillman, J.; Nygren, L.; Kahiluoto, H.; Ruuskanen, V.; Tamminen, A.; Bajamundi, C.; Nappa, M.; Wuokko, M.; Lindh, T.; Vainikka, P.et al. Bacterial protein for food and feed generated via renewable energy and direct air capture of CO_2: Can it reduce land and water use? *Global Food Secur.* **2019,** *22*, 25.

(132) Nasseri, A.; Rasoul-Amini, S.; Morowvat, M.; Ghasemi, Y. Single cell protein: production and process. *Amer. J. Food Tech.* **2011,** *6* (2), 103.

(133) Grimmer, H. R.; Thiagarajan, N.; Nitschke, E. Conversion of Methanol to Liquid Fuels by the Fluid Bed Mobil Process (A Commercial Concept). *Studies Surf. Sci. Catal.* **1988**, *36*, 273.

(134) Yurchak, S. Development of Mobil's Fixed-Bed Methanol-to-Gasoline (MTG) Process. *Studies Surf. Sci. Catal.* **1988**, *36*, 251.

(135) Liederman, D.; Yurchak, S.; Kuo, J. C.; Lee, W. Mobil methanol-to-gasoline process. *J. Energy* **1982,** *6* (5), 340.

(136) IEA **2021**. *Solar PV*. IEA. Paris. https://www.iea.org/reports/solar-pv. Accessed 1 Sept. 2022.

(137) IEA **2021**. *Wind Power*. IEA. Paris. https://www.iea.org/reports/wind-power. Accessed 1 Sept. 2022.

(138) The White House. **2021**. *FACT SHEET: President Biden Signs Executive Order Catalyzing America's Clear Energy Economy Through Federal Sustainability*. https://www.whitehouse.gov/briefing-room/statements-releases/2021/12/08/fact-sheet-president-biden-signs-executive-order-catalyzing-americas-clean-energy-economy-through-federal-sustainability/?utm_source=link. Accessed 1 Sept. 2022.

4 Selected Quotes

“In principle, starch and sugar could be produced artificially from CO_2 with greater efficiency and with much lower environmental impacts than industrial agriculture.”

“A high degree of control over the product stereochemistry is critical for synthesis of safe and digestible carbohydrates.”

“The deployment of artificial carbohydrate synthesis at Gt/y scales will require a successful global energy decarbonization with inexpensive and plentify renewable energy.”

“This work strongly motivates future research to develop catalytic materials and processes and to conduct more rigorous technoeconomic analysis considering lifecycle emissions, capital costs, and additional costs to accommodate the non-dispatchable nature of renewable energy.”