Utilization of Bio-CO_2 and Bio-Methane for Fuel Production: Integration Solid Oxide Electrolyzer, Low Energy Plasma Reformer with Fischer-Tropsch Synthesis

S. Elangovan, J. Hartvigsen, M. Hollist, and J. Elwell

OxEon Energy, 257 River Bend Way, Suite 300, North Salt Lake City, UT 84054, USA

Transition to renewable energy is essential to achieve climate protection objectives. Besides storing electricity for later use, fuel production using renewable energy is an essential part of reducing fossil dependance. The highest value application in current markets is the production of liquid transportation fuels such as sustainable aviation fuels (SAF) from sustainable, ideally biogenic carbon resources. A system is presented for processing anaerobic digester gas for liquid hydrocarbon production. Bio-CO_2 is processed through a solid oxide electrolysis cell and bio-CH_4 through a low energy plasma reformer. The combined synthesis gas is supplied to a Fischer-Tropsch reactor for the production of liquid hydrocarbons. The combination of technologies nearly doubles the yield of biofuel by utilizing the bio-CO_2 in addition to the bio-CH_4. The product fuel is all bio-carbon but it also embodies renewable electric energy in a high-value, storable and transportable liquid hydrocarbon.

Introduction

OxEon Energy's team has led the development of solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC) technology for over 30 years. The reversibility of the solid oxide cell stacks allows for both power production and the generation of H_2 using the same device (1). Additionally, the SOEC stack developed by OxEon for MOXIE (Mars Oxygen ISRU Experiment) has demonstrated the use of Mars atmosphere CO_2 as an electrolysis feedstock (2), expanding the scope of operation for SOECs. These reversible Solid Oxide Cell (rSOC) devices can be paired with catalyst reactors to produce additional chemicals and fuel, such as the Fischer-Tropsch synthesis (FTS) of liquid hydrocarbons from SOEC generated synthesis gas. An illustration showing how these technologies can interface for cross-sector energy conversion is shown in Figure **1**.

Transition away from fossil fuels to renewable energy is essential to achieve climate protection objectives. Besides storing electricity for later use, fuel production using renewable energy is an essential part of reducing fossil dependance. Hydrogen production is receiving the greatest attention as a carbon free energy carrier with the potential to fuel future fleets of hydrogen fuel cell vehicles, to store grid electricity to accommodate asynchronous generation and load, and to a lesser extent to displace heating fuels. However, the highest value application in current markets is the production of liquid transportation fuels such as sustainable aviation fuels (SAF) and low (fossil) carbon diesel fuel. Liquid hydrocarbon fuels only achieve the decarbonization goals if they replace fossil fuels and are produced from sustainable, ideally biogenic carbon resources.

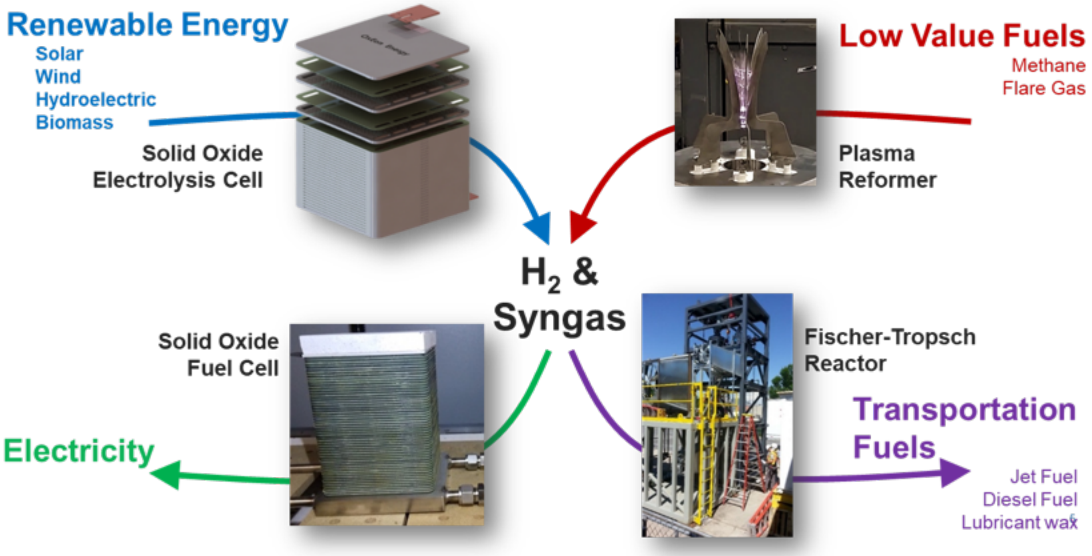

Figure 1. Cross-sector energy conversion solutions possible with four complementary technologies: SOEC, SOFC, plasma reformation, and Fischer Tropsch reactor.

OxEon's technologies are being applied to bridge the electrical and materials energy sectors to provide pathways for renewable electric energy as a storable and transportable liquid hydrocarbon that can be used in the existing vehicle fleet that will be on the road and in the air for decades to come. A power to fuels technology to convert biogenic carbon to high value, energy dense, liquid transportation fuels is presented. Anaerobic digester gas is the feedstock for the system, processing the bio-CO_2 through an SOEC and the bio-CH_4 through a low energy plasma reformer for the production of synthesis gas, also known as syngas. The combined syngas streams are supplied to a Fischer-Tropsch (FT) reactor for production of liquid hydrocarbons. The combination of technologies offer several advantages: the yield of biofuel nearly doubles by use of the bio-CO_2 compared to bio-CH_4 alone, cooling the FT reactor generates all the steam needed in the SOEC reducing the effective operating voltage (accounting for raising steam) from > 1.5 V/cell to < 1.3 V/cell, oxygen by-product from the SOEC is used in the autothermal reformer, as is some of the FT produced water. The product fuel is all bio-carbon, demonstrating a pathway for production of liquid hydrocarbons from renewable electric energy.

SOEC and SOFC systems

OxEon Energy uses a scandia-stabilized zirconia (ScSZ) electrolyte-based cell design (approximately 130 mm x 130 mm), with nickel-cermet fuel electrode and perovskite-based air electrodes. Green electrolyte is tape cast, then fired to produce a dense electrolyte approximately 250 microns thick. Electrode inks are applied via screen printing, then fired to form porous electrode layers. Heritage SOEC stacks utilized ferritic stainless-steel interconnects, which though reasonably thermally matched to the cell materials, still exhibited enough thermal expansion difference to prevent the use of a hermetic glass seal between the layers. As a result, heritage stacks have open anode channels, necessitating a collection mechanism external to the stack for the high purity O_2 produced. The MOXIE system requirements of operating in a near vacuum environment, through multiple, rapid thermocycles, resulted in significant changes to heritage SOEC stack design. A new interconnect material, specifically created to have a near perfect thermal expansion to the ScSZ electrolyte supported cell, was first developed for use in the MOXIE stack. Because of the optimized thermal match, the high chromium (95Cr-5Fe-Y_2O_3, CFY) interconnect and the ScSZ electrolyte supported cell can achieve a hermetic glass seal, allowing for a fully sealed anode perimeter capable of internally manifolded O_2 collection within the stack (3).

SOEC stack operation for CO_2 electrolysis has two major operational challenges: oxidation of the cathode (CO_2 reduction electrode) in the presence of dry CO_2 and formation of coke when the extent of electrolysis reached beyond a certain CO/CO_2 ratio (4, 5, 6). Both oxidation (near the CO_2 inlet) and coking (near the CO_2 outlet), would not only deactivate the cathode, they could also disrupt the cathode microstructure resulting in permanent damage. The MOXIE system incorporated a product recycle to introduce reducing gas (CO) to the stack with the CO_2 feed to prevent oxidation and limited the extent of CO_2 utilization to avoid the formation of coke. Work conducted under a recently completed NASA SBIR succeeded in developing a redox tolerant cathode, still using a nickel-based electrode with a modified composition. Stacks incorporating the new cathode composition have demonstrated complete recovery from oxidation events as well as demonstrated operation at voltages above the theoretical carbon formation limit (7). Stacks have also been run with the new cathode material in steam electrolysis, dry-CO_2 electrolysis, and a range of H_2O/CO_2 coelectrolysis modes. Steam electrolysis demonstrates the highest steam conversion and when run in a multi-stage stack system, >99% steam utilization has been demonstrated (8). Dry CO_2 electrolysis operation is limited by the CO reduction potential, although limited operation above that potential has been demonstrated to date without a carbon forming event. Co-electrolysis operation has shown that the product H_2/CO ratio tracks the inlet H_2O/CO_2 ratio, providing the ability to tailor the syngas composition based on downstream operations. Co-electrolysis has also shown to have a productivity nearer dry CO_2 than steam, with a modest performance dependence on the H_2O/CO_2 feed ratio observed. A current density sweep is shown for the three operation modes (steam, dry-CO_2, and coelectrolysis with a 3:1 $H_2O:CO_2$ feed ratio) in Figure 2.

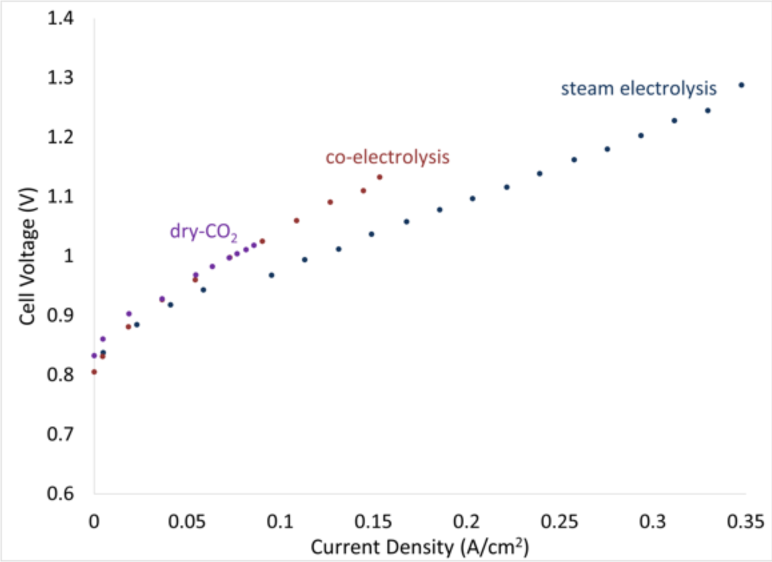

Figure 2. Comparison of current sweeps for steam, dry-CO_2, and co-electrolysis (3:1 $H_2O:CO_2$ feed) SOEC operation.

The new interconnect material and design employed for the MOXIE mission stack has since been scaled to match the 130 mm x 130 mm total cell footprint for OxEon's heritage stacks with support from a NASA NextSTEP award. This work was geared towards scale-up of the demonstration sized MOXIE stack to mission-scaled stacks capable of supporting a manned mission to Mars. The size of the mission scale stacks was ultimately limited by the interconnect size that could be manufactured with the available production presses used to press the powder metal. The scale-up in stack size resulted in a cell area five times larger than the MOXIE system cell area. Stack heights have also been increased to 65-cells, 6.5 times taller than the 10-cell MOXIE stacks, for a total stack capacity 33-times greater than the original demonstration stack (see Figure 3). It is of note that there is no loss of efficiency between the MOXIE-scale and mission-scale stacks as efficiency is a function of the cell operating voltage and both are operated well below the thermal neutral voltage. The cell current scales with area and the mission-scale stacks have demonstrated the expected 5x increase in current per cell relative to the MOXIE cells. Similarly, the total voltage scales with the number of cells in each stack, and no unexpected effects have been seen with the largest stacks operated to date.


Figure 3. Comparison of SOXE stacks from MOXIE (left) and mission-scale (right).

The successes of the MOXIE stack installed and operating on NASA's Perseverance Rover are applicable to efficient resource utilization on this world. As fuel costs rise and the proportion of energy from renewables increases, the business case for using SOEC with SOFC becomes more attractive. Storing off-peak nuclear and intermittent renewable energy by electrolysis of steam and CO_2 using SOEC devices is both technologically feasible and economically promising, and is receiving increasing attention from government funding sources, private investors, and public utilities. rSOC technology offers the benefit of using a single system comprised of solid oxide cells (SOC) and a balance of plant (BOP) to operate as both a fuel cell and an electrolyzer. In SOFC mode, H_2 is typically fed to the fuel electrode where it is electrochemically oxidized to produce power, H_2O, and heat. In SOEC mode, the cell is operated in reverse with an external power source applied across the cell to convert steam to hydrogen. In both modes the stack is operated between 750 ^{o}C and 850 ^{o}C. Two rSOC demonstration systems (20 kW$_e$ and 30 kW$_e$) are scheduled for installation during 2023. The 30 kW$_e$ system will be coupled to a thermal energy distribution system at the Idaho National Laboratory (INL) that will be configured to mimic an industrial source of low-grade heat. A solid model of the overall system design, consisting of three 4-stack quad assemblies, is shown in Figure 4.

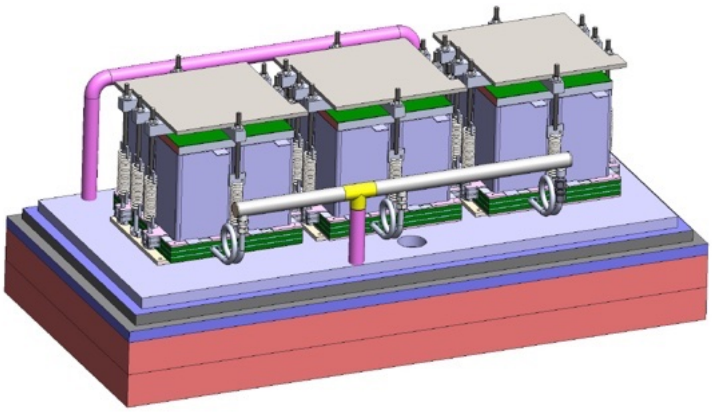
Figure 4. OxEon's rSOC 30 kW SOEC/ 10 kW SOFC system design for installation at INL.

Fischer Tropsch Synthesis

First demonstrated in 1923 by Franz Fischer and Hans Tropsch, early commercial FT development occurred primary in Germany during the 1930s and 1940s (9). The FT process converts associated gas to high value liquid hydrocarbon fuels. By producing storable and transportable fuels, the FT process provides an opportunity to circumvent the economic and logistical challenges of transporting gas to market. There is an emerging market for FT technology aimed at a variety of small distribute resources including biomass, biogas, coal-biomass blends, stranded gas, associated gas, and CO_2 co-electrolysis as intermittent renewable energy storage options. Biomass to liquid (BTL) technology has many prospective feedstocks with the potential to be carbon neutral and biomass gasification processes have been developed to the point where costs may be comparable to coal-based gasification (10). FT technology to capture and convert these fuel sources to liquid fuels would require smaller systems that can be transported to the site versus site-built plants. BTL has previously been eschewed in FT technology because of the impractical shipping costs to move materials to FT synthesis sites and the logistics surrounding batch processing. The challenge in developing these resources is producing a small-scale plant at the same cost per bpd capacity as large plants. To accomplish this task, OxEon Energy has developed a system that uses larger diameter reactor tubes with a heat transfer insert to manage thermal control of the system. OxEon's FT design requires fewer reactor tubes than the traditional fixed-bed industry design and uses standard pipe sizes for reduced system fabrication costs. These portable systems have been designed for a 10-20 bpd production target.

Optimization of the FT reactor tube diameter and shape of the heat transfer insert has been done via an iterative process involving simulation modeling and verification testing. The latest round of simulation work was done in partnership with Lawrence Livermore National Laboratory with the support of a High-Performance Computing for Energy Innovation (HPC4EI) award and resulted in the design currently being used in several demonstration systems for FT liquid fuel production from CO_2 (11). An example of the initial fin geometry, the simulation generated optimized geometry, and an actual extruded part are shown in Figure 5.

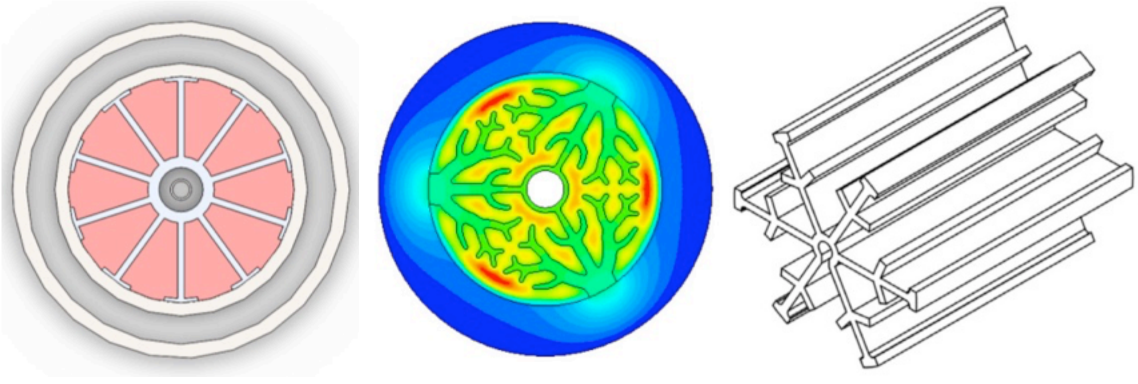

Figure 5. Evolution of fin simulation from initial problem statement (left), simulation optimized geometry (center), and a non-optimized extruded part (right).

OxEon has demonstrated FT operation with a variety of syngas sources including syngas produced via natural gas reformation, reverse water gas shift (RWGS) of CO_2, and co-electrolysis of steam and CO_2. Extensive performance mapping with the modular FT reactor design has also informed catalyst characteristics such as pore size, support shape, and precious metal promoter loading to allow for targeted FT product production. The product distribution for a custom prepared FT catalyst tested in 2020 and an updated version of the same catalyst tested in 2023, adjusted to increase the chain growth propagation probability (alpha), is shown in Figure **6**. The new catalyst was tailored to shift the product distribution to longer chain lengths and reduce methane selectivity.

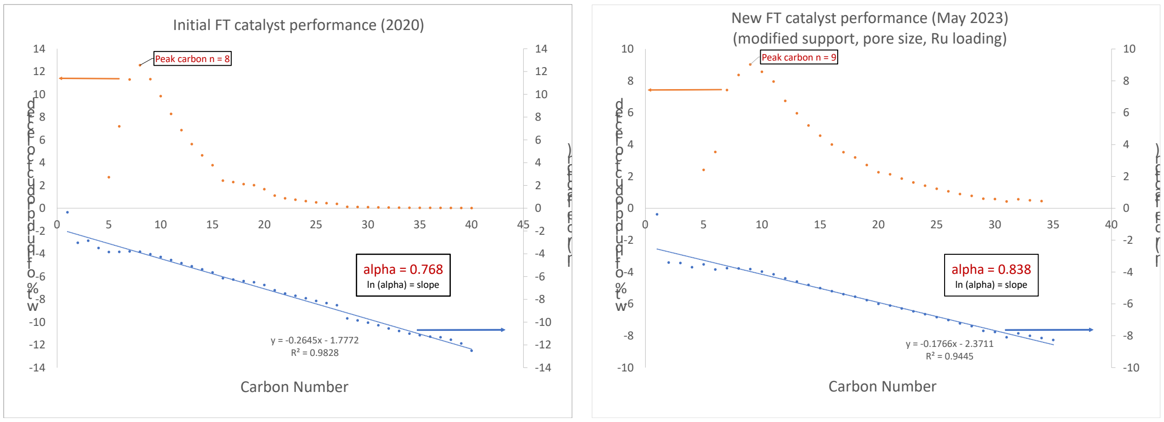

Figure 6. FT liquid product distribution curve by carbon number with chain growth propagation probability fit.

Plasma Reformer

OxEon's non-thermal plasma reformer consists of a pair, or multi-phase pairs, of electrodes immersed in a flowing reactant gas stream. The reactant stream generally consists of air or oxygen, steam, and the hydrocarbon feed to be reformed. For the applications discussed in this paper, the feed to be reformed is methane, but the reformer has been demonstrated to be fuel flexible. Heavy hydrocarbons such as JP-8 have been successfully processed in the plasma reformer for SOFC operation. A high electric potential difference is imposed on the electrode pairs, typically 9-12 kV_{AC}, which creates a potential gradient of 3-4 kV/mm at the electrode position of nearest approach. This is sufficient to achieve ionization of the gas between the electrodes, which allows a current flow between the electrodes as shown in Figure 7. The flow of feed gas forces the plasma arc streamwise along the path between the diverging electrodes until the distance becomes large enough that the arc

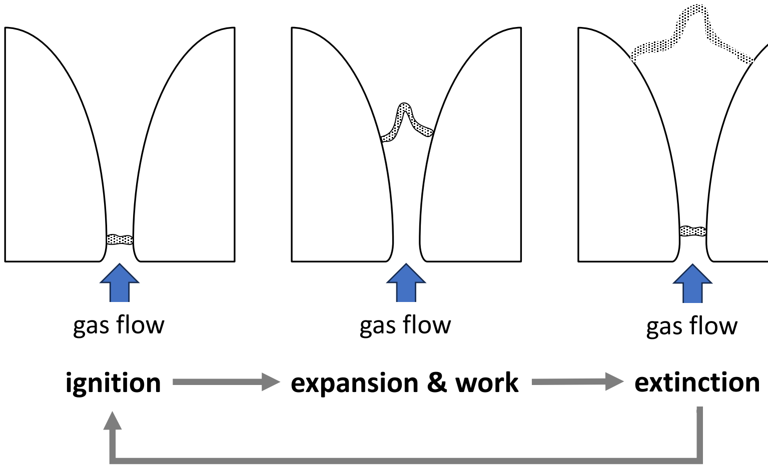

Figure 7. Non-thermal plasma arc operation.

extinguishes, and another immediately forms. This process is typically measured in milliseconds. A photo of the operating arc for a 3-pair electrode reformer is shown in Figure 8.


Figure 8. Operation of 3-pair electrode reformer.

The reformer uses the non-thermal plasma to form radicals, ions, and excited species to promote the reforming reaction much as would occur with a solid reforming catalyst. Because a catalyst is not used in the plasma reformer, it is sulfur insensitive, allowing for sulfur to be removed later in the gas phase, if required for downstream processes. The energy needed to drive the endothermic reformation reaction can be realized by burning a portion of the fuel or by heat integration with the rest of the system. The unit may be started in partial oxidation mode and then switched to steam reforming once temperatures are sufficient to maintain the reaction. The electrical energy required to power the plasma is $< 2\%$ of the heating value in the input fuel.

OxEon has experience in designing, constructing, and successfully operating non-thermal plasma reformers in both endothermic (internal partial oxidation) and exothermic (externally fired or integrated) modes, with optimized thermal integration based on application. The initial laboratory-scale reformer capable of processing ~ 5 kWt fuel, has been scaled to units able to accommodate a fuel input exceeding 100 kWt (12).

System for fuel production from bio-CO_2 and bio-CH_4

With the support of a Bioenergy Technologies Office (BETO) award from the Department of Energy (DOE), a process for conversion of both bio-CO_2 and bio-CH_4 from anaerobic digester gas is being developed for a demonstration system capable of producing 4-6 gpd of FT liquid fuels. An SOEC system will be used to convert steam (raised by exotherm in FT reactor) and bio-CO_2 to syngas (CO & H_2). A plasma reformer will convert the bio-CH_4 to syngas, using the plasma to catalyze the reaction of the methane with steam and oxygen (supplied as oxygen enriched air). The oxygen enrichment is made possible by using the byproduct O_2 from the SOEC system. The syngas generated by the SOEC and plasma reformer are combined to feed an FT reactor to produce liquid hydrocarbon fuels. Steam for reforming and electrolysis units are produced by cooling the exothermic FT reactor and recycling water produced in the FT reaction. A simplified process block diagram is shown in Figure 9.

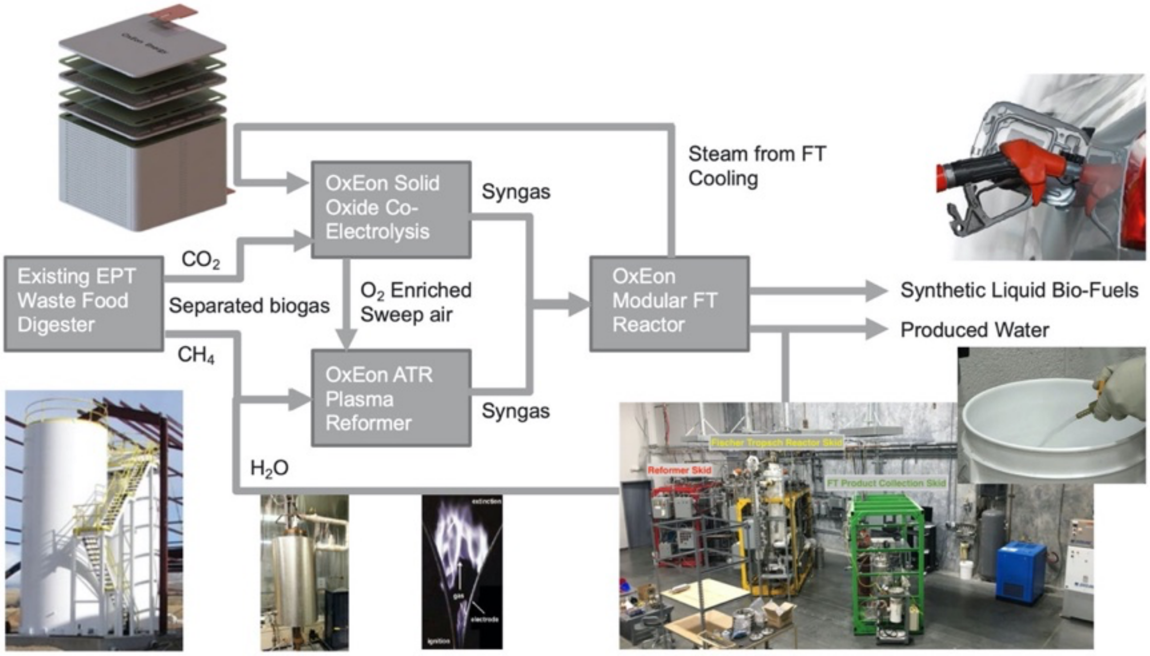

Figure 9. Simple process block diagram for liquid fuel production from anaerobic digester gas.

Subsystem Verification

Individual subsystem verification of the SOEC, plasma reformer, and FT technologies were conducted to demonstrate key performance targets ahead of integrated system design and fabrication. Go/No-Go targets were set for each subsystem and demonstrated performance was evaluated by the BETO office and an independent engineer. The SOEC verification was performed with a H_2O/CO_2 feed ratio of 1.9 and ~5% H_2. Gasses used for the verification testing came from gas tanks to simulate bio-CH_4 and FT exotherm raised steam. A stack electrical efficiency of 122% (V_{tn}/V_{op} = 1.34/1.099) resulted in CO_2 conversion of 51% and a syngas product with a H_2/CO ratio of 2.15. The plasma reformer was operated with natural gas, water, and O_2 enriched air (~40% O_2) to simulate a bio-CH_4 feed with FT produced water and SOEC produced O_2. A cold gas efficiency of 81%, carbon selectivity to CO of 81%, and a plasma power of 295 W were observed during operation. Additionally, analysis of the plasma produced syngas showed 0.15 mol% CH_4, no detectable amount of C_2, and a H_2/CO ratio of 2. Fischer Tropsch verification testing was done with a syngas produced from reformed natural gas with a H_2/CO ratio comparable to the compositions produced during verification of the SOEC and plasma reforming units. The conversion of CO in the FT was 85% and H_2 conversion was 94%. Selectivity of feed CO to C_{5+} was 79%, for an overall CO to C_{5+} (conversion * selectivity) of 67%. Analysis of the liquid hydrocarbons produced shows a product distribution with a peak at C_9-C_{10}. An overview of each subsystem's performance targets and verification results is shown in Table 1, confirming that each technology is capable of meeting the program requirements for an integrated system.

Table 1. Subsystem go/no-go performance targets.

SOEC

	Target	Verification Results
CO2 conversion	> 40%	**51%**
Syngas H2/CO ratio	1.8 to 2.2	**2.15**
stack electrical efficiency (i.e. Vop < 1.34 V/cell)	>100%	**122%**

Plasma Reformer

	Target	Verification Results
Plasma Power	< 350 W at 0.45 PF	**295 W at 0.45 PF**
CGE	> 76%	**81%**
CO selectivity	> 80%	**81%**
Reformate residual CH4	< 1 mol%	**0.15%**
Reformate C2	< 0.2 mol%	**not detected**

Fischer Tropsch

	Target	Verification Results
CO Conversion	> 80%	**85%**
H2 Conversion	> 80%	**94%**
CO Selectivity to C5+	> 76%	**79%**
Overall CO to C5+	> 67%	**67%**
Mass balance closure	> 92% on C	**96%**
Product Distribution Cn peak	> C9	**C9-C10**

System Integration and Design

After successful completion of the subsystem technology verification, design of the integrated system started. Primary efforts for 2023 have so far focused on preparing the full system design for an internal Critical Design Review (CDR), which requires the completion and review of several key items, including: system P&ID, drawing tree, system CAD drawings, bill of materials (BOM), failure mode and effects analysis (FMEA), program level risk and issue registry, and fabrication readiness. Project goals for the full, integrated system informed system design such that the final demonstation system will be capable of > 50% biogenic carbon to fuel, with a minimum of 500 hours operation, and 100 gallons of biofuel produced from the combined methane and CO_2 digester inputs. The FT produced biofuel will be converted to standard fuels with post system upgrading.

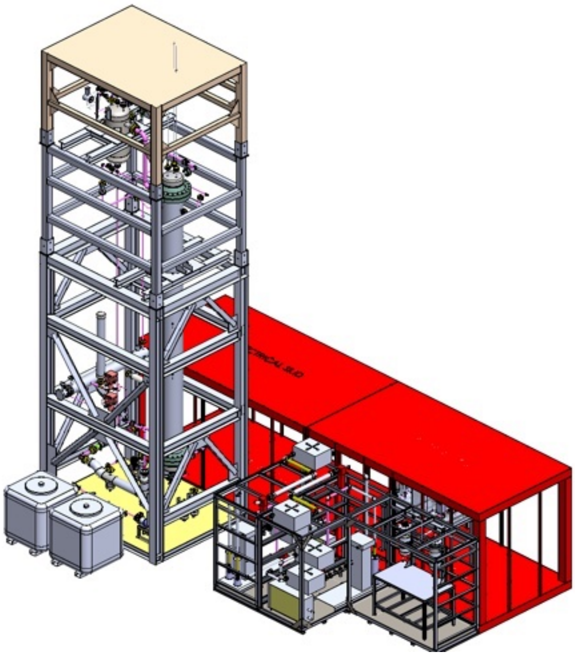

Figure 10. Rendering of integrated system for fuel production from bio-CO_2 and bio-CH_4.

The integration of the three technologies has several thermal and performance advantages over the individual technologies. The FT reaction is exothermic, so the heat removed via an evaporitive water cooling jacket is used to raise steam for the SOEC system. This heat is also used to preheat the FT feed syngas produced by the SOEC and plasma reformer. Unreacted FT tailgas is burned within the SOEC thermal enclosure to provide any make-up heat needed to counter ambient losses. The O_2 produced by the SOEC stack is used to feed the plasma reformer oxygen enriched air and the water produced by the FT reaction is also used as a feed to the plasma reformer. By using both the anaerobic digester CO_2 and CH_4 gasses, the yield of total biofuel is nearly doubled. A rendering of the integrated system is shown in Figure 10.

Fabrication

Due to the complexities of integrating multiple technologies, the design has been broken down into subsystems to allow for a staged approval process. The subsystems are: 1) FT reactor and steam cooling system, 2) Hot Section Unit (HSU) which contains the electrolysis stacks, 3) Plasma Reformer, 4) syngas compression and storage system, and 5) balance of plant (BOP). As subsystems complete the rigorous CDR process and as the items that were identified as long-lead items early in the process are received, fabrication has been allowed to start in phases. Fabrication for both the FT reactor cooling vessel and the syngas compression skid are underway with pictures of the progress shown in Figure 11.

Figure 11. Fabrication of syngas compression skid (left) and FT cooling vessel (right).

Conclusion

OxEon's technology portfolio offers flexibility in cross-sector energy conversion for a variety of solutions for potential renewable energy production. An integrated system for producing liquid hydrocarbons from anaerobic digester gas has been presented and will be fabricated and commissioned in the next year. The demonstration system will run for a minimum of 500 hours and produce 100 gallons of FT liquid hydrocarbons. The product fuel will be all bio-carbon and demonstrate a renewable pathway for the production of high-value, storable and transportable liquid hydrocarbon.

Acknowledgments

The work presented has been supported in parts by the DOE EERE Bioenergy Technology Office (BETO), award DE-EE0008917, a NASA Headquarters Space Technology Mission Directorate (STMD) Tipping Point Award, contract 80LARC20C0001, a NASA Next Space Technologies for Exploration Partnership (NextSTEP) award, contract 80HQTR19C0006. The content is solely the responsibility of the authors and does not necessarily represent the official views of any government agency.

References

1. J. Pike, S. Elangovan, J. Hartvigsen, D. Larsen, T. Hafen, M. Hollist, A. Gomez, A. Yarosh, and J. Elwell, "Reversible SOEC/ SOFC System Development and Demonstration," 15th European SOFC & SOE Forum, A0504 (2022).
2. J. Hoffman, M. Hecht, D. Rapp, J. Hartvigsen, J. Sooho, A. Aboobaker, J. Mcclean, M. Andrew, E. Hinterman, M. Nasr, S. Hariharan, K. Horn, F. Meyen, H. Okkels, P. Steen, S. Elangovan, C. Graves, P. Khopkar, M. Maden, G. Voecks, P. Smith, K. Araghi, and D. Eisenman, "Mars Oxygen ISRU Experiment (MOXIE)—Preparing for human Mars exploration," *Science Advances,* vol. 8, no. 35 (2022).
3. J. Elwell, J. Hartvigsen, S. Elangovan, D. Larsen, M. Hollist, and T. Hafen, "Overcoming Technical Challenges to Advance the MOXIE Solid Oxide Electrolysis Stack from TRL3 to 9, Early Challenges to Successful ISRU Oxygen Production on Mars," *51st International Conference on Environment Systems*, Minneapolis, Minnesota, ICES-2022-211, (2022).
4. J. Hartvigsen, S. Elangovan, D. Larsen, J. Elwell, M. Bukil, L. Frost, and L. Clark, "Challenges of Solid Oxide Electrolysis for Production of Fuel and Oxygen from Mars Atmospheric CO_2," *ECS Transactions,* vol. 68, no. 1, pp. 3563-3583 (2015).
5. J. Hartvigsen, S. Elangovan, and L. Frost, "OxEon Energy Demonstration of Manned-Mission Scale ISRU Process Systems," *49th International Conference on Environmental Systems,* ICES-2019-257, (2019).
6. J. Hartvigsen, S. Elangovan, J. Elwell, D. Larsen, and L. Clark, *Proc. 12th European SOFC & SOE Forum 2016,* Lucerne (2016).
7. T. Hafen, T. Rane, D. Larsen, J. Pike, J. Hartvigsen, J. Elwell, and S. Elangovan, "Solid Oxide Electrolysis Cathode for Increased Robustness for ISRU Application," *51st International Conference on Environmental Systems*, Minneapolis, Minnesota, ICES-2022-280 (2022).
8. M. Hollist, J. Hartvigsen, J. Elwell, S. Elangovan, A. Gomez, D. Claus, M. Wilson, G. Jackson, C. Dreyer, G. Sowers, D. Dickson, J. Schmit, and N. Emadi, "Solid Oxide Electrolysis Based Lunas PSR Ice Processing System for Propellant Hydrogen and Oxygen Production," *51st International Conference on Environmental Systems,* Minneapolis, Minnesota, ICES-2022-275 (2022).
9. C. Bartholomew and R. Farrauto, *Fundamentals of Industrial Catalytic Processes, 2nd Ed.,* Ch. 6.5, John Wiley & Sons, New Jersey (2006).
10. S. Ail, S. Dasappa, "Biomass to liquid transportation fuel via fischer tropsch synthesis–technology review and current scenario," *Renew. Sustain. Energy Rev. vol.* 58, pp. 267–286 (2016).
11. J. Barrera, J. Hartvigsen, M. Hollist, J. Pike, A. Yarosh, N. Fullilove, and V. Beck, "Design optimization and integrated cooling inserts in modular Fischer-Tropsch reactors," *Che. Eng. Sci.,* vol. 268 (2023).
12. J. Hartvigsen, S. Elangovan, M. Hollist, P. Czernichowski, and L. Frost, "Non-thermal Plasa Reformation of Liquid Fuels," *ECS Transactions,* vol. 35, no. 1 (2011).