FINAL TECHNICAL REPORT

Executive Summary

Hawaii Energy and Environmental Technologies Initiative

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For the period December 1, 2009 to September 30, 2015

HNEI
Hawai'i Natural Energy Institute
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This report summarizes work conducted under Grant Award Number N00014-19-1-0310, the Hawaii Energy and Environmental Technologies Initiative 2009 (HEET09), funded by the Office of Naval Research (ONR) to the Hawaii Natural Energy Institute (HNEI) of the University of Hawaii at Manoa (UH). This continued efforts initiated under previous HEET awards on critical technology needs associated with the development of advanced fuel cells and fuel cell systems, an expanded effort on fuel processing and purification, the extraction and stability of seabed methane hydrates, and testing and evaluation of alternative energy systems for the Pacific Region. Testing and evaluation of alternative energy systems includes heat exchangers for Ocean Thermal Energy Conversion (OTEC), grid-scale battery energy storage, photovoltaic (PV) systems, a fast-fill hydrogen fueling station, energy efficiency test platforms, and alternative biofuels development.

Under HEET09 fuel cell testing and evaluation continued with upgrades to the test stand along with further evaluation of fuel and airborne contaminant impact testing on fuel cell performance. The impact of fuel and airborne contaminant mixtures on fuel cell performance was continued. In support of the fuel cell bus demonstration program in Hawaii Volcanoes National Park (HAVO), another ONR activity, the effect of relevant contaminants and their mixtures were characterized to set air filter specifications. The potential synergy between different classes of airborne contaminants was also explored using a wetting agent that can affect product liquid water management in a fuel cell and promote the transport of ions towards and into the membrane, ultimately lowering fuel cell efficiency. Fuel cell hardware-in-loop and system simulation activities were focused on the benefits of novel fuel cell/battery hybrid system architecture for UAV applications. These were determined by testing the hardware controller and assessing its impact on UAV flight duration for a given propulsion and ancillary load profile. In support of the Naval Research Laboratory, HNEI conducted testing of NRL's variable current battery discharge method intended to improve the specific energy of a lithium-ion battery pack.

In support of the development of bioactive fuel cells, quantitative characterization of the electrode properties and cell performance were performed in order to enhance fundamental understanding of the underlying mechanism in electrobiocatalysis. This work was conducted in two parts, first to develop and characterize chitosan co-block polymers to immobilize multiple enzymes that can more fully oxidize complex energy fuels, and secondly to develop integrated *in situ* characterization methodologies, to better understand the charge transfer process involved by more direct measurement and correlation. Polar sensitive fluorophores in combination with fluorescent spectroscopy and microscopy techniques were used to probe the chemical microenvironments of native and hydrophobically modified chitosan polymer matrices used to immobilize enzymes. Results indicate that electrostatic forces dominate the interaction between fluorophores and polymer when both are freely suspended in solution. Secondly, unique

capabilities were demonstrated using spectroscopic imaging ellipsometry and electrochemical techniques to investigate mediator immobilization on platinum electrodes.

For Navy application, there is particular interest in liquid biofuels that can be introduced into the current fuel supply chain. This task identified operational challenges and analyzed issues related to the introduction of liquid biofuel, focusing on the variability caused by primary feedstock sources, conversion methods, storage methods, and the presence of contaminants.

In subtask 2.1, Biofuel Characterization Planning, high priority, critical testing capabilities were developed and interfaced with the supply chain. These capabilities were identified in the previous phase of HEET and included equipment, personnel, and lab facilities to support the Navy's greater use of alternative fuels blended with petroleum F76 diesel and JP5 jet fuel. Under this award, "fit-for-purpose" properties of the fuels were identified including their compatibility with fuel tank and piping materials, their compatibility with elastomer seals in engines and fuel delivery equipment, and their capacity to maintain levels of microbial and corrosion activity comparable to, or lower than, petroleum. Storage stability testing capabilities for fuel quality were down-selected from the selected list of methods to assess special equipment requirements for fuel quality.

In Subtask 2.2, Plasma Arc Processing, the use of a non-thermal reverse vortex flow (RVF) gliding-arc reformer for liquid fuels was explored. Previous work had focused on non-thermal, RVF stabilized gliding-arc plasma reforming of methane. Under this subtask, the same system was adapted for the reforming of marine diesel (F-76), hydroprocessed renewable diesel (HRD-76) and dodecane; liquid fuels that could be reformed into hydrogen rich gas for shipboard applications. Ultrasonic atomization of the fuel was used to axially inject fuel into the reformer. Injected fuel vaporized due to elevated temperatures in the reactor. Vapor clouds were eliminated by insulating the upper half of the reaction chamber. Parametric and factorial tests resulted in dodecane conversion that remained fairly constant across all of the tests while the selectivity, hydrogen yield, efficiency, and other parameters varied greatly. Decreasing power input, increasing fuel input, and increasing steam input improved system performance.

In Subtask 2.3, Thermocatalytic Conversion of Synthesis Gas into Liquid Fuels, catalyst characterization and activity of Zr or Mn containing Ru/Q10 were investigated for Fischer–Tropsch synthesis in a stirred slurry tank reactor. The addition of Zr or Mn in Ru/Q10 enhanced CO conversion, C5+ selectivity and space time yield under the tested conditions. The catalyst activity was highly stable during the period of reactor operation. Catalyst characterization results suggest that a small amount of Zr or Mn addition can increase the surface atomic concentration of Ru and inhibit the oxidation of Ru species, resulting in enhanced catalyst activity and stability.

The objective of 2.4, Novel Solvent Based Extraction of Bio-oils and Protein from Biomass, was to optimize methods and compositions of co-solvent mixtures for the one-step extraction of bio-oils and protein from biomass, and to further develop unit operations capable of fractionating and purifying both products. Three main tasks were completed: (1) to quantify the degree to which 1-step extraction using a hydrophilic co-solvent system extracts protein from corn and oil seeds; (2) to determine the extent to which proteins denature in the co-solvent system; and (3) to optimize the composition of the co-solvent for protein extraction. In this work, an ionic liquid –

methanol co-solvent was shown for the first time to effectively co-extract phorbol esters and bio-oil from jatropha kernel biomass in a single extraction step. Under optimized conditions for simultaneous extraction of bio-oil and phorbol esters, 30 wt% ionic liquid, [C2mim][MeSO4] and 70 wt% methanol, nearly all the bio-oil was extracted and auto-partitioned to a separate immiscible phase. Additionally, approximately 98% of the phorbol esters were extracted from the original biomass. The co-solvent did not extract significant amounts of protein which remained with the jatropha biomass even after washing steps. In addition to achieving effective co-extraction of both bio-oil and phorbol esters, the low phorbol esters - high protein content of the de-lipified biomass also possessed high potential as an animal feed.

In Subtask 2.5, Biochemical Conversion of Synthesis Gas into Liquid Fuels, the effect of CO on microbial activity was investigated in a gas tight bioreactor, revealing the toxicity of CO in a typical biomass syngas (CO>10%). A thermal reactor with Cu/ZnO catalyst was developed to convert CO into CO_2 and hydrogen. A dual reactor system was built up for continuous gas circulation between the bioreactor and the catalytic reactor to reach a very high CO conversion (> 90%). Three major conclusions were drawn from the work: the microbial strain cannot work directly on syngas because of the high CO content (>10%) and its toxicity to microbes; the strain can work on residual gas from other processes if CO content is 5% or below, and; a dual reactor system can effectively reduce the CO content of syngas for its direct utilization and conversion into biopolyester by the microbes.

Subtask 2.6 Biocontamination of Fuels, examined the microbial contamination of biofuels and the associated impacts on fuel stability, biofouling, and corrosion of fuel-related components. Development focused on a DNA based rapid molecular detection method and investigation of microbiologically induced corrosion. Results suggest that corrosion also occurs due to the direct metabolism of fuel components. This metabolism can provide basal support for the development of complex microbiological communities that include sulfate reducing bacteria and others that may also play a role in biofouling and corrosion. Detection of this specific metabolic pathway is fundamental to development of an effective control methodology. The research is now focused on finding specific genetic elements that are expressed during fuel metabolism using Moniliella wahieum Y12T as a model. Prokaryotic isolates have also been obtained and will be included in subsequent work.

Under Subtask 2.7 Biofuel Corrosion, static immersion tests were conducted in water/biofuel mixtures using unfiltered and filtered fuels in the anaerobic, sterile aerobic, and aerobic conditions. The results indicated that presence of microorganisms in the unfiltered biofuel resulted in the most severe corrosion rate of steel after 6 months in the anaerobic condition. The corrosion products on steel immersed in the biofuel phase were identified as mainly iron formate hydrate and iron oxalate hydrate. The formation of iron formate and iron oxalate suggests the presence of organic acids (i.e., formic acid and oxalic acid) in the biofuel.

Under Subtask 2.8, Waste Management Using the Flash-Carbonization™ Process, fundamental measurements were conducted of the specific isobaric heat capacity of pure water at elevated pressure to enable design of advance waste treatment systems. The aim of this study was to compare experimental results with values predicted by the IAPWS-95 formulation, in which most of the data are based on measurements of Sirota's group in the former Soviet Union in the period from 1956 to 1970. The present calorimetric results for the specific heat capacity of pure water were found to be substantially in disagreement with the values obtained using the IAPWS-95 formulation, especially at high temperatures, where the differences were greater than 20%.

Task 3, Methane Hydrates comprised four activities: hydrate energy, environmental impacts of methane release from seafloor hydrates, hydrate engineering applications, and international collaborative R&D.

Work on hydrate energy focused on fundamental laboratory studies of methane hydrate formation and dissociation in porous media, plus determining the effects of transition metal salts on hydrate behavior. Most of the transition metal salts tested inhibited methane hydrate formation at high concentrations, but none to the extent of sodium chloride except for ferric chloride. FeSO4 and CuSO4 at concentrations up to 2 mol% were observed to have minimal impact on hydrate stability. At lower concentrations (0.5 mol%), some of the salts appeared to promote hydrate formation, an effect that is also observed with alcohols.

When methane hydrate forms in porous media, the data suggests that a small shift in its phase boundary will occur. The implication of this result is that, over a range of pressures relevant to deep ocean sediments, the generally-employed phase boundary for a simple water-methane binary system tends to over predict hydrate melting temperature. Lower melting temperatures means that natural hydrate deposits in seafloor sediment are more vulnerable to purposeful or inadvertent increases in temperature. While this can be advantageous for certain methane recovery strategies, it raises concerns about outgassing and seafloor stability in a warming climate. Additional experiments appear to be warranted to confirm this phenomenon for a broader range of porous media properties and to more definitively quantify the shift in the phase boundary and to understand the underlying mechanism.

Microbial processes in the sediment and the water column are believed to play a major role in determining methane levels throughout the marine environment. Combined use of molecular analysis, chromatography and microcalorimetry was attempted with Beaufort Sea samples to elucidate the aerobic biological metabolisms by which microbes can regulate methane level in both the water column and near-surface. The development of submodels of microbial methane sources and sinks for integration into an ocean general circulation model also progressed during this period.

A preliminary experimental study of hydrate desalination and biofiltration was completed as part of the goal to explore the use of gas hydrates for various engineering applications. The data suggest that hydrates can be used to substantially decrease the salt content of low salinity water, but may not be able to significantly remove biological contaminants.

To foster international collaborative R&D on methane hydrates, HNEI supported and helped to organize the 8th International Workshop on Methane Hydrate R&D that was held in Sapporo, Japan in June 2012, as well as the 9th workshop held in Hyderabad, India in November 2014.

Task 4, Alternative Energy Systems focused on Ocean Thermal Energy Conversion, grid energy storage, PV systems, hydrogen production and fueling, energy efficient building platforms, variable powered ice maker, and alternative biofuels for Navy applications.

Under 4.1, Makai Ocean Engineering continued work to design, construct and test subscale heat exchangers to validate performance for Ocean Thermal Energy Conversion applications. Under this award, shakedown testing of the heat exchanger test facility was completed, the control system was developed and validated, development and testing of the brazed aluminum evaporator and the shell and tube condenser were completed, and the hollow extrusion corrosion samples were evaluated. The brazed aluminum evaporator uses brazed aluminum fins in the ammonia channels and square extruded passages for the seawater channels. The fins enhance heat transfer and the extruded channels eliminate exposing brazed joints to the corrosive seawater environment. The shell and tube condenser showcases the use of tubular friction stir welding – a new manufacturing technique – to join tubes to the tubesheet. The use of aluminum alloys and friction stir welding combine the desirable corrosion resistance of the alloy and manufacturing method, as well as a lowered cost of manufacturing. Major improvements in instrumentation, data collection, and control software enabled a wide range of testing conditions and relatively short transient time between testing points. The preliminary results of the corrosion testing program indicate localized corrosion will determine the viability of aluminum heat exchangers.

Under Subtask 4.2, Grid Storage, a grid-scale Battery Energy Storage System (BESS) was installed, connected to the grid and commissioned on the Island of Hawaii. It has been operating for three years, cycling over 3 gigawatt-hours in energy throughput. A second BESS, intended for the island of Molokai, was developed through the factory acceptance test phase. In an effort to realize these two BESS installations, HNEI formed and led public-private partnerships between UH, utility owners, hardware manufacturers, algorithm developers, and independent power producers.

On the Island of Hawaii, the 1 MW, 250 kWh BESS installed at a 10.6 MW wind farm can be controlled by either of two real-time algorithms: a primary frequency response algorithm, and a wind power smoothing algorithm. An Altairnano, lithium-ion titanate battery was chosen for an extended cycling lifetime and faster charge/discharge rates compared to the more common carbon anode electrochemistry. The two algorithms, frequency response and wind smoothing, were developed in tandem with the hardware, and were put through a series of acceptance tests. Over 100 switching experiments were conducted targeting a variety of grid conditions (day/night, windy/calm, etc.) and a variety of algorithm parameter settings (gain, limit on maximum power, and a “dead band” in which the algorithm does not respond to small fluctuations). The results show that the BESS reduces the overall frequency variability by 30-50% under typical grid conditions.

A 2 MW, 397 kWh BESS planned for the Molokai grid system is intended to provide the very fast response time needed to balance the intermittency in PV power generation on the low inertia grid system. While still under development, the Molokai BESS has helped identify current technological barriers related to BESS and inverter response times, as well as meter sensing delays. An improvement in this area is likely to have applications in real-world micro-grids under heavy penetration from intermittent renewable energy resources. HNEI will continue to test both systems under other awards to assess grid benefit and long-term battery health.

Under Subtask 4.3, PV module and inverter technologies were tested to characterize performance and durability under differing environmental conditions. PV test platforms were installed at Hawaii Project Frog classrooms on Oahu and Kauai for side-by-side comparison of grid-connected PV systems. Efforts focused on three areas: instrumentation for data collection and subsequent performance analysis based on two years of collected data; design of larger test platforms for future installation on Maui and at MCBH on Oahu, and; development of a new data acquisition system (DAS) with added capabilities including measurement of open-circuit voltage and short-circuit current.

In August 2013, 2.6kW PV arrays were installed on the rooftops of classrooms at Ilima Intermediate School on south Oahu and at Kawaikini Charter School in Lihue, Kauai. These energy-neutral buildings were being studied as part of the energy efficiency task of this ONR award. At the Ilima site, two PV material technologies, heterojunction with intrinsic thin layer (HIT) and thin film made of copper, indium, gallium and diselenide (CIGS) were compared side-by-side. At Kawaikini three PV technologies were compared, HIT, CIGS, and monocrystalline with two different system architectures, string vs microinverter. Data collection was initiated in November 2013 for two years of operation at both locations.

The larger test platforms were designed for 25kW and 100kW, comprised of a broad range of module manufacturers, system architectures, and module technologies, including mono and polycrystalline, bifacial, HIT, and thin films (Cadmium Telluride (CdTe) and CIGS). The 100kW MCBH test platform is design to be installed on two carport structures to support the hydrogen filling station, another HNEI/ONR project, offsetting the electrical load of the electrolyzer at the station.

The Power Park Support Subtask 4.4 expanded on work begun under a US Department of Energy funded effort to deploy a 350 bar hydrogen production and fueling station at HAVO. Due to operational changes, this system was deployed at the Marine Corps Base Hawaii (MCBH) on Oahu to support the ONR General Motors Equinox fuel cell electric vehicle project. With funding from this award, the system was modified by adding a 700 bar fast fill capability. The new 350/700 bar fast fill station became operational on 19 November 2014. It has successfully completed over 300 fills without any operational downtime.

Under Subtask 4.5 Energy Test Platforms, energy efficient building platforms were deployed and evaluated for potential mass-deployment to the Pacific region. Working with Project Frog, HNEI installed three test platforms at two sites and assessed the structures in terms of manufacturing and installation cost effectiveness as well as logistical efficiency. The components of this systematized kit-of-parts for use in the Pacific islands includes structure, envelope, construction materials, energy generation and management, sensors and controls, and integrated building technologies The research further evaluated the integration of clean energy generation technology within the test platforms.. The assembly of the test platform at Ilima Intermediate School was completed and ownership transferred from UH to the Department of

Education on September 30, 2011. The two test platforms at Kawaikini were completed and transferred March 15, 2013.

During the process, Frog identified two ways to improve future deployments. Optimizing the packaging and shipping procedures would decrease the costs by 17%-26%; and creating a certified installer network would allow use of 100% locally sourced labor and management.

After the first complete year of data collection in 2014, the three platforms performed as designed. The structure in the hotter Oahu microclimate performed at the “High Estimate” which assumed significant dependence on air conditioning, resulting in an actual electric site EUI of 7.8 kWh/sf-yr (excluding solar). The two predominantly naturally ventilated structures in the more temperate Kauai location produced twice as much energy than was used, realizing an average electric site EUI of about 4.7 kWh/sf-yr, achieving the “Optimal Performance” target. This difference in performance may be attributable to two factors: differences in micro-climates and difference in policies, awareness and user response to the internal environment.

A second objective under this subtask was to install, test and evaluate small wind turbine technologies to determine the relative effectiveness of differing designs, the impact of different climatic conditions. HNEI contracted the Golden Gate National Parks Conservancy to install 1 kW wind turbines adjacent to, and connected with the test platforms located at the Crissy Field Center in the Presidio of San Francisco, a proven wind resource for collection of comparative wind energy data. Vertical axis technology, turbines manufactured by Venco Power, Windspire Energy and Tangarie Alternative Energy Power were selected. A data acquisition system was installed to monitor wind turbine performance as well as building performance of the Center. Simultaneous wind speed and turbine output was recorded for 816 days with minute-level data. Actual performance was compared to expected performance for both wind resource and turbine generation. Both Windspire turbines operated from October 6, 2012 through December 31, 2014, however the Venco turbines had intermittent operating issues and the Tangarie turbine operated for only 268 days, having failed by June 30, 2013.

Under Subtask 4.6, a variable powered ice-maker (VPI) was procured and tested in a subtropical climate, at NELHA. Initial testing using salt water produced high quality sea water ice that was used by local aquaculture companies at the Natural Energy Laboratory of Hawaii Authority to freeze their fish. Over the course of several months, the high heat levels experienced in the system enclosure coupled with the aggressive corrosive environment caused the electronic control equipment to degrade and eventually fail. A major design issue identified was the use of two compressors to turn down the system in the event of a loss of power. While the system was able to meet moderate power variability, when it was tested with an instantaneous loss of power one of the two compressors successfully shut down as it was programmed to do but vapor-locked, and could not be restarted for up to 40 minutes until the vapor lock naturally cleared. A solution is to use one compressor. Given these issues it was not possible to test the system’s ability to desalinate saltwater. If this system is still of interest to ONR, it would need to be redesigned to address the design issues identified during this experiment.

An alternative biofuels assessment was conducted by Green Era LLC. The assessment comprised four areas: a site survey of agricultural lands in Hawaii; a crop assessment; production, harvesting, and handling methodologies, and; feedstock, processing, and waste handling for a number of thermochemical, biochemical and hybrid conversion technologies that could be used to convert the selected feedstocks into usable, sustainable, high-value energy products.

Hawaii BioEnergy reported the results of an assessment of the feasibility of growing microalgae as a biofuel, including the challenges of both an open, mixotrophic algal system, and a heterotrophic system.