



NRL/MR/6360--19-9971

6.1 New Start: Conversion of CO₂ Waste Into Energetic Molecules (FY15-FY19)

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January 20, 2021

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 20-01-2021			2. REPORT TYPE NRL Memorandum Report			3. DATES COVERED (From - To) 10/1/2014-9/30/2019		
4. TITLE AND SUBTITLE 6.1 New Start: Conversion of CO ₂ Waste Into Energetic Molecules (FY15-FY19)						5a. CONTRACT NUMBER		
						5b. GRANT NUMBER		
						5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Heather D. Willauer, James R. Morse, and Jeffrey W. Baldwin						5d. PROJECT NUMBER		
						5e. TASK NUMBER		
						5f. WORK UNIT NUMBER 1C27		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory 4555 Overlook Avenue, SW Washington, DC 20375-5320						8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6360--19-9971		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research One Liberty Center 875 North Randolph St., Suite 1425 Arlington, VA 22203-1995						10. SPONSOR / MONITOR'S ACRONYM(S) ONR		
						11. SPONSOR / MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A: Approved for public release; distribution is unlimited.								
13. SUPPLEMENTARY NOTES								
14. ABSTRACT A synthetic fuel process that combines carbon dioxide (CO ₂) and hydrogen (H ₂) to make drop-in replacement jet fuel when and where it is needed to support persistent and sustainable Navy and joint forces mission and warfighting capabilities is envisioned. Before such a process can become feasible, however, highly selective catalytic materials must be developed to convert CO ₂ to energetic molecules to be used as fuel. This 6.1 NRL New Start Program provided CORE funding to help researchers maintain a level of support needed to develop chemistries and new materials in the quest to use environmental CO ₂ as a carbon source for synthetic fuel production.								
15. SUBJECT TERMS Synthetic fuel Carbon dioxide Catalyst Conversion								
16. SECURITY CLASSIFICATION OF:				17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON		
a. REPORT	b. ABSTRACT	c. THIS PAGE	Heather D. Willauer					
Unclassified	Unclassified	Unclassified	Unclassified	Unlimited	32	19b. TELEPHONE NUMBER (include area code) (202) 767-2673		
Unlimited	Unlimited	Unlimited						

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EXECUTIVE SUMMARY

A synthetic fuel process that combines carbon dioxide (CO₂) and hydrogen (H₂) to make drop-in replacement jet fuel when and where it is needed to support persistent and sustainable Navy and Joint Forces mission and warfighting capabilities is envisioned. However before such a process can become feasible, highly selective catalytic materials must be developed to convert CO₂ to energetic molecules to be used as fuel. This 6.1 NRL New Start Program provided CORE funding to help researchers maintain a level of support needed to develop chemistries and new materials in the quest to use environmental CO₂ as a carbon source for synthetic fuel production.

A multidisciplinary team and approach was used to achieve five major milestone developments that culminated in the transition of CO₂ hydrogenation from a TRL-3 to TRL-7 together with support from OPNAV. Along with these milestones, the program produced 7 refereed journal articles, 1 book chapter, 1 NRL Memorandum report, 1 letter report, 1 patent, and 17 presentations at conferences. The full references for these materials are provided in Appendix A.

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6.1 NEW START: CONVERSION OF CO₂ WASTE TO ENERGETIC MOLECULES

1.0 MOTIVATION

Strategic and defense oriented alternative energy and fuel development are high priority goals of SECNAV, OPNAV, ONR, and DOD [1-3]. To help meet these goals, the development of unique alternative energy approaches such as the conversion of anthropogenic carbon dioxide (CO₂) to high-value hydrocarbons to be used for energy storage is a topic receiving significant attention by researchers at NRL [4-20]. The primary limitation in using CO₂ as a building block for the production of hydrocarbons is the high energy barrier for oxidation, reduction, and polymerization reactions. While electrochemical and photochemical CO₂ conversion processes in water continue to improve in efficiencies, challenges remain with low hydrocarbon yields and difficult scalability for these synthetic approaches [21]. In contrast, thermochemical processes are one of the few proven methods for producing relatively high yields (> 45%) of hydrocarbons greater in carbon number than methane [4-8, 12, 22].

NRL is actively developing a two-step thermochemical approach to convert CO₂ and hydrogen to energetic molecules [4-8]. **Step-1** addresses the conversion of CO₂ and H₂ to olefins (short-chain unsaturated hydrocarbon molecules) by an iron-supported catalyst. **Step-2** consists of conversion of olefins to liquid hydrocarbons ranging from C₆-C₁₇ by oligomerization over supported nickel and/or zeolite catalysts, or alternatively conversion of methanol to olefins and higher hydrocarbons over zeolite based catalyst. In the past year, NRL has demonstrated the integration of these processes and has successfully produced laboratory-scale quantities of liquid hydrocarbons.

While CO₂ conversion as high as 60% have been achieved at the laboratory-scale in **Step-1** of the NRL two-step thermochemical approach, by far, the key scientific challenge and roadblock that NRL continues to study at the basic science level is how to accomplish greater CO₂ and H₂ conversion efficiencies and to effectively direct product selectivity to intermediate hydrocarbons such as olefins (C₂-C₉) and methanol. Water formed in the primary reactions involved in (**Step-1**) CO₂ hydrogenation is known to negatively influence catalyst activity and product selectivity [23-25]. Computational modeling and kinetic analysis of data obtained from our smallest laboratory-scale fixed-bed reactor showed that reducing the effects of water vapor on the catalyst activity would shift the equilibrium at the catalyst surface to produce the desired intermediates such as olefins or methanol to values greater than 80% over intermediates such as CO or methane. What is not well understood is how to modify the catalyst material and reaction conditions to prevent and or minimize the catalyst sites from becoming blocked by competitive water vapor absorption while at the same time maintaining the catalyst activity for CO₂ hydrogenation. We propose to design and synthesize novel silica-and carbon-based composite materials that have water stability, thermal stability, and CO₂ hydrogenation activity. By controlling the catalyst properties, we will prevent competitive water absorption at the catalyst surface and improve product selectivity and yield over the current CO₂ hydrogenation catalysts.

The second scientific challenge and road block involves **Step-2** of the NRL two-step thermochemical approach to convert CO₂ and hydrogen to energetic molecules. This is the selective catalytic conversion of the intermediates (olefins or methanol) produced from the

hydrogenation of CO₂ in **Step- 1** to C₉-C₁₆ region in **Step-2** at the lowest possible pressures (200 to 300 psi) and temperatures (100 to 300 °C). Currently this step requires pressures in excess of 400 psi with temperatures as high as 700 to 1000 °C, where conversion efficiencies are plagued by the complexity of **Step-1** product streams containing water vapor and unreacted CO, CO₂, and H₂. What is not well understood is how to change the catalyst properties (strength and number of acid sites, pore size, channel structure, nickel loading, and water stability) and reaction conditions to reduce competitive hydrogenation of the product stream from **Step-1**. Such control would facilitate product shift to C₉-C₁₆ region in high yield at low temperatures and pressures.

We propose to design and synthesize new metal organic frameworks (MOFs) that have water stability, thermal stability, chemical stability, and shape selectivity for selective oligomerization to C₉-C₁₆. The advantage of using MOFs over traditional inorganic zeolite frameworks and nickel supported catalysts is that they have a compartmentalized design feature, where both inorganic metal nodes and organic linking component may be incorporated and modified independently [26,27]. This modular nature of MOF structure suggests a versatile design platform that can be tuned to target specific catalyst performance properties such as selectivity and stability at low pressures and temperatures. Because of the versatility and modular nature of these materials, the basic science understanding has the potential to be used in other diverse areas of catalysis and gas storage. For example MOFs are currently receiving significant attention for their ability to capture and store CO₂, H₂, and CH₄. To date, MOFs have been used to achieve the highest surface areas and methane storage capacities for any physisorbent, and may be synthesized for specific performance criteria such as adsorption and desorption rates for specific gases. From the basic synthetic knowledge gained in this program, new materials in the future could be tuned to have both the ability to absorb reactant gases (e.g., CH₄, H₂, CO₂, CO) and react them *in situ* for the production of higher hydrocarbons. The *in situ* production of higher hydrocarbons would eliminate additional energy needed to release, compress, and catalytically convert the gases to higher hydrocarbons.

While the catalyst composition and morphology are indeed the most significant variables in both CO₂ hydrogenation and olefin oligomerization reactions, it has been well established that strong relationships exist between catalyst composition and reaction conditions (reactor type, gas-hourly space velocity or GHSV, reactor temperatures and pressures). This has been shown to lead to changes in kinetic rate equations and the kinetic parameters obtained by these equations [22,28]. Specifically, differences in the transport of reactant and product gases and the catalyst particle characteristics result in differences in the reaction kinetics. The final challenge remains to understand and determine the effects of channel reactor environment on the kinetics of the reactions in both **Step-1** and **Step-2** of the NRL thermochemical approach to convert CO₂ and hydrogen to energetic molecules using already established NRL computational models. This commercial channel reactor technology has been proven to scale-up traditional Fischer-Tropsch synthesis (carbon monoxide and hydrogen (syngas)) by simply increasing tubular length and number and therefore should be suitable for a shipboard technology in the distant future where stringent size and weight constraints exist. Modular units based on this commercial technology are being designed for other offshore and remote synthetic hydrocarbon fuel synthesis from syngas [29,30]. We propose to determine the effects of this scalable reactor environment on the NRL two-step thermochemical approach. The effects of catalyst packing and gas transport on CO₂ hydrogenation will be determined by measuring product selectivity and yield utilizing a well characterized CO₂ baseline hydrogenation catalyst.

By understanding how to design and tailor catalyst materials to exhibit stability (water and thermal) and catalyst activity for both **Step-1** and **Step-2** of the NRL thermochemical approach, along with the knowledge of how the channel reactor environment effects reaction kinetics, we will be able to enhance product selectivity and yield of the integrated process while minimizing the overall energy requirements. If we are successful, we will be in a position to transition and scale-up this two-step approach to converting CO₂ waste into energy-rich hydrocarbons.

A strategy to transform CO₂ molecules to energy-rich materials is applicable to multiple current Naval S&T focus areas such as Power & Energy and Autonomy and Unmanned Systems [3]. The two-step approach proposed here can be tailored to produce specific feedstocks such as liquid fuel or methanol, methane, ethylene, carbon monoxide, that can reformed and used directly in hydrogen or solid oxide fuel cells (SOFCs). The transition potential for this technology is high, but relies on understanding and controlling the fundamental catalytic mechanisms in both **Step-1** and **Step-2**. This understanding and control is essential to increase rate, selectivity, and viability of the reaction process and proposed technology. Our environmentally-friendly synthetic strategy will yield strategic and monetary benefits by producing high-value, energy-dense products from CO₂ molecules at higher throughput by implementing the appropriate reaction media and reaction conditions.

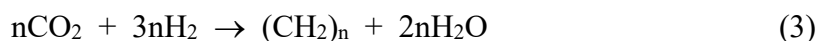
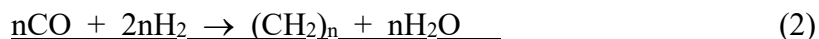
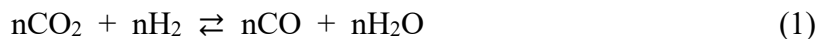
2.0 OBJECTIVE

Understand and control fundamental catalytic physical and chemical properties to develop selective water-stable catalysts for thermochemical hydrogenation reactions by addressing key water-induced catalyst deactivation mechanisms.

3.0 APPROACH

3.1 New Synthetic Materials and Approaches for Advancing CO₂ and H₂ to Intermediates (Step-1)

NRL's objective is to increase CO₂ conversion efficiencies to greater than the 60% already demonstrated in our laboratory-scale process [4-8], while maintaining current process selectivity and efficiencies. There are essentially two primary reactions (equations 1 and 2) identified in CO₂ hydrogenation.



A thermodynamically favorable side reaction associated with CO₂ hydrogenation is the highly competitive methanation reaction (Eq 4) [22].



Another competing side reaction is the Boudouard reaction (Eq 5).



The water formed in the primary reactions involved in CO₂ hydrogenation (Equations 1-4) and typical FT synthesis have been reported to affect the catalyst active sites causing a decrease in conversion and loss in product selectivity [23-25].

New and improved synthetic approaches will be developed to design catalyst composite materials with structures that stabilize metal catalyst active sites against degradation under reaction conditions that produce water as a primary by-product. The degradation may result in thermally-induced sintering and agglomeration, mechanical attrition, as well as re-oxidation or accelerated crystallization of the metal oxide surface [31]. By effectively removing water vapor from the catalyst active sites, the equilibrium at the catalyst surface will favorably shift to the production of desired intermediates such as olefins or methanol over intermediates such as CO or methane (Equations 1-3). If successful, carbon dioxide conversion selectivity and efficiency will increase while reducing catalyst deactivation and increasing catalyst lifetimes.

We propose to develop and synthesize silica- and carbon-based composite materials because it has been shown in the literature that mesoporous carbons and silicas may serve to direct the self-assembly of catalytic nanoparticles as well as enhance thermal stability, catalytic activity, and water stability [32]. Catalyst composites synthesized with silica have been found to improve stability in water, as reported for BaTiO₃ [33], HZSM-5 zeolite [34], as well as for iron-based catalysts for CO₂ hydrogenation [35]. With respect to carbon composites, deposition of mesoporous carbon films by impregnation with sugars (e.g., sorbitol) [36] or encapsulation of catalysts in carbon nanotubes [37] have each been found to enhance the activity of catalysts by improving metal dispersion as well as prevent leaching of the metal into aqueous reaction media. In addition, the mesoporous materials have been shown to impart a high concentration of the iron carbide phase from the contained oxide which is essential in promoting chain growth in the hydrogenation reaction [38].

In these studies CO₂ and H₂ will be used as a model system in the laboratory bench-scale reactor to initially evaluate each catalysts performance. Results of these studies will be used to down-select the CO₂ hydrogenation catalyst material to be used in the channel reactor and in the integrated channel reactor.

3.2 New Synthetic Materials and Approaches for Advancing Intermediates to C₉-C₁₆ (Step-2)

One of the challenges is to integrate **Step-1** and **Step-2** of the NRL two-step thermochemical approach to convert CO₂ and hydrogen to energetic molecules. Operating this integrated system at the lowest possible pressures (200 - 300 psi) and temperatures (100 - 300 °C) would provide a novel, cost-effective method for fuel production from CO₂ and H₂. In order to achieve this, the

complex product stream from **Step-1** must be selectively oligomerized to the C₉-C₁₆ region in quantities greater than 60%. Metal-organic frameworks (MOFs) will be synthesized and tested in the laboratory scale reactor as a water-stable, low-pressure alternative to commercial zeolite materials.

Zeolite-like imidazolate frameworks (ZIFs) are a family of MOFs whose microporous structures have been found to resemble those of commercial zeolites, and similarly are exceptionally stable to different chemical and thermal treatments (typically *ca.* 550 °C in N₂) [39]. Although showing framework rigidity and permanent porosity like their zeolite counterparts, ZIF-based materials often exceed the pore sizes of zeolites by 2-fold. This point is encouraging from the standpoint of oligomerization catalyst development, as often it is the small pore size of the zeolites that prevent product release and result in catalyst deactivation over time [40]. The feature of an imidazolate-based linker between metal nodes also suggests that functionalizing the linker (e.g., -NH₂ group) could provide an accessible site for post-synthetic metal exchange (e.g., -NH₂---Ni) – resulting in a metal with open coordination sites available for oligomerization catalysis under conditions of lower pressure (e.g., 200-450 psi) and temperature (*ca.* 120 °C) associated with the use of Ni-exchanged amorphous silica-aluminas for the selective and high conversion of ethylene and propylene to higher olefins [41].

The second MOF candidate that we will synthesis for oligomerization catalysis is ZrO₂-based UiO-66. These MOFs are frequently cited as having very high chemical and thermal stability, where some examples maintain structural integrity even upon exposure to boiling water baths or mineral acids of high concentration for prolonged periods of time [42]. Much of their stability is attributed to the extraordinarily strong coordination bonds formed between carboxylate-terminated linkers and the metal oxide clusters [43].

In these studies ethylene will be used as a model system in the laboratory bench-scale reactor to initially evaluate each MOF's oligomerization performance. Water, CO, CO₂, and H₂ will then be introduced into the reaction to measure how they individually and collectively effect ethylene oligomerization. Results of these studies will be used to down-select the MOF catalyst material to be used in the channel reactor and in the integrated channel reactor.

3.3 Commercially-modified, single- channel reactor technology unit

NRL has a commercially-modified single-channel scalable reactor unit which will allow NRL to conduct a parallel research effort to understand and determine the effects of reactor environment on reaction kinetics. The channel reactor was specifically designed to improve radial heat transfer within the reactor since the overall reaction described in equations 1- 4 are exothermic in nature. These improvements in heat transfer are believed to prevent hot spots and coking of the catalyst material. As a result, enhanced reaction conversions and product yields are anticipated due to improved catalyst lifetime and optimal performance from reduced degradation effects.

Catalyst materials developed for both **Step-1** and **Step-2** that have been well characterized in the laboratory bench-scale reactor will be used in the channel reactor to compare catalyst performance under several different reactor conditions. These conditions include temperature, pressure, flow rate, and packing of the reactor. These data will be used to update current well-

established computational models derived for our laboratory-scale fixed-bed reactor to establish if and how the reaction kinetics change in the channel reactor environment.

4.0 PLANS

4.1 Year 1

The first goal of year one will be to develop and synthesize silica-modified catalysts. Two approaches will be studied based on the mode of introduction of the silica into the catalyst matrix. In the first approach, silica will be co-precipitated with salts of iron and other promoters. The second approach will be the impregnation of supported iron catalyst with tetraethylortho silicate (TEOS) both before and after deposition of iron and promoters. Synthetic efforts will focus on the controlled synthesis of each catalyst with dependable morphology. Each of the catalysts will be fully characterized for structure (XPS, XRD, SEM, TEM) as well as thermal and hydrostability (TGA, DSC) both before and after measuring CO₂ hydrogenation performance in the laboratory-scale reactor. Microporosimetry will be used to measure BET surface area, total pore volume, and pore radius of catalysts both before and after thermal and water stability tests to determine structural integrity. We will determine how silica morphology, mode of silica and metal loading, pretreatment and reaction conditions affect CO₂ hydrogenation performance. This performance is assessed by measuring product yield, selectivity, and catalyst stability over the time of the reaction. Results will be compared to a well-characterized baseline catalyst that has achieved over 60% CO₂ hydrogenation.

The second goal of the first year will be to use NRL's well-characterized baseline catalyst in the channel reactor environment to begin establishing a method to optimize the gas transport properties to the catalyst sites by systematically varying the GHSV.

The third goal of the first year is to synthesize and characterize the ZIF MOF and further functionalize the formed ZIF with nickel. The ZIF will be synthesized under conventional solvothermal conditions, where modifications to scale-up for gram quantities will be optimized according to methods reported by industry (e.g., BASF) in the literature [44,45]. Characterization of structure for the obtained ZIF MOFs will include XPS, XRD, SEM, TEM and thermal analysis completed using TGA, DSC, and DTA. Microporosimetry will obtain BET surface area measurements as well as pore volume and radius for both before and after thermal and water stability tests to determine structural integrity.

Accomplishments in Year 1:

- Determine the effects of silica-modified catalyst on CO₂ conversion, hydrocarbon selectivity, and yield.
- Correlate spectroscopy results of the silica-modified catalyst with CO₂ conversion, hydrocarbon selectivity, and yield.
- Determine gas transport properties in the channel reactor by changing GHSV for the baseline catalyst and measure the hydrocarbon selectivity, conversion, and yield.
- Demonstrate synthesis and control over the ZIF MOF properties in gram quantities to be tested in the laboratory scale-reactor.

4.2 Year 2

The goal of the second year will be to synthesize carbonaceous materials by two approaches. In the first approach, commercially available carbohydrates will be used as precursors for the synthesis of iron oxides supported on nano- to microscale carbon spheres. Iron oxide will be incorporated using iron nitrate by cohydrolysis-carbonization route recently reported in the literature [46]. The resulting $\text{Fe}_x\text{O}_y/\text{C}$ composite materials are expected to exhibit both thermal stability and water stability (e.g., reduced sintering) from the containment of formed iron oxides in the carbon matrix. In the second approach, mesoporous silica (e.g., SBA-15) will be first impregnated with commercially available carbohydrate and then carbonized. This carbon-coated SBA-15 will be used as the support for CO_2 hydrogenation catalysts after undergoing subsequent impregnation with solutions of iron and promoter nitrate salts followed by calcination. Each of the catalysts will be fully characterized for structure (XPS, XRD, SEM, TEM, microporosimetry) as well as thermal and hydrostability (TGA, DSC) both before and after measuring CO_2 hydrogenation performance in the laboratory scale reactor. We will determine how the carbon composite morphology, mode of carbon and metal loading, pretreatment and reaction conditions affect CO_2 hydrogenation performance. This performance is assessed by measuring product yield, selectivity, and catalyst stability over time of the reaction. Results will be compared to a well-characterized baseline catalyst that has achieved over 60% CO_2 hydrogenation as well as the silica-modified catalyst formed in Year 1.

The second goal of the second year will be to continue the examination of NRL's well-characterized baseline catalyst in the channel reactor environment to begin establish a method to optimize the gas transport properties to the catalyst sites by systematically varying the temperature and pressure.

The third goal is to synthesis and characterizes ZrO_2 -based UiO-66 MOFs that have been functionalized with nickel. UiO-66 will be synthesized under conventional solvothermal conditions, where scale-up to gram quantities will be optimized according to methods reported by industry (e.g., BASF) in the literature [44,45]. Characterization of structure for the obtained MOFs will include XPS, XRD, SEM, TEM and thermal analysis completed using TGA, DSC, and DTA. Microporosimetry will obtain BET surface area measurements as well as pore volume and radius for both before and after thermal and water stability tests to determine structural integrity.

Accomplishments in Year 2:

- Determine the effects of carbonaceous catalyst properties on CO_2 conversion, hydrocarbon selectivity, and yield.
- Correlate spectroscopy results of the carbonaceous catalyst with CO_2 conversion, hydrocarbon selectivity, and yield.
- Determine gas transport properties in the channel reactor by changing the temperature and pressures for the baseline catalyst and measure the hydrocarbon selectivity, conversion, and yield.
- Determine the effects of ZIF MOF on ethylene oligomerization reaction
- Determine the effects of ZIF MOF on ethylene oligomerization reaction in the presence of H_2 , CO , CO_2 , and water.

- Demonstrate synthesis and control over the ZrO₂-based UiO-66 properties in gram quantities to be tested in the laboratory scale-reactor.

4.3 Year 3

The goal of the third year will be to down-select the best approach for stabilizing the CO₂ hydrogenation catalyst. We will demonstrate the catalyst in the more complex channel reactor system. In this year we will also have integrated **Step-1** and **Step-2** at in the channel reactor to demonstrate the application of the new materials in the complex system.

Accomplishments in Year 3:

- Down-select new CO₂ hydrogenation catalyst.
- Determine the effects of ZrO₂-based UiO-66 on ethylene oligomerization reaction.
- Determine the effects of ZrO₂-based UiO-66 on ethylene oligomerization reaction in the presence of H₂, CO, CO₂, and water.
- Demonstrate the integration of Step-1 and Step-2.

5.0 RESULTS AND DISCUSSION

5.1 The Role of Catalyst Environment On CO₂ Hydrogenation In A Fixed-Bed Reactor

The continuously stirred tank/thermal reactor (CSTR) simulates conventional slurry phase reactors that are used for large-scale industrial applications. The physical size and nature of the slurry phase reactor is not ideal for producing operational fuel at sea or in remote locations. Thus the challenge remains to find low cost modular chemical reactor solutions that are scalable and provide efficiencies and the operational ability to be used for off-shore and remote synthetic fuel production applications. Companies at the forefront of developing these systems are using fixed-bed design concepts.

NRL observed that moving from a continuously stirred tank/thermal reactor (CSTR) to a fixed-bed reactor has had a significant impact on the catalytic activity of the Fe promoted CO₂ hydrogenation catalyst at similar GHSV and temperature. Hydrocarbon selectivity was reduced from 62.4% (CSTR) to 30.5% (fixed-bed reactor). Kinetic and modeling analysis indicated this change in catalyst activity observed in a fixed-bed reactor environment may be attributed to the increased interaction between water and the catalyst surface as water accumulates along the fixed catalyst bed during the hydrogenation reaction. Due to the nature of the CSTR, water vapor formed during the reaction leaves the catalyst suspended in the mineral oil and does not accumulate in the CSTR unlike in the fixed-bed reactor. Water formed under typical Fischer-Tropsch (FT) conditions is known to influence catalyst activity primarily by re-oxidizing the catalyst. Unlike traditional Fischer-Tropsch reactions (FT) there are two moles of water produced for every one mole of CO₂ consumed as shown in equations 1-4. Since *in-situ* water removal in the fixed-bed reactor is not ideal or practical, mineral oil was added as a start-up solvent to simulate the chemical/solvent environment of the slurry phase reactor.

The negative impact that water formation has on the catalyst environment during CO₂ hydrogenation reactions in a fixed-bed reactor was reduced by the addition of a start-up solvent, (mineral oil) to a fixed-bed reactor as a pretreatment. A Macrolite®-supported iron-based catalyst was used as the model catalyst to determine the impact of pretreatment with mineral oil on product selectivity, CO₂ conversion, and catalyst stability over a range of reaction temperatures (280 °C, 300 °C, and 320 °C). At the lower reaction temperatures (280 °C, 300 °C), CO₂ conversion and C₂-C₅+ yield was increased by as much as 17% and 25% respectively by addition of start-up solvent.

Characterization of the catalyst microstructure by Powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) after CO₂ hydrogenation showed the formation of an iron manganese oxide phase in the absence of the start-up solvent. The addition of a new iron manganese oxide phase supports the differences observed in catalyst activity between reactions with and without mineral oil. Since the oxide phase has been identified as the active phase for WGS and RWGS, for reactions that do not have mineral oil, it is postulated that the conversion of iron carbides into iron oxides causes a decrease in FT activity and an increase in RWGS activity. This change in catalyst activity results in a shift in product selectivity from C₂-C₅+ hydrocarbons to carbon monoxide.

Modeling and kinetic analysis of the data suggested that the non-polar nature of the start-up solvent coating the catalyst particle decreases oxidation of the catalyst phase by reducing water adsorption. Reduced water adsorption on the catalysts sites results in the increase in the FT reaction rate. This led to an increase in hydrocarbon yield and water yields and decreases in the CO yield consistent with the experimental data. These results were documented in refereed journal article, Bradley, M. J.; Ananth, R.; Willauer; DiMascio, F.; Williams, F. W. "The role of catalyst environment on CO₂ hydrogenation in a fixed-bed reactor," *Journal of CO₂ Utilization* 2017, 17, 1-9 [47]. The results provide key insights into the scale-up of these systems in commercial fixed-bed reactors that will be presented later in this report.

5.2 The Effect of Copper Addition on the Activity and Stability of Iron-Based CO₂ Hydrogenation Catalysts

There has been some promising data that adding copper in small amounts to a supported iron catalyst can drastically improve activity. Some modeling efforts of CO₂ hydrogenation on the iron copper intermetallic (100) phase support the hypothesis that small amounts of copper will be beneficial to the system. There is also extensive work on how catalyst change as a result of exposure to syngas conditions but there is very little characterization work being done on FeCu/K catalysts in CO₂ hydrogenation conditions.

In response to this gap in the literature, NRL reported on the activity, composition, morphology, and kinetics of adding copper to well characterized iron-based catalysts with the aim of optimizing a new, more efficient CO₂ hydrogenation catalyst. Additionally, a detailed model for the fixed-bed reactor was developed to derive and understand the kinetics governing the activity and selectivity of the iron-based catalyst containing copper metal. The model considers mass transfer between the catalyst particles and within a given particle. The species diffuse into individual particles and react inside the pores, and exchange mass with fluid flowing within the interstitial space of particle bed. The model also considers heat transfer associated with

exothermic reactions occurring in the particles in the fixed-bed. The fluid mixture and packed bed properties depend on temperature, composition, and porosity. The model predictions are compared to the experimental data for the catalyst containing copper metal.

In an effort to improve both activity and durability of iron-based catalysts on an alumina support, copper (10%-30%) has been added to the catalyst matrix. The addition of 10% copper significantly increases the CO₂ conversion, and decreases methane and carbon monoxide selectivity, without significantly altering the crystallinity, and structure of the catalyst itself. The FeCu/K catalysts form an inverse spinel crystal phase that is independent of copper content and a metallic phase that increases in abundance with copper loading (>10% Cu). At higher loadings, copper separates from the iron oxide phase and produces metallic copper as shown by SEM-EDS. Addition of copper appears to increase the rate of Fischer-Tropsch reaction step as shown by modeling the chemical kinetics, inter and intra particle transport of mass and energy. The data obtained at different temperatures enable us to derive activation energy for the FT reaction when copper is included. It was found the diffusive transport is relatively fast compared to the reaction rate in the particles, and support particle porosity has significant effect on the conversion and yield. These results were documented in refereed journal article, Bradley, M. J.; Ananth, R.; Willauer, H. D.; Baldwin; Hardy, D. R.; Williams, F. W. "The Effect of Copper Addition on the Activity and Stability of Iron-Based CO₂ Hydrogenation Catalysts," *Molecules* 2017, 22, 1579 [48]. The results provide key insights into potential catalyst systems for long term stability as NRL looks to transition these technologies to commercial fixed-bed systems.

5.3 Potassium-promoted Molybdenum Carbide as a Highly Active and Selective Catalyst for CO₂ Conversion to CO

The most commonly used catalysts for CO₂ hydrogenation are slight variations of Fe and Co-based Fischer-Tropsch (FT) catalysts. The current optimal NRL developed catalyst, K-Mn-Fe/Al₂O₃, achieves a CO₂ conversion of 41.4% and a selectivity towards C₂-C₅+ hydrocarbons of 62.4% at a gas hourly space velocity (GHSV) of 0.0015 L g⁻¹ s⁻¹, but controlling the selectivity to a specific type of olefin remains a challenge. Although there are promising catalysts for CO₂-FT, the complexity of CO₂-FT suggests that the alternative route of feeding CO produced from reverse water-gas shift (RWGS) into a FT reactor must also be considered. For industrial RWGS, operating temperatures are very high, typically at or above 600 °C at 2.8 MPa, over ZnO/Al₂O₃ and ZnO/Cr₂O₃ catalysts. Because methane (CH₄) is thermodynamically favored below 600 °C, these catalysts require high temperatures to selectively produce CO, which also results in substantial deactivation. To make fuel synthesis from CO₂ viable, a low-cost and stable RWGS catalyst is first required, which can achieve high selectivity to CO over a wide range of conversion and operating temperatures.

Recently, Pt-based catalysts have been investigated for RWGS, but they are expensive, and thus, unviable for an industrial scale CO₂ conversion process. As an alternative, transition metal carbides (TMCs) are low-cost, with similar electronic properties to precious metals. Density functional theory (DFT) calculations over the TMC, molybdenum carbide (Mo₂C) demonstrate that Mo-terminated Mo₂C has many properties similar to transition metals including Ru, Fe, Co and Ni catalysts, all of which are active for CO₂ conversion. DFT calculations by Shi et al. further illustrate that CO₂ dissociation (CO₂ → CO + O) is more favorable than

CO₂ hydrogenation (CO₂ + H → HCOO or COOH) over Mo₂C, suggesting high CO selectivity. Reactor experiments over unsupported-Mo₂C powder catalysts for RWGS at 300 °C and 0.1 MPa show 8.7% conversion and 93.9% selectivity towards CO, confirming the DFT calculations. Another study over Mo₂C nanowires also reports high activity and CO selectivity at 600 °C. The high intrinsic activity of Mo₂C originates from CO₂ binding in a bent configuration, leading to spontaneous breakage of a C=O bond, leaving CO and O bound to the surface. The CO can desorb from the surface, while the oxy-carbide (O-Mo₂C) is restored to the active carbide through hydrogenation. Results of this study demonstrate that potassium-promoted molybdenum carbide supported on γ -Al₂O₃ (K-Mo₂C/ γ -Al₂O₃) is a low-cost, stable and highly selective catalyst for RWGS over a wide range of conversion. These findings are supported by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations.

CO₂ conversion in a fixed-bed environment as high as 23% and the highest CO yield of 22.2% and selectivity of 96.5% ever reported at low temperatures of 300 °C at 300 psi. When the temperatures were increased to 400 °C at the same pressures, conversion and selectivity increased to 40% and 98%. XPS measurements determined the dispersion of K on K-Mo₂C/ γ -Al₂O₃ catalyst causes the active Mo to stay in a reduced active state. The XRD measurements supported the formation of metallic Mo as the active phase. DFT CO₂ dissociation profiles indicated that the addition of K to the catalyst enhanced CO₂ adsorption and facilitates its dissociation to CO by lowering the activation energy barrier by 2.8 kcal mol⁻¹. The catalyst profile over 68 hours found only a 2.2% deactivation on steam versus the 11.0% for industrial catalyst after 75 hours on stream. The results were documented in refereed journal article, Porosoff, M.D., Baldwin, J.W.; Peng, X.; Mpourmapakis, G.; Willauer, H.D. “Potassium-Promoted Molybdenum Carbide as a Highly Active and Selective Catalyst for CO₂ Conversion to CO,” *ChemSusChem* 2017, 10, 2408-2415 [49]. The catalyst performance obtained by this research led to the filing of Navy Case #104187, US application number 15/616,024 and PCT application number PCT/US17/36397, filed June 7, 2017 [50].

5.4 Elucidating the Role of Oxygen Coverage in CO₂ Reduction on Mo₂C

Since molybdenum carbide (Mo₂C) is a promising and potential cost effective catalyst for the conversion of CO₂ to CO it was worth exploring the mechanism occurring on the catalyst surface and the understanding of the catalyst structure under the reaction conditions. A study employed first principles calculations to understand the CO₂ dissociation mechanism on β -Mo₂C (001) under different oxygen coverage on the catalyst surface (oxycarbide). The results demonstrated that with increasing oxygen coverage, there is an electronic modification on the catalyst surface (e.g. d-band shift on Mo atoms), that in turn, tunes the interactions of the adsorbates and the CO₂ dissociation barriers. Interestingly, the studies reveal linear relationships between the oxygen coverage and electronic modification with the reactivity of the catalyst. The results show that CO₂ can adsorb and dissociate on the oxygen covered Mo₂C surface, even in the presence of surface oxygen up to 0.5 monolayer (ML). Specifically, the activation of CO₂ on Mo₂C involves charge donation from the surface to CO₂ through both carbon and oxygen atoms. The binding energy of oxygen on the Mo₂C surface increases as the surface O-coverage increases, until it reaches a maximum at 1ML coverage. CO₂ binding energy decreases with the increase in surface oxygen atoms and CO₂ can no longer chemisorb at high oxygen coverage (O-coverage >

0.5ML). The high exothermicity of dissociated state of CO₂ (CO* and O*) is found to be significantly reduced with oxygen coverage, and CO desorption energies decrease with increasing oxygen coverage. Finally, it should be noted that even though the Mo₂C surface can become an oxy-Mo₂C surface under reaction conditions, our study shows that CO₂ can still adsorb and dissociate at low O-coverage (<0.50ML). The results rationalize a series of previously reported experimental observations and documented in a refereed journal article, “Elucidating the role of oxygen coverage in CO₂ reduction on Mo₂C,” M. Dixit, X. Peng, M.D. Porosoff, H.D. Willauer, G. Mpourmpakis. *Catalysis Science & Technology*, 2017, pages 5469 to 5796 [51].

5.5 An economic basis for littoral land-based production of low carbon fuel from nuclear electricity and seawater for naval commercial use

Three separate U.S. military databases were used to estimate the U.S. Navy operational fuel needs at sea. Defense Science Board data were used to estimate the FY2013 total fuel delivered—at-sea price being paid by the USN per gallon between \$6 and \$7. Using published capital cost data and a range of nuclear electrical energy scenarios, costs ranging between \$1.48 to \$8.67 per gallon are estimated for producing 82,000 gallons per day of fuel in littoral land-based locations. These costs also reflect differences in how the process is constructed and operated.

This study defines two possible scenarios. The first scenario the fuel process is designed, built, and operated commercially by the private sector. The second scenario the fuel processes are designed, built, and operated by the Navy much like the existing Military Sealift Command (MSC) fuel supply ships are currently operated. The cost range from \$2.86 to \$ 8.67 per gallon commercially compared to \$1.48 to \$4.46 per gallon in the Navy scenario. The fundamental driving cost difference between the two scenarios is the capital construction costs. These costs for the Navy are not financed as commercial entities. Thus, a 50 year lifetime for all parts of the system including the reactor along with operational cost reduces the cost per gallon significantly. The study also found that the single highest cost for the total process in each scenario would be the cost of the power source. In this particular study, regardless of the future nuclear configuration chosen for a littoral land-based fuel synthesis process, the range of cost estimates for PWR technologies evaluated clearly indicated the nuclear capital cost would most likely fall between \$1200/kW to \$7500/kW of electricity.

The study found that initial littoral land-based production of fuel closer to the point of use would significantly reduce the Fully Burden Cost of Fuel (FBCF) associated with logistical storage and delivery of the fuel. Currently the U.S. Navy is paying an average standard price of \$2.97 billion dollars annually for fuel. They are delivering an average 516 million gallons out to sea at an estimated FBCF of \$3.4 billion dollars annually. Initiating a littoral land-based fuel process would fix the cost of fuel for the Navy over the next 50 years and reliance on expensive, vulnerable, foreign sources of petroleum based fuel would be reduced.

This analysis has established a reasonable economic rationale for potentially replacing fossil fuel for the entire U.S. Navy’s at sea usage using a group of littoral land-based facilities. In addition, the paper provides naval strategic and logistic analysts with the broad constraints and framework within which to specifically address detailed future planning to accomplish this goal wherever it might be warranted by operational advantages. All results and observations were documented in

the referred journal entitled “An economic basis for littoral land-based production of low carbon fuel from nuclear electricity and seawater for naval commercial use,” Willauer, H. D.; Hardy, D. R.; Moyer, S. A.; DiMascio, F. Williams, F. W.; Drab, D. M. Energy Policy, 2015, 81 pages 67-75 [52].

5.6 Economic comparison of littoral production of low carbon fuel from non-fossil energy sources and seawater

While the previous analysis focused on the littoral production of low carbon fuel utilizing nuclear electricity, this analysis focuses on the economics of producing low carbon fuel at specific strategic locations using wind, photovoltaic (PV), and mobile nuclear light water reactors.

The US Department of Energy (DOE) National Renewable Energy Laboratory’s (NREL) evaluated 22 naval installations in efforts to identify potential technologies to enhance combat capabilities, provide great energy security, while at the same time the technologies had to be environmentally sustainable. With the help of these analysis, NRL sought to determine the size, cost, and configuration of a sustainable low carbon fuel producing process at the remote sites of Diego Garcia, Guam, and Djibouti.

The Naval Support Facility Diego Garcia is one of the most strategically important U.S. military installations. Located over 2,750 miles (4,500 km) south of Iraq and Afghanistan, the base has served as a critical refueling station during the Persian Gulf War, Operation Desert Fox, and the Afghanistan War. Due to its location in the middle of the Indian Ocean, the base relies solely on petroleum based resources to provide power and electricity to the island. In addition, this base, like remote fossil fuel poor nations, relies entirely on imported petroleum based resources to support all naval operations in, around, and from the installation. The island’s potential renewable resources, extremely small land mass, and its importance in US military operations provides one of the most challenging cases for assessing how its renewable and alternative energy resources could be exploited and used to ensure its maximum sustainable energy security and strategic importance for the US Navy.

The amount of fuel (nearly 8% of all Navy operational fuel at sea) that is delivered and utilized on Diego Garcia alone, coupled with the extremely small land area, and potential environmental restrictions, represent just a few of the many challenges of taking advantage of the renewable energy on the island for producing drop in low carbon fuel.

The analysis provided a variety of scenarios that show it is possible to supply up to 100% of all the power and energy needs of Naval Support Facility Diego Garcia without importing any fuel for the foreseeable future. Furthermore, it was shown that through various potential combinations of renewable energy including land-based wind, land based PV arrays, and floating PV arrays that this can be done with favorable economics for the Navy when compared to current FY14 FBCF.

Using published capital cost estimates and a range of solar and wind renewable electrical energy scenarios, costs ranging between \$6.40 and \$12.57 per gallon of standard fuel are estimated for a 129,000 gallons/day fuel process. The cost estimate for a floating nuclear electrical scenario is

between \$4.66 and \$9.47 per gallon. Larger area potential sites of strategic naval and/or commercial importance such as Guam and Djibouti provide additional operational scenarios.

An initial technical assessment report by NREL in 2011 suggests that the island of Guam can support between 315 MW to 631 MW (7600 MWhr/day to 15000 MWhr/day) of electrical energy by solar PV. They have also identified 30 MW of potential electrical energy from wind turbines, and further assessments are still needed to determine more scenarios that can take advantage of Guam's Class V wind classification (7.9 m/s, Table 5). While renewable energy on Guam is conceivable for future DOD energy savings, the island is susceptible to typhoons that cause problems with floatable PV arrays and turbines. Wind turbine locations are also constricted based on the interferences they cause to radar systems. While Guam has a larger land mass than Diego Garcia, the amount of fuel it consumes yearly (~230,000,000 gallons) offers another challenge to producing sustainable low carbon fuel from renewable electrical energy.

Camp Lemonnier, Djibouti (CLDJ) Africa is a US Naval Expeditionary Base that is home to the Combined Joint Task Force-Horn of Africa (Camp Lemonnier). The base is the only permanent US military base in Africa that supports over 4,000 U.S. joint and allied forces military and civilian personnel, and U.S. Department of Defense contractors. The Camp is located in the town of Ambouli on the southern side of the Djibouti-Ambouli International Airport. In 2007 it was publicized that the Camp would be expanded from 0.15 miles² to nearly 0.78 miles² in an effort to transfer the base from an "expeditionary" base to an enduring facility. Like most remote military facilities, CLDJ must contend with multiple challenges with respect to energy and water.

Djibouti is a small fossil fuel poor country located on the horn of Africa. It is bordered by Eritrea, Ethiopia, Somalia, the Red Sea, and the Gulf of Aden. Djibouti has a limited supply of fresh water, a harsh climate, and it relies heavily on its western neighbor Ethiopia for energy (Singh, 2015). Due to the unreliable nature of the Djibouti's electrical grid, CLDJ generates almost all of its own electricity by onsite diesel generators. Table 6 shows the fuel grade, quantities, and calculated FBCF used to support CLDJ annually. A total of 19.5 million gallons annually or 53.3 thousand gallons a day is used by CLDJ for both mobility needs and electrical generation needs. Tables 2 and Table 6 show that CLDJ requires only 41% of what is required to support Diego Garcia.

Due to the camp's ever evolving mission and its extensive current expansion, it is important for the camp to have a flexible sustainable infrastructure. As a result the Naval Facilities Engineering and Expeditionary Warfare Center (NAVFAC EXWC) are executing projects to promote energy sustainability and water conservation at CLDJ. As a part of this effort NAVFAC EXWC determined in a 2008 assessment that solar-generated electrical power might be one of the best options for incorporating renewable power at CLDJ. CLDJ is located in an area of the world that has some of the highest solar irradiation levels, a minimum of 6 kWh/m²/day. Dividing this number by 24 hours in a day gives a power rating 0.25 kW/m². Table 6 shows that on average 53,300 gallons of fuel needs to be produced daily to support CLDJ. Former NRL analysis indicates that 134 MW of power (3216 MWh/day) is required to produce this quantity of fuel from CO₂ and H₂ in seawater. The size of the PV arrays to produce all the power needed for the fuel at CLDJ can be derived by using solar irradiance, the approximate efficiency of solar panels, and the available land at CLDJ. If all the available 0.15 miles² of land (2 km²) could be used at CLDJ to produce electricity by PV arrays at 16% efficiency then approximately 78 MW

of power (1872 MWhr/day of electricity) would be available and as a result more land would have to be obtained for such a process to be considered feasible. NAVFAC EXWC also determined from a PV demonstration in 2010 that the arrays were subject to dust build up from frequent dust storms in the summer that resulted in a 30% loss in electrical output. In another demonstration in 2012 it was found that the panels had to be washed approximately three times per week to maintain system performance.

Electricity from photovoltaic renewable generation has been demonstrated to be feasible and promising for promoting energy sustainability for certain applications at the Camp. The ability to secure and maintain over 0.78 miles² or about 2 km² of PV arrays for a fuel process in such a harsh environment may pose several physical, economic, and security challenges. The total cost per gallon of fuel by PV array presented in Table 4, \$2.29/gallon (Navy) and \$3.63/gallon (commercial), would increase by the cost to lease additional land for the process, the cost associated with accruing more water and systems needed to clean and maintain the panels, and personal to secure and maintain the panels.

NAVFAC EXWC has also investigated the use of wind turbine power at CLDJ. They found that poor wind speed and height restrictions due to the Camps location next to an airport rendered this particular source as not a strategically or economically viable option.

The military examples evaluated in this analysis provide a framework for how such a process could be used commercially to supply stored energy as a sustainable fuel source for remote countries poor in fossil fuel resources. This information may also be used by policy analysts to support alternative energy implementation strategies and greatly expand the naval and commercial role in nuclear and renewable energy aimed at sustainable production of low carbon fuel. All results and observations were initially documented as an official NRL Memorandum report “An economic basis for littoral land-based production of low carbon fuel from renewable electrical energy and seawater for naval use: Diego Garcia evaluation,” Willauer, H. D.; Hardy, D. R.; DiMascio, F. Williams, F. W.; NRL/MR/6300-15-9635, August 13, 2015 [53]. The evaluation was further supported by collaborations with George Washington University and expanded upon to include the naval strategic locations of Guam and Djibouti. This collaboration resulted in the referred journal entitled “Economic comparison of littoral production of low carbon fuel from non-fossil energy sources and seawater,” Willauer, H. D.; Hardy, D. R.; Baldwin, J. W., DiMascio, F. Williams, F. W.; Bradley, M. J; Hoheisler, R. Journal of Cleaner Production 2018, 170 pages 1473 to 1483 [54].

5.7 Large-Scale Testing of NRL CO₂ Hydrogenation Catalyst: Quick Look Results Analysis

Through the current support of NRL’s 6.1 basic research program and OPNAV N45, NRL has been developing and testing catalyst for the hydrogenation of CO₂ to high-value hydrocarbons in a laboratory-scale fixed-bed plug flow thermochemical reactor process. It is envisioned that these hydrocarbons will one day be used to augment industrial chemical processes and produce operational fuel on land or at sea. The NRL technology before this test series was at a Technology Readiness Level of **TRL-3** (fuel synthesis).

In order to evaluate the feasibility of scaling up these catalysts for commercial applications and transitioning the technology from a **TRL-3** to a **TRL-6**, it is imperative to determine the effects of reactor environment on catalyst performance and reaction kinetics in large-scale reactor units over a period of one to two months. OxEon Energy, formally known as Ceramatec, is a leader in research and development on single-channel scalable modular reactor units for production of hydrocarbons from syngas (CO and H₂). These modular systems have been employed by OxEon Energy in ONR STTR in which OxEon Energy was a subcontractor to IntraMicron and for a U.S. Airforce (USAF) funded program for production of jet fuel. While OxEon Energy is still in the research and development stage, it offers a unique opportunity for NRL to adjust CO₂ hydrogenation catalyst systems to operate efficiently in the future commercial OxEon Energy units. It also enables NRL to utilize Ceramatec expertise in catalyst scale-up and implementation to optimize the NRL catalyst composition, catalyst packing in the large unit, and engineering the catalysts for these systems.

The objective of these studies was to evaluate the performance of NRL CO₂ hydrogenation catalysts in a OxEon Energy commercial single-channel scalable modular thermochemical reactor unit for the purposes of transitioning the technology from a **TRL-3** to a **TRL-6**. The following key parameters were measured to evaluate the catalyst performance at these large scales:

- CO₂ conversion
- Product yield
- Product selectivity
- Effect of gas stream recycling
- Catalyst scale-up
- Catalyst loading
- Catalyst stability

In this test series a OxEon Energy commercial single-channel modular thermochemical reactor was loaded with approximately 6,090 grams of NRL iron-based catalyst for the continuous hydrogenation of CO₂ at OxEon's facilities in Salt Lake City, Utah.

Currently the laboratory-scale fixed-bed plug flow thermochemical reactor process requires 20 grams of catalyst for evaluation in a 9 to 12" long stainless steel tube (3/8" ID, 1/2" OD). The catalyst bed occupies 8 to 10" length of the stainless steel tube. The catalyst quantities required for the evaluations were easily synthesized at NRL using known incipient wetness impregnation (IWI) techniques and their size ranged from 100 to 600 microns.

In a typical CO₂ hydrogenation experiment, 10 mL of mineral oil is added to the catalyst and the catalyst was reduced in-situ by flowing 100 mL/min H₂ at 300 °C and 20 bar for 18 hours. Three mass flow controllers (Brooks Instruments, USA) were used to control the flows of CO₂, H₂, and N₂ into the reactor. Immediately following reduction, hydrogenation of CO₂ was conducted at 20 bar and 300 °C with a H₂/CO₂ ratio of 3:1 and a 10 mL/min N₂ internal standard at 20 bar and gas hourly space velocity (GHSV) of 9.6×10^{-4} L/s-g. The GHSV is defined as standard liters per second of total carbon dioxide and hydrogen flow divided by the grams of total elemental Fe, Mn, and K metals in the reactor. The effluent gases were passed through a cold trap, at 10 °C to condense the water vapor and any heavy liquid hydrocarbons formed in the reactor. The effluent

gases were analyzed in real time using an inline gas chromatograph (GC) (Agilent Technologies, Fast RGA analyzer). Hydrocarbons were separated using an HP-AL/S column (Agilent Technologies, 19091P-512, 25 μm x 320 μm x 8 μm) and detected with an FID detector. Fixed gases (H_2 , CO_2 , CO , N_2) were separated on a Unibead IS column (4 ft, 60/80 mesh in UltiMetal) and a 5 \AA molecular sieve column (8 ft, 60/80 mesh) and detected with a TCD detector. The GC was calibrated using a mixture of gases with known molar ratio (MESA Specialty Gas, USA). Time-on-stream (TOS) for the catalyst was 48 hours.

The OxEon Energy large-scale single-channel modular thermochemical reactor is a single tube that is nominally 4.5 inches in outer diameter. The catalyst occupies approximately 49.5" of the reactor tube assembly. The center of the tube contains an internal cooling fin (to disseminate the heat throughout the catalyst bed that is generated during exothermic reactions). OxEon Energy developed this reactor along with the cooling fin after having several years of experience working with the hydrogenation of syngas (CO and H_2) to hydrocarbons using cobalt and iron based catalysts. Equation 2 above shows the exothermic nature of the Fischer Tropsch (FT) reaction ($\Delta_{\text{R}}\text{H}_{300^\circ\text{C}} = -166 \text{ kJ/mol}$). OxEon Energy is able to use a larger tube size because of the thermal management structure that distributes the heat throughout the catalyst bed produced by the exothermic FT reaction. Optimizing the FT reaction in the larger reactor tube size will drastically reduce the number of tubes required for a process. This is intended to reduce long-term fabrication and catalyst servicing costs. OxEon Energy was funded by the USAF to build a multi-tube reactor process that contains 7 of the 4" tubes. This translates into a 2 barrel/day pre-pilot demonstration using syngas (CO and H_2) as feedstock for production of fuel. The intent is to scale the modular process up to 100 barrel/day process using the same tube size. OxEon Energy's future capabilities highlights the significance of this test series as NRL begins evaluating for the very first time its hydrogenation catalyst in the OxEon Energy singular 4" reactor tube using CO_2 and H_2 as the feedstock.

In these large-scale studies uniform industrial quantities of catalyst were needed to fill the OxEon Energy commercial single-channel modular thermochemical reactor bed. NRL provided the a catalyst formulation (support 100%, potassium 16.5%, manganese 12%, iron 17% by mass) to Water Star Inc. for the large-scale synthesis of over 10 Liters (~ 12,000 grams) of catalyst material that contained particles ranging from 0.6 mm to 2 mm in diameter. Before OxEon Energy loaded the catalyst into the reactor it was reduced, passivated, and soaked in mineral oil for 12 hours. Approximately 9 ml of mineral oil was used for every 20 grams of catalyst. This is similar to the amounts used in the laboratory scale studies.

Initially three catalyst/shot mixtures were loaded in the reactor. The first section of the reactor contained 202 grams of catalyst and 1,950 grams of aluminum shot. The middle section was loaded with 1212 grams of catalyst and 4,530 grams of aluminum shot, and the last section contained 606 grams of catalyst and 1,080 grams of aluminum shot. This gave a total catalyst loading of 2020 grams and a total shot load of 7,560 grams of shot. This catalyst/aluminum mixture filled about four feet of the reactor length. The lowest concentration of catalyst at the top of the reactor was the first to see the hydrogenation gases.

The iron-based metal catalyst (support 100:16.5:12:17 ratio of support: potassium: manganese: iron) that was synthesized by Water Star Inc. only contained 31% active metal on a support. Therefore of the 2020 grams of catalyst loaded into the reactor, only 626 grams of the catalyst

was active. The support is typically needed to increase catalyst surface area and provide catalyst stability.

A 3:1 ratio of H₂/CO₂ was flowed over the catalyst at GHSV ranging between 1.4 x 10⁻³ and 8.0 x 10⁻⁴ L/s-g. Nitrogen was used as the internal standard and all experiments were carried out at 300 °C and 20 bar. The effluent fixed gases (H₂, CO₂, CO, N₂) and CH₄ from the reactor were analyzed in real time using an inline GC (Inficon) equipped with a TCD detector. The system was designed so that when the products exit the reactor they go to a hot trap and heavy hydrocarbons such as wax (typically seen if FT reactions using cobalt-based catalyst) are drained and the remainder of the hydrocarbons and non-converted synthesis gas goes to the fin tube to cool to room temperature. The gases then proceed through a chiller to a cold trap (cold trap is maintained at -4 °C) where the light oil and water are condensed and captured and separated periodically. The non-condensate gasses pass through a tee and are split such that part of the stream goes to flare and the other part goes to the recycle compressor. The composition of both gas streams are identical and the recycled feed is then blended back into the reactor at a ratio of 2:1 recycle feed to fresh feed (CO₂ and H₂). In this configuration some molecules of H₂ and CO₂ may go one pass through the catalyst and to flare, while others may make the recycle trip 1000 times. The flaring/removal of 1/3 of the gas stream is important to keep methane, and unwanted byproduct of this reaction to reasonable levels. Labview was used for the inline GC analysis to ensure that the GHSV and CO₂:H₂ ratio remained constant during the recycling process. The long chain effluent from the reaction (i.e. hydrocarbons greater than C-2) was analyzed separately using a GC (Bruker 456) equipped with a flame ionization detector.

Based experiences associated with thermal runaway that can occur during FT reactions, OxEon Energy loaded the thermochemical reactor with only 2,020 grams of the iron-based catalyst (626 grams of the catalyst was active). After the initial hydrogenation reactions with CO₂ and H₂ indicated that there would be no difficulty in managing the exothermic behavior of the reaction, the experiment was stopped so that the reactor could be reloaded with the full amount of catalyst. The catalyst was increased from 2020 grams to 6,090 grams. As a result the active metal loading was increased from 626 grams to 1888 grams.

Three specific approaches are used in this test series to reduce the effects of water on the catalyst activity and one additional features was used to minimize thermal degradation of the catalyst. The first approach involves the addition of a start-up solvent (mineral oil) to the reactor environment as a pretreatment. NRL found during laboratory scale CO₂ hydrogenation studies that mineral oil increased the overall hydrocarbon yield by decreasing the amount of CO while maintaining the same conversion efficiencies. It was also found that the mineral oil preserved the catalyst active phase longer and prevented oxidation of the active catalytic phase. The modeling and kinetic analysis of the data supports and explains these results by showing how the polar nature of the mineral oil coating the catalyst particle reduced the water adsorption on the catalyst sites. The reduced water adsorption on the catalysts' sites results in the increase in the FT reaction rate.

The second approach involves the use of a different catalyst support. The use of gamma alumina support for the distribution of the catalyst active metal surface is a common practice in the design of catalyst systems. The support's role is to increase the surface area for metal loading and provide catalyst stability. However, water can cause the hydroxylation of the gamma alumina

support causing the support to change phases from gamma alumina to Boehmite, lose surface area, and become more acidic in nature. NRL changed the catalyst support from gamma alumina to Macrolite® engineered ceramic media (M2) (Fairmount Water Solutions) having a bulk density of 73 lbs/ft³. Macrolite® is a chemically inert aluminosilicate that primarily consists of nepheline syenite spherical particles with an average diameter of 55 micrometers. Laboratory-scale fixed-bed plug flow reactor confirmed the catalyst performance and long term stability on this support.

The third and fourth approach are design features provided by Ceramtec. The first is a recycling element used to reduce the catalyst exposure to the water produced during the FT reaction. Syngas conversion on the first pass over the catalyst bed is limited to less than 50% and the water produced during the reaction is condensed. The unconverted syngas and byproducts from the first pass over the catalyst bed are recycled until a total conversion greater than 80% is achieved. The second is the internal cooling fin, this feature has been modeled, tested, and proven effective in distributing the heat throughout the catalyst bed that is generated from exothermic FT reactions. This is essential to preventing hot spots inside the catalyst bed that can lead to thermal runaway and sintering and agglomeration of the active metal catalyst phase resulting in a decrease in catalyst efficiency.

The catalyst run with CO₂ and H₂ was challenging for OxEon Energy based on their initial infrastructure. OxEon Energy currently uses natural gas and a OxEon Plasma Reformer to make syngas on site from a plumbed natural gas source inside the facility. This continuous source of syngas provides the ability to run the reactions at great lengths uninterrupted. The experiments for NRL were a bit more challenging because the large quantities of CO₂ and H₂ had to be supplied by an outside source and could not be generated on site as needed. As a result the feedstock was monitored closely and the reactions were periodically stopped over weekends.

Catalyst testing began with the full catalyst load of 6,090 grams (1888 grams active metal) and average GHSV at the beginning of the test of 1.4×10^{-3} L/s-g. This comprised of 4.6×10^{-4} L/s-g of fresh feed (3:1 H₂:CO₂) and 9.4×10^{-4} L/s-g recycled gas (CO, H₂, CO₂, hydrocarbons less than C-6). The reactor started out at (290 °C and 10 bar) and was brought to nominal temperature and pressure (300 °C and 20 bar). The first analysis of the products was reported one day later and six days later.

At a total GHSV of 1.4×10^{-3} L/s-g, CO₂ conversion for these conditions was on average 53%. The methane selectivity varied from 11.5% to 25.8% and CO selectivity slowly increased slowly over time from 11.5% to 17.2%. Hydrocarbon selectivity ranged from 63 to 78%. Differentiating the hydrocarbon product stream at this point in the analysis was not possible so the olefin paraffin ratio is not reported. The oil collected (defined as hydrocarbons that are C-6 and higher) during this time was 6 kg. When the GHSV was reduced from 1.4×10^{-3} to 8.0×10^{-4} L/s-g and the reactor was operated under these conditions an increase in CO₂ conversion from an average of 53% to an average of 69% was observed. The methane and CO selectivity were reduced to 12% and 9%. While the hydrocarbon yield increased to 79% the olefin/paraffin ratio was only 3. Thus one third of the short chain hydrocarbons (less than C-6) produced were saturated and can't be further oligomerized to higher hydrocarbons. The liquid fraction collected over 48 hours of running these operating conditions was 22.7 kg. This is an increase to an average of 73% per day of liquid hydrocarbon production.

A comparison was made between the total ion chromatograms taken by a GC mass spectrometer for a petroleum derived JP-5, a Camelina derived JP-5, CO₂/H₂ synthesized fuel at the laboratory scale, and CO₂/H₂ synthesized at the large-scale. These chromatograms provide a fingerprint of the fuel by identifying the hydrocarbon region which the fuel primarily contains. The highlighted region of the chromatograms show that the petroleum based JP-5 and Camelina derived fuels have very different fingerprints but that the majority of the fuel consists of hydrocarbons ranging between C₉-C₁₆. Both of these fuels meet the military specification MIL-DTL-5624 for JP-fuel. When comparing these fuels to those produced at the laboratory and large-scale, it was shown that the majority of the liquid hydrocarbons produced in the synthesis process fall in the same highlighted region. The lighter and heavier hydrocarbons can be easily removed from the fuel using common distillation methods.

Further subsequent measurements were taken with the recycling system turned off so that only fresh feed (CO₂ and H₂) were fed into the reactor. The goal was to determine the impact of gas recycling on the activity of the catalyst and the products of the reaction. During these measurements, the GHSV was 4.6×10^{-4} L/s-g. These reactor conditions are the closest to those run at the laboratory scale. At the laboratory scale, there is no mechanism in place to recycle the product stream over the catalyst. Under these single pass conditions, CO₂ conversion is reduced to 26% and the methane selectivity is reduced to 6%. CO selectivity is increased by 69% to 80%. Hydrocarbon selectivity was reduced by 39% to 42% and the olefin/paraffin ratio increased to an average of 4. When the catalyst was run in the NRL laboratory-scale fixed-bed plug flow thermochemical reactor under identical reactor conditions, a 57% loss in CO₂ conversion at 11% was found. The CO selectivity was reduced by 56%, the hydrocarbon selectivity was increased by 36%, and the methane selectivity was identical at 6%. These results are significant because they indicate that at the large-scale the 56% increase in CO₂ conversion favors the formation of CO. Since the reaction conditions are similar, the observed change in product distribution may be attributed to the change in scale and design of the large-scale thermochemical reactor.

Long term catalyst stability is an important for the commercial feasibility of the catalyst process, therefore the used catalyst was regenerated by flowing hydrogen over the catalyst bed until no methane was detected by the GC (Agilent Technologies) equipped with a TCD detector. Then nitrogen with air to make 1% O₂ was flowed over the catalyst bed. The O₂ content was gradually increased until no further CO₂ was measured by the GC. This method essentially removed all hydrocarbon and carbon remaining on the catalyst and also dried the catalyst bed. After catalyst regeneration the reaction was resumed at a GHSV of 9.2×10^{-4} L/s-g with the recycling feature. The results indicate that the catalyst was regenerated as the CO₂ conversion, hydrocarbon selectivity, and hydrocarbon liquid fraction returned to levels initially reported at the beginning of the catalyst run. These results are extremely significant as they demonstrate the ability to regenerate the catalyst which suggest long term viability of maintaining catalyst activity.

In conclusion, the performance of NRL iron-based catalyst in a OxEon Energy commercial single-channel modular thermochemical reactor unit was evaluated in this test series. In a typical laboratory-scale CO₂ hydrogenation reaction, 20 grams of NRL synthesized catalyst is evaluated in a small fixed-bed plug flow thermochemical reactor. In this test series the catalyst was commercially synthesized and 6,090 grams of catalyst were loaded in the OxEon Energy

modular reactor. This 300 x scale-up in the CO₂ hydrogenation reaction enabled NRL to evaluate the reactor environment on catalyst performance and determine how this performance compares to laboratory testing. Initial results indicated that at the large scale CO₂ conversion was 56% higher than the laboratory scale and that the increase in CO₂ conversion favored the formation of CO. When the product stream was recycled, CO₂ conversion was increased from 26% to 69% and CO selectivity was reduced in favor of hydrocarbon formation. OxEon Energy demonstrated that the NRL iron-based catalyst could successfully be regenerated and with minimum loss in activity. All results and observations were documented in the NRL Letter Report, Willauer, H. D.; Bradley, M.J.; Hardy, D. R.; Frost, L.; Hartvigsen, J. “Large-Scale Testing of NRL CO₂ Hydrogenation Catalyst: Quick Look Results Analysis” NRL Letter Report 6360.2/156, 20 August 2016. These results were critical as they demonstrated successful scale-up of NRL iron-based catalyst in OxEon Energy commercial single-channel modular thermochemical reactor unit. This is the first step in transitioning the technologies from a TRL 3 to TRL6 [55].

5.8 The Global Potential For Converting Renewable Electricity To Negative-CO₂ Emissions Hydrogen

In parallel efforts of converting CO₂ waste into energetic molecules, NRL has been at the forefront of developing technologies to capture the CO₂ from seawater. The interest in these NRL technologies led to a collaborative effort between NRL and scientists from the University of California, Santa Cruz and University of Colorado Boulder to combine saline water electrolysis with mineral weathering powered by any source of non-fossil fuel-delivered electricity. The research found that combining these technologies could on average, increase energy generation and CO₂ removal by greater than fifty times relative to biomass energy plus carbon capture and storage (BECCS), at equivalent or lower cost. This electrogeochemistry avoids the need to produce and store concentrated CO₂, instead converting and sequestering CO₂ as already abundant, long-lived forms of ocean alkalinity. Such energy systems could also greatly reduce land and freshwater impacts relative to BECCS, and could also be integrated into conventional energy production to reduce its carbon footprint. Further research is needed to determine the realizable capacity, economics and net environmental benefit of such systems. We also stress that the negative-emissions energy field is in its infancy and therefore the methods discussed here are unlikely to be the only ones ultimately worth considering. CO₂ management strategies and research and development policies in the future therefore need to anticipate and encourage the emergence of additional approaches. This will maximize our chances of safely and cost-effectively increasing sustainable energy production while helping stabilize atmospheric CO₂, the climate and ocean acidification below the rapidly approaching critical thresholds. All results and observations were documented in the referred journal by Rau, G. H.; Willauer, H. D.; Ren, X. J. The Global Potential For Converting Renewable Electricity To Negative-CO₂ Emissions Hydrogen. *Nature Climate Change* 2018, 8, 621-625 [56].

5.9 Synthetic Fuel Development

The book chapter covers a brief history of how synthetic fuel development occurred and the role of fossil fuels in the different processes. Synthetic fuels have progressed along with science and technology developments as new materials and spectroscopic techniques have enabled the

development of better catalysts and reactor designs. This chapter also points out that any big synthetic fuel breakthroughs (the Bergius process, the FT, and MTG) came from the desire to become petroleum independent following a national threat of war, an oil embargo, or crisis. Currently synthetic fuel catalyst have been extended to thermochemical approaches for the conversion of anthropogenic carbon dioxide as intermediates for chemicals and fuel production. This coupled with the future advances in renewable energy and carbon dioxide capture from the environment offers promising solutions to mitigate anthropogenic carbon dioxide increases.

Today the role of synthetic fuels and its sources in the future is up for much debate. Fossil fuels currently account for 88% of the global energy sources. How this trend changes with increase in global population, advances in renewable sources, renewable storage, transport technologies, transportation technologies, changes in fossil fuel availability, and environmental policies will ultimately come down to economics as opposed to national and international wars, embargos, and crisis of the 20th century. The push towards what is considered to be abundant natural gas to replace coal and oil as it burns cleaner may in the long run be used by more nations to produce synthetic fuel.

The amazing recent advances in DAC and promising developments for utilizing seawater as a carbon source combined with renewable electricity could potentially energize synthetic fuel development in the near future as the world seeks solutions to solve increases in anthropogenic CO₂. The observations were documented in the book entitled “Future Energy 3rd edition, Chapter 26 “Synthetic Fuel Development,” H. D. Willauer and D. R. Hardy [57].

6.0 CONCLUSIONS

NRL is developing and demonstrating technologies to produce operational fuel (JP-5/F76) on land and at sea for the Navy. This 6.1 New Start Program provided CORE funding to continue to conduct the sustained basic and applied research necessary to develop the chemistries required to convert highly stable environmental CO₂ to drop in replacement fuels for the Navy and DOD. With the help of this program, additional funding was received from OPNAV to collaborate with industrial partners to scale-up NRL catalyst formulations for demonstration and evaluation in a commercial modular continuous flow chemical reactor system. This achievement transitioned the technology from a **TRL-3** to **TRL-7**. In addition, these funds helped to support the concurrent effort of developing technologies to successfully capture CO₂ from seawater as part of the larger program of developing a future Navy capability. Producing any amount of operational fuel in theater as needed would minimize logistic efforts, maximize war-fighting efforts, while achieving strategic fuel autonomy and security.

This program produced 7 papers in refereed journals, 1 book chapter, 1 NRL Memorandum report, 1 NRL Letter report, 1 patent, and 17 presentations at conferences. The full references for these materials are provided in Appendix A.

7.0 MILESTONES

- Developed water stable CO selective catalyst (>98%) that operate under low temperature and pressure conditions (300 to 450 °C).

- Determined the water stabilizing effect start-up solvent has on Fe-based catalyst in CO₂ hydrogenation reactions.
- Developed a bimetallic catalyst that is more water stable than typical Fe-based catalyst by adding copper that is known to be more water tolerant.
- Transitioned CO₂ hydrogenation reactions from TRL-3 to TRL-7.
- Demonstrated 70% CO₂ conversion on the commercial scale along with recycling and catalyst regeneration.

8.0 RECOMMENDATIONS FOR FUTURE STUDIES

The NRL team is leading the field of CO₂ hydrogenation and its unique multidisciplinary approach has a proven history of innovations and transition. As NRL continues to push scientific frontiers and innovation, it is critical for the team to maintain basic and applied research efforts in the development of CO₂ catalysts. In the spirit of these goals, NRL is currently pursuing further understanding and control of fundamental catalyst-support interactions. These interactions have proven to significantly influence the stability and selectivity of catalysts for thermochemical hydrogenation reactions.

9.0 REFERENCES

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APENDIX A

Oral Presentations

1. Invited: Heather D. Willauer, “Converting Seawater Into Fuel: Game Changer Technology”, Energy Efficiency in Shipping, September 10-11, 2014, London, UK.
2. Invited: LT Wesley Monillas, Heather D. Willauer “#4515, Navy Fuels,” ONR-RC 2015 Winter Program Review, 22-25 January 2015, Arlington Virginia.
3. Bruce D. Patterson, Reto Holzner, Armand Kurum, Christopher Rossel, Heather D. Willauer, Jeroen A van Bokhoven “Liquid Fuel Production on Artificial Islands”, Energy Science Technology International Conference & Exhibition, 20-22 May 2015, Karlsruhe Convention Centre, Germany.
4. Invited: LCDR Felice DiMascio, Heather D. Willauer “#4515, Navy Fuels,” ONR-RC 2016 Winter Program Review, 28-31 January 2016, Arlington Virginia. .
5. Matthew J. Bradley, Ramagopal Ananth, Felice DiMascio, Dennis R. Hardy, Jeffrey W. Baldwin, and Heather D. Willauer, “Combating the detrimental effects of water in Fe-based CO₂ hydrogenation catalysts,” American Chemical Society Spring 2016 National Meeting, San Francisco CA March 13-17, 2016.
6. Matthew J. Bradley, Ramagopal Ananth, Felice DiMascio, Dennis R. Hardy, Jeffrey W. Baldwin, and Heather D. Willauer, “Combating the detrimental effects of water in Fe-based CO₂ hydrogenation catalysts,” Division of Catalysis Science and Technology Sci-Mix, American Chemical Society Spring 2016 National Meeting, San Francisco CA March 14, 2016.
7. Marc D. Porosoff and Heather D. Willauer, “Development of catalysts for CO₂ hydrogenation to olefins,” Gordon Research Conference, 12-17 June 2016, Colby Sawyer College in New London, NH.
8. Invited: Heather D. Willauer “Operational Fuel Production from Seawater,” March 2016 NSA Federal Laboratory Symposium, The Laboratory for Telecommunications Sciences (LTS) at 8080 Greenmead Drive, College Park, MD 20740, March 29-31, 2016.
9. Invited: Heather D. Willauer, “Seawater to Fuels,” Naval Safety and Environmental Training Center 2016 Professional Development Symposium Energy Track, March 17, 2016.
10. Marc D. Porosoff and Heather D. Willauer, “Development of catalysts for energy and environmental applications,” American Institute of Chemical Engineers (AIChE), San Francisco Union Square, CA, November 6, 2017.
11. Heather D. Willauer, Matthew J. Bradley, Marc D. Porosoff, Felice DiMascio, Jeffrey W. Baldwin, Dennis R. Hardy “Sustainable Energy Production from Seawater,” DoD Science, Technology, and Innovation Exchange, ByteCubed meeting facility, Arlington Virginia, August 25, 2017.
12. Invited: Heather D. Willauer, Sustainable Energy Production from Seawater, Microbial Electrosynthesis Meeting/Workshop, Hosted by NRL with funding from ONR & DOE

Advanced Research Projects Agency-Energy (ARPA-E), Washington DC., November 3-4, 2017.

13. Invited: Heather D. Willauer and Felice DiMascio “Navy Fuels,” ONR-RC 2-18 Winter Program Review, Arlington Virginia. January 25-28, 2018.
14. Invited: Heather D. Willauer “Operational Fuel Production from Seawater,” Sea-Air-Space: The Navy League’s Global Maritime Exposition Learn. Compete. Win. Gaylord Convention Center, National Harbor, MD. April 11, 2018.
15. Invited: Heather D. Willauer, James R. Morse “Operational Energy From Seawater, DOE Hydrogen and Fuel Cells Program Annual Merit Review and peer Evaluation Meeting, Marriott Wardman Park Hotel, Washington DC June 13-15.
16. Invited: Heather D. Willauer “Carbon Sequestration,” Federal Laboratory Consortium (FLC) Energy Webinar Series. November 2, 2018.
17. James R. Morse, Heather D. Willauer, “The Role of Transition Metal Carbide Catalysts in the Transformation of CO₂ into Fungible Fuels,” Spring MRS Conference, 2019.

Refereed Journal Articles, Reports, Patents

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