

Single-Step Production of Alcohols and Paraffins from CO₂ and H₂ at Metric Ton Scale

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ecarbonization of the energy industry is one of the greatest challenges of the modern era and must be achieved to address climate change.¹ Accomplishing this task will require development of new technologies across energy generation and storage, as well as carbon capture and utilization, together with the redeployment of old technologies that enable low-carbon infrastructure. There has been incredible traction over the past several years for the electrification of light vehicle transportation using batteries, for example, to enable utilization of renewable electricity for transportation rather than fossil fuels.² However, there are significant infrastructural and technological challenges to electrify other modes of transportation, which accounts for approximately 14% of global greenhouse gas emissions.³ This is especially true in cases where the low energy density of batteries precludes their use, due to the substantial mass that would be required to store sufficient energy for mobility.

Applications such as aviation, rocket propulsion, heavy maritime transport, and others require high energy density fuels, and electrofuels derived from carbon dioxide and water can enable production of circular, high energy density compounds that are compatible with much of today's chemical and fuel infrastructure.⁴⁻⁸ Several high-impact areas of academic research, including renewable Power-to-X,^{9,10} CO₂ electroreduction,^{11,12} green H_2 production,¹³ and solar fuels or artificial photosynthesis,¹⁴ are dedicated to producing these chemicals and fuels using only renewable energy and globally available resources.¹⁵ Systems that convert CO_2 and H_2O into hydrocarbons and are, at a high level, similar to the fundamental photosynthetic processes enabling life on our planet, in that their only chemical byproduct is O_2 . Plants use photosynthesis to convert CO₂, H₂O, and solar energy into chemical energy by creating sugars, cellulose, and other complex carbon-based compounds. This effectively stores the energy from the sun in the chemical bonds of a carbon-based compound. While this process has been supporting the Earth's ecosystem and balancing carbon dioxide concentration in our atmosphere for billions of years, the rate at which humanity is releasing CO_2 into the atmosphere by burning fossil fuels is too high for plant-based photosynthesis to mitigate. Carbon dioxide capture and utilization technologies, on the other hand, can capture and convert CO_2 at much higher rates.¹⁶

Once CO_2 is captured, there are several pathways to produce alcohols or hydrocarbon fuels. The most readily available technologies include reverse water-gas shift (RWGS), that first converts the CO_2 into CO using green H₂, with the aim of



Figure 1. Industrial methods to convert CO_2 , H_2O , and renewable electricity into synthetic fuel, including ethanol, methanol, or fuelrange paraffins. Water electrolysis coupled with legacy RWGS and FT is shown in (a), while more novel two-step methods include CO_2 electrolysis (b) and CO_2 hydrogenation (c).

using additional H_2 to produce syngas that can then be transformed into chemicals or fuels using systems like technologically proven Fischer–Tropsch (FT) or methanol production systems (Figure 1a).¹⁷ Another approach to high energy density fuels based on CO₂ electrolysis first produces CO from CO₂ that can be combined with green H_2 ,¹⁸ or directly produces a combination of CO and H_2 .¹⁹ As a second step, the CO and H_2 syngas is converted to fuels using conventional FT or methanol synthesis (Figure 1b). A third and less common approach is the one we have taken, direct CO₂ hydrogenation using green H_2 to produce compounds typically made from syngas, such as higher alcohols including ethanol, and paraffins (Figure 1c).

Since 2017, we have been researching hydrogenation technology for CO_2 conversion with the goal to achieve world-scale production of commodity chemicals and fuels, starting with alcohols and alkanes.^{20–22} Over the course of the research and development process, a substantial amount of high-purity ethanol is generated from R&D operations. This prompted the launch of three consumer goods, vodka, spirits,

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Figure 2. Left: The ACCTC at the Shepard Energy Centre 860 MW power plant, where a slipstream of flue gas is used for CO₂ utilization pilot systems. Right: The CO₂ hydrogenation skid and product tote inside its enclosure. (Image credit: Air Company)

and sanitizer that are made using the ethanol that we produce as a byproduct of the R&D process. All three are the first of their kind, made using ethanol produced in a single reaction step from CO_2 . The primary product of our laboratory-scale, prototype, and pilot systems, however, is the data that results, and the learnings developed to drive further scale-up of the technology.

Pilot-Scale Deployment. In 2021, we deployed our CO₂ hydrogenation technology on the pilot scale, converting CO₂ captured from the flue gas of the Shepard Energy Centre, an 860 MW a natural gas-fired power plant in Calgary, Alberta, Canada (Figure 2).²³ The Alberta Carbon Conversion Technology Centre (ACCTC) draws a slipstream of flue gas containing approximately 6.6% CO₂ into a monoethanolamine (MEA)-based scrubbing system, removing approximately 80% of the CO₂ in the flue gas to provide a water-saturated stream of CO₂ with oxygen and nitrogen impurities.²⁴ The CO₂ stream was fed into the pilot fixed bed flow reactor skid. The engineering, procurement, and construction (EPC) firm selected for the prototype and pilot systems was Zeton, Inc.²⁵ The reactor was charged with approximately 100 kg of our catalyst, which was synthesized in-house. The catalyst itself is a confidential mixture of earth-abundant metals supported on alumina; the patent-pending composition and method of manufacture is currently proprietary. The pilot reactor first began producing alcohol products in the beginning of December of 2020.

Saturated CO_2 was output from the amine capture system at ambient pressure and fed into three stages of compression to reach pressures adequate for alcohol synthesis. Intermittent spikes in O_2 , N_2 , and NO_x required that the catalyst and system be designed with suitable robustness to handle feedstock gas impurity concentrations over 1%. Our New York facilities, on the other hand, all utilize biogenic CO_2 captured from corn fermentation facilities which is higher purity at the source. We previously conducted a quantitative comparison between biogenic and postcombustion CO_2 capture, using data from our deployment, and published the results.²⁴ As we scale up, we aim to primarily use a mixture of biogenic and air-captured CO_2 , with capture from flue gas as a secondary source.

The pilot system was deployed for over 8000 h with a CO_2 design capacity of 960 kg/day for maximized production under single-pass conversion conditions, and 175 kg/day for maximized carbon efficiency when product gases are recycled.

During the deployment, the system achieved the stability required at-scale for further commercialization. Extensive data was collected to assess catalyst stability and the effect of changes in temperature, pressure, feed gas ratios, and impurity content. In December of 2021, the system was temporarily shut down and transported to Brooklyn, New York, where it will continue to operate for R&D and to produce feedstock materials for our products.

The CO₂ conversion process that we use in our prototype and pilot reactors enables conversion of >90% of inlet CO₂ to products, with straightforward recovery of the remaining <10% at larger scale, leading to a carbon efficiency >90% for the process. This is achieved by engineering the catalyst and reactor to enable full recycle of the unreacted CO₂, H₂, and any byproduct gases back into the reactor inlet (Figure 3)



Figure 3. High-level process diagram showing (a) inputs and outputs from the pilot system during its Calgary R&D deployment, and (b) the system's permanent site in New York. High-purity ethanol is distilled downstream from the mixture of alcohols and water.

simplifying the process in that there is no venting of any tail gas except for a small (<100 mL/min) slipstream for gas detection.²⁶ Because of the high solubility of CO_2 in product liquid, the product comes out of the gas–liquid separation system as a carbonated mixture of water, paraffins, and alcohols with minimal dissolved H₂. While utilizing quantities of CO_2 on the order of 100s of kilograms per day at the pilot scale, continuous recovery of the dissolved CO_2 was not required for the product alcohols and paraffins to be cradle-to-gate carbon negative in internal lifecycle analyses (LCA). However, at

larger scales, the dissolved CO_2 will be recovered and fed into the reactor to optimize carbon yield.

When operating in full recycle, i.e., all the fed-in CO_2 and H_2 are converted into liquids with tail gas vents closed, the system utilized approximately 175 kg of CO_2 per day, generating approximately 40 gallons of liquid products and filling a standard 275-gallon tote in less than 1 week. Figure 4 shows



Figure 4. Weeklong consumption and production of water, alcohols, and paraffins from the pilot system. Over the course of a week, over 1 metric ton of product is made.

the CO_2 and H_2 consumption, as well as the liquid production from a typical week of operations recycling all unreacted feed gas, except for the CO_2 dissolved in the aqueous liquid product that was vented on the pilot scale but will be recovered on larger scales. Liquid production fluctuated ± 5 gallons depending on several factors, such as reactor heat and pressure variations. These occurred as the outside temperature fluctuated over the course of routine operations in an unweathered tent, deployed outdoors in Calgary.

By changing reactor and catalyst conditions, we further demonstrated control over the relative distribution of alcohols (methanol, ethanol, and *n*-propanol) and paraffins, while additional research in our New York R&D facility aims to identify reactor conditions that optimize output of individual compounds while suppressing impurities. For example, under certain conditions, ethanol production could be optimized for production of consumer products, while under others, paraffin production could be optimized to produce larger quantities of long-chain hydrocarbons from CO₂. Separation of the paraffins from the product liquid was performed using simple oil-water separation, while alcohols (primarily methanol and ethanol) are separated via distillation to achieve AA grade methanol, and United States Pharmacopeia (USP) grade ethanol. While the ethanol is used as feedstock for our consumer goods, volumes on the order of 100 gallons of fuel-range paraffins produced from CO₂ are currently undergoing further testing for suitability as sustainable aviation fuel.

Ethanol, methanol, and fuel-range paraffins are produced in significant quantities, with the paraffins ranging from hexane to octacosane and the majority of the compounds present being between octane and eicosane. Aviation fuel, specifically Jet-A, is comprised partially of alkanes with carbon numbers between 8 and 18.²⁷ With recent focus on decarbonization of the aviation industry,²⁸ our technology has the capability to

produce potential sustainable aviation fuel (SAF) feedstock efficiently, directly from CO_2 and H_2 , with the aim to ultimately produce a synthetic paraffinic kerosene (SPK) suitable for transportation use. As we improve our technology, we believe it has the potential to replace legacy Fischer– Tropsch systems by simplifying a two-step conversion process (RWGS and FT) into a single step of CO_2 hydrogenation to fuel-grade paraffins. Notably, if CO_2 is fed into a system with a standard FT catalyst product selectivity is pushed toward methane production, inhibiting the FT chain growth process.²⁹ Our process and catalyst suppress methane production, so that none is detected in our recycle system. Ultimately, the economics of CO_2 and H_2 conversion to fuels may be improved by this one-step process.

Product distribution from the FT process is characterized by chain growth of CH_x reaction intermediates on the surface of the FT catalyst. It is generally accepted that *CH₂ surfacebound monomers undergo chain growth by CO insertion and subsequent reduction with H_2 into $*C_vH_z$ intermediates of different carbon numbers.³⁰ These intermediates undergo further hydrogenation or dehydrogenation to form paraffins, olefins, and other hydrocarbon compounds. In the FT process, the C-C coupling of active species on the surface of the FT catalyst is challenging to control, which leads to a statistical distribution of hydrocarbon products. The distribution of hydrocarbons in FT is predicted by the Anderson-Schulz-Flory (ASF) model.³¹ The ASF model depends on chain growth probability, which is influenced by the nucleophilicity of the catalyst, reductive chemical potential of the active site, the effectiveness of the catalyst for C-C coupling, and other reaction conditions.

In a typical ASF distribution, lighter hydrocarbons (smaller than pentane) are produced with high selectivity if there is a low chain growth probability. At larger chain growth probabilities, heavier hydrocarbons with a carbon number greater than 21 are expected. Current industrial FT processes that make synthetic crude oil produce widely distributed hydrocarbon products with a carbon number between 1 and 80.³² This requires substantial downstream treatment, such as fractionation and hydrotreating, to produce a hydrocarbon mixture suitable for use as aviation fuel. As such, the overall economics of FT processes is decreased when specific types of fuel are desired. For example, an industrial FT process that follows the ASF model without any significant deviation has a maximum primary reactor selectivity for products with a carbon number between 10 and 20 of approximately 39%, requiring further downstream refining to get a narrow distillate range cut for fuel production.³³

The process by which paraffin production occurs in our system appears distinct from typical FT systems (Figure 5) and may instead be related to alcohol formation. Conventional FT systems generate paraffins through chain growth of $*CH_2$ by repeated insertion of CO followed by further reduction. This process usually generates side-product olefins via β -hydride elimination and olefin isomerization.³⁴ The produced internal olefins can further react to form methyl-alkanes, which account for the majority of the branched alkanes in an FT product stream. However, in our system, only straight chain paraffins were observed under operating conditions. This suggests that secondary hydrogenation has much faster kinetics than olefin isomerization. Additional internal research tuning down our catalysts' reductive potential resulted in terminal olefins, alcohols, carboxylic acids in differing ratios. This indicated



Figure 5. Gas chromatogram with peak identification by mass spectrometry for paraffins produced from CO_2 in the pilot plant. Inset: Photograph of liquid sample collected under paraffin-selective conditions showing aqueous and nonaqueous layers.

that potential chain growth and alcohol formation pathways may proceed through olefin and carboxylic acid intermediates. The observed olefins could, therefore, be generated by dehydrogenation as observed in traditional FT systems, or via a more novel alcohol dehydration mechanism, since methanol, ethanol and other higher alcohols are required coproducts in the output stream. Through continued R&D efforts, we hope to gain further mechanistic insights that will allow us to fine-tune our process.

Ultimately, what our team has demonstrated through the deployment of this pilot system is a simplified and direct conversion of CO_2 to alcohols and paraffins on an industrially relevant scale. Within a process that mimics photosynthesis but operates at a higher rate and efficiency, our goal is to eliminate the need for additional RWGS and FT steps when using CO_2 as a feedstock. The pilot system operated with high per pass conversion and high carbon efficiency, achieving over 8000 h of operation, allowing for the conversion of over 50 tons of CO_2 to alcohols and paraffins, demonstrating both the stability and scalability of our process.

Importantly, we gained insight into reactor and catalyst operational conditions that promote selectivity toward specific products, allowing us to suppress unwanted side products such as methane, and to fine-tune the ratio of alcohols to paraffins. As part of this deployment, we collected a significant amount of catalyst stability and performance data that enables us to gain further understanding of our system as we scale-up. This pilot-scale deployment has allowed us to demonstrate the scalability of our single-step process, and we are now pursuing further scale-up to make meaningful impact toward climate change mitigation.

Outlook. Fischer–Tropsch and syngas-to-alcohols technologies have served the oil and gas industry for decades for production of synthetic chemicals and fuels. With this pilot deployment, our new CO_2 hydrogenation process has been shown to be industrially robust and scalable, with the aim to replace Fischer–Tropsch and syngas-to-alcohols technologies with a single-step alternative in cases where CO_2 is the preferred carbonaceous feedstock rather than CO. We are

currently in the process of scaling the catalyst and technology from the pilot scale to a substantially larger commercial demonstration system. As the byproduct of this scale-up R&D, our consumer goods act as first examples of premium products made sustainably from CO_2 and enable consumers to support the development of this technology toward scales that can have a true impact toward addressing climate change.

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Notes

The authors declare the following competing financial interest(s): U.S. Patent Application No. 63/298,402 by S.W.S., C.C, and M.G. contains work described in this paper. Views expressed in this Energy Focus are those of the authors and not necessarily the views of the ACS.

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