

FINAL TECHNICAL REPORT

Executive Summary

Hawaii Energy and Environmental Technologies Initiative

Office of Naval Research

Grant Award Number N00014-11-1-0391

For the period January 1, 2011 to September 30, 2016



HNEI

Hawai'i Natural Energy Institute

University of Hawai'i at Mānoa

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EXECUTIVE SUMMARY

This report summarizes work conducted under Grant Award Number N00014-11-1-0391, the Hawaii Energy and Environmental Technologies Initiative 2010 (HEET10), funded by the Office of Naval Research (ONR) to the Hawaii Natural Energy Institute (HNEI) of the University of Hawaii at Manoa (UH). The overall objective of HEET10 effort was to use Hawaii as a model for development, testing, and integration of distributed energy systems for the Pacific Region. HEET10 included efforts to meet critical technology needs of the Navy associated with fuel cell testing and evaluation, synthetic fuels processing and production to accelerate the use of liquid biofuels for Navy needs, the extraction and stability of seabed methane hydrates, and alternative energy systems. Testing and evaluation of alternative energy systems includes work on Ocean Thermal Energy Conversion (OTEC), grid-scale battery energy storage, support for hydrogen fuel operations at the Marine Corps Base Hawaii and on the Island of Hawaii, building energy efficiency test platforms, and end-use high value energy efficiency technologies.

The final report and all technical reports as well as publications produced through these efforts are available on HNEI's website at <http://www.hnei.hawaii.edu/node/346>.

Under Task 1, subtask 1.1, new diagnostic capabilities for fuel cell testing and evaluation were added and the evaluation of stacks for UUV and UAV applications continued. The use of pressure swing adsorption technology to remove airborne contaminants was investigated as a replacement for incumbent air filters. Rapid, ex situ catalyst and membrane materials screening capabilities were implemented to isolate contaminant impacts on fuel cell performance. Gas analysis capabilities were upgraded with the commissioning of a gas chromatograph/mass spectrograph to identify contaminant decomposition reactions within a fuel cell. A prototype tracer system was acquired to quantify product liquid water, assess the extent of flow field channel blockages by the intrusion of flexible gas diffusion media, and determine the existence of flow bypass and uneven flow distribution lowering cell efficiency. The potential of voltage noise measurements to identify, in real time, specific failure modes was explored. An adaptable reactant gas recirculation system representative of real system operating conditions was built to study water and contaminant accumulation processes. A commercial automotive fuel cell stack design was adapted for operation in an oxygen-fed UUV. The effect of duty cycling on the durability of a commercial stack for a UAV application was determined by comparing load following (fuel cell system) and constant load (fuel cell/battery hybrid system) cases. HNEI also conducted testing of NRL's variable current battery discharge method intended to improve the specific energy of a lithium-ion battery pack.

Under subtask 1.2, Novel Fuel Cells, thin films suitable for biofuel cell electrodes were fabricated from unique materials comprised of modified chitosan polymer. Results showed that films of controlled thickness could be reproducibly produced using the technique of spread-coating, and that chemical modification of the chitosan biopolymer with hydrophobic chemical

groups could extend the range over which a linear response between film thickness and deposition rate could be achieved. These results were deemed important as having the ability to understand how the introduction of hydrophobic modification - a technique shown to introduce solution-based micelle structure and micellar aggregates that support enzyme immobilization - affects film thickness and morphology of spread coated thin films will aid the long term development and deployment of chitosan-based biofuel cell electrodes.

Task 2, Technology for Synthetic Fuels Production sought to identify and address issues related to liquid biofuel variability caused by primary feedstock sources, conversion methods, storage methods, or the presence of contaminants.

Subtask 2.1 focused on plasma reforming of renewable biogas to produce hydrogen rich streams that can be upgraded for fuel cell applications. Additionally hydrogen sulfide contamination was characterized. For this investigation, a non-thermal plasma reactor was modified and parametric tests, factorial tests, and response surface methodology was conducted sequentially to identify optimum reactor operating conditions to minimize specific energy requirements.

The thermocatalytic production of hydrocarbons from synthesis gas was examined in subtask 2.2, with emphasis on catalyst evaluation. The effects of pore size on ruthenium-silica catalyst performance were investigated for Fischer–Tropsch synthesis, and the catalysts were characterized. The addition of small amounts of zirconium and manganese improved catalytic activity and stability for Fischer–Tropsch synthesis. Results were published and are available on HNEI’s website.

Under subtask 2.3, novel solvents to extract bio-oils and proteins from biomass were investigated. The three objectives were to quantify a 1-step extraction of phorbol esters from oil seeds using a hydrophilic co-solvent system, determine the extent to which the phorbol esters can be recovered from the co-solvent, and determine the extent to which the extracted biomass is toxin-free and suitable as an animal feed.

The objective of subtask 2.4 was to investigate biochemical pathways for conversion of synthesis gas into liquid fuel molecules (gasoline and diesel fuels). Unique microbial species were used to convert syngas to a mid-stage product. Fuel costs could be reduced by reusing the hydrolysates of cell debris, however current biodiesel production through microbial carbon dioxide fixation was found to be economically infeasible.

Subtasks 2.5 and 2.6 were focused on fit-for-purpose testing of biofuels to determine their susceptibility to biocontamination and propensity for creating biocorrosion, respectively. In subtask 2.5, biocontamination of fuels, two isolates from a petroleum-contaminated sample were used to study the biodegradation of sulfur containing hydrocarbon inherently present in all diesel fuels. Glycerol was found to stimulate both rhamnolipid production and dibenzothiophene degradation, and optimal molar ratios were determined. Under subtask 2.6, the influence of fungi on the corrosion of 1018 steel was investigated. The influence of the fungi *Paecilomyces saturatus* on the corrosion of 1018 steel was investigated in B100, B20, and ULSD fuel-water mixtures for a three-month exposure. The 1018 steel coupons remained in the passive state (due to the presence of the air-formed oxide film) in the B100 and B20 fuel-water mixtures; whereas, the 1018 steel coupons corroded actively in the ULSD fuel-water mixture. The presence of

biodiesel appeared to have a beneficial effect on corrosion even in the presence of the fungi. Corrosion rates decreased as the biodiesel content in the fuel-water mixtures increased. For all cases where the steel actively corroded, the thick layer of iron corrosion product was identified as lepidocrocite.

Subtask 2.7 explored using the Flash-Carbonization™ process to convert waste streams into carbon products. Fundamental measurements of carbon yield as a function of conversion technology and process parameters were determined using corncob as a model fuel. Elevated pressure secured the highest fixed-carbon yields. Findings show that secondary reactions involving vapor-phase species are at least as influential as primary reactions in the formation of charcoal. Size reduction handling of biomass, significantly reduces the fixed-carbon yield, with whole corncob carbonized at elevated pressure producing the highest yield of charcoal. By comparison, fluidized-bed and transport reactors cannot realize high yields of charcoal from biomass. Results have been published in a journal paper and are available on HNEI's website.

Task 3 work on methane hydrates focused on methane hydrate stability and related environmental issues; hydrogen fuel storage in binary hydrates; and promoting international research collaborations. Fundamental laboratory studies were performed on hydrate formation and dissociation in porous media and determining the effects of transition metal salts on hydrate behavior. Hydrates that form in relatively fine sands were found to melt at lower temperatures than hydrates that occur in larger void spaces. Most of the transition metal salts tested in the present study inhibited methane hydrate formation at high concentrations, but none to the extent of sodium chloride except for ferric chloride. As a continuation of our studies of the microbiology of methane and other hydrocarbons in seafloor sediments and the oceanic water column, a novel gas-tight bioreactor was designed and fabricated. The purpose of this bioreactor was to increase target microorganism density to levels required to investigate microbial methane cycling. During HEET 10, an investigation also was initiated to explore the use of gas hydrates as a storage medium for hydrogen fuel for propulsion applications, and laboratory facilities and protocols were designed, fabricated, and tested. Finally, to foster international collaborative R&D on methane hydrates, HNEI supported and helped to organize the 8th and 9th International Workshops on Methane Hydrate R&D.

Task 4, ocean energy focused on continued development of OTEC heat exchanger technology (subtask 4.1), and analysis and testing to support development of lower cost Sea Water Air Conditioning (subtask 4.2). HNEI subcontracted Makai Ocean Engineering to provide heat transfer performance; and corrosion and biofouling testing of heat exchangers for use in OTEC power plants. Makai completed the design, fabrication, installation, and performance testing of the Lockheed Martin Graphite Foam heat exchanger. However it did not have the anticipated improvement in performance compared to the plain shell and tube design. The Lockheed Martin Enhanced Tube heat exchanger was also designed, fabricated, installed, and performance tested, and showed a significant improvement in performance versus the plain tube heat exchanger. Additionally, three years of corrosion testing was concluded on hollow extrusion samples.

Subtask 4.2 characterized environmental conditions within the receiving waters of a Seawater Air Conditioning (SWAC) system. This included discharge plume analysis conducted by Makai

Ocean Engineering as well as procurement of three wave buoys to support future time series water quality analysis in support of SWAC development.

Task 5 involved laboratory and field efforts to investigate battery energy storage. Under subtask 5.1 Lithium-ion batteries were evaluated to minimize battery cell degradation at the cell and small-pack level for grid energy storage applications. Key performance metrics of alternative Lithium-ion cell chemistries were explored including cycle life, useable energy and power, power energy density, and power efficiencies. It was found that batteries with titanate negative electrodes have better capacity retention than batteries using graphite. Titanate based batteries were investigated further and their durability against mild overcharge was established. It was shown that, upon overcharge, these cells are prone to some gassing and that it could limit their performance if the gas remained trapped in-between electrodes. This effort allowed the invention of a new patent-pending methodology for online state of health tracking that could be applicable to large Battery Energy Storage (BESS) systems. In order to be able to test the larger cells used in the grid-scale BESS, HNEI established a new battery testing laboratory within the Hawaii Sustainable Energy Research Facility and expanded existing software tools to visualize characteristics of cell chemistry performance and degradation.

Under subtask 5.2, research continued on three grid-connected battery energy storage systems intended to assess range of ancillary services under different grid operational conditions on three islands. Research efforts for the Hawaii Island grid primarily focused on regulating grid frequency using an Altairnano 1MW, 250kWh battery system procured and installed under HEET09. HEET10 findings illustrated how local battery storage support of the 10MW Hawaii wind farm can cause grid-wide issues. However, it was found that battery cycling can be greatly reduced to extend lifetime while still providing a significant portion of the grid-wide benefit. A second Altairnano 1MW, 250kWh BESS was procured, installed on Oahu, and tested to simultaneously provide power smoothing as well as voltage regulation within an electric substation serving large industrial loads. A third BESS was installed on Molokai, an Altairnano 2MW, 397kWh system, and facility acceptance testing completed. Testing and evaluation of the BESS located on Oahu and Molokai will be conducted under future APRISES awards.

Under Task 6, grid-connected PV systems on Oahu and Maui were evaluated. Continuing previous ONR-funded work, performance and durability of different PV and inverter technologies under differing environmental conditions were characterized. The PV systems under test represent grid-connected, residential and small-scale commercial systems. This work has created a framework of knowledge on PV test platform design, installation, testing, instrumentation and data analysis methodologies. Accomplishments under HEET10 include development of new test protocols and data collection methodologies,; installation of a carport-based PV test platform in South Maui, advancement of data analysis tools, including an innovative dissociation of the DC performance ratio into current and voltage performance, and detailed analysis of the first month of performance data from the Maui site and a year of data from UH Manoa. Data collection and analysis from both sites will continue under future APRISES awards.

Task 7 focused on four main areas of hydrogen development: fueling support and analysis for the Navy/Marine Corps demonstration fuel cell vehicle project on Oahu; fueling support for the

forthcoming operation of demonstration fuel cell buses at Hawaii Volcanoes National Park on Hawaii Island with a hydrogen dispensing system; assessment of the capacity for production of hydrogen and biomass from agriculture in Hawaii, and; assessment of alternative pathways to meet the projected growth in demand for hydrogen in Hawaii, mainly gasification of municipal solid waste and importation of natural gas in small-scale container vessels.

Under subtask 7.1 HNEI supplied hydrogen in support of the Navy/Marine Corps demonstration of General Motors Equinox fuel cell electric vehicles, first using hydrogen imported from the mainland and then via operation of a dual pressure 350/700 bar fast fill hydrogen fueling station at the Marine Corps Base Hawaii. This subtask also included analysis of the station's technical performance.

In anticipation of the future deployment of two hydrogen fuel cell shuttle buses at Hawaii Volcanoes National Park, a high air contaminant environment, subtask 7.2 supported development of a hydrogen dispensing system on the Island of Hawaii. The buses will be used to test a novel (patent pending) air filtration system developed by HNEI to protect the shuttle bus fuel cell power systems from airborne contaminants. In future operations, hydrogen will be delivered from the Natural Energy Laboratory Hawaii Authority located on the west side of the island using hydrogen transport trailers. Additionally under this subtask, a hydrogen dispenser boost pump system was developed and tested to reduce hydrogen transport costs.

Subtask 7.3 explored production of hydrogen fuel from agriculture in Hawaii as an alternative to importing oil. Pacific Biodiesel Technologies was contracted to conduct an operations sensitive assessment of the capacity for the local production of fuels and biomass to assess the potential for DOD operations and/or hydrogen production. The project site was transitioned from Oahu to Hawaii Island in order to support the Navy and US Department of Agriculture goal of establishing a biofuels commercialization program. The project emphasized broad assessments of the potential agricultural crop production, products and co-products, and process technologies available to produce advanced biofuels on Hawaii Island.

Subtask 7.4 assessed alternative pathways to meet the projected growth in demand for hydrogen in Hawaii, primarily gasification of municipal solid waste and importation of natural gas in small-scale container vessels. Technology and economic issues were addressed and recommendations put forth for development of hydrogen infrastructure with capacity to meet potential targeted demand to produce hydrogen for fuel cell vehicles.

Task 8 included four topics relating to energy efficiency in buildings. Under subtask 8.1 two second-generation energy-neutral test platforms were designed and installed by Project Frog of San Francisco on the UH Manoa campus. Construction was completed and the University began to use the platforms as functioning classrooms in August 2016. Under subtask 8.2 two Project Frog platforms installed at the Kawaikini New Century Public Charter School on Kauai were monitored. Actual performance was compared to the predictive models developed during the design phase. Under subtask 8.3, MKThink was contracted to develop a data management platform to improve the acquisition, management and analysis of structured and unstructured data in order to improve decisions related to sustainable energy solutions. Subtask 8.4 focused on an evaluation of available desiccant dehumidification technologies and their potential

applications to improve thermal comfort in tropical and subtropical environments. As part of this assessment, energy-saving air-management processes were evaluated considering technical and economic aspects pertinent to retrofits and new building development in Hawaii. .

Task 9, Algal Production Studies focused on improving the economics of mixotrophic growth systems through exploration of four areas: Environmental Controls, Organic Acids Feeding Strategies, Lipid Accumulation Strategies, and Strain Sourcing and Selection. HNEI subcontracted this effort to Hawaii BioEnergy to source indigenous microalgae and test in laboratory and outdoor open cultures.