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EXECUTIVE SUMMARY

This report summarizes work conducted under Grant Award Number N00014-13-1-0463 the Asia Pacific Research Initiative for Sustainable Energy Systems 2012 (APRISES12), 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 APRISES12 was to develop, test, and evaluate distributed energy systems, emerging technologies and power grid integration using Hawaii as a model for applicability throughout the Pacific Region. APRISES12 encompassed fuel cell research, contaminant mitigation and evaluation; battery testing; seafloor methane hydrates extraction and stability; synthetic fuels processing and production to accelerate the use of biofuels for Navy needs; alternative energy systems for electric power generation and integration into smart microgrids, and energy efficient building platforms. Testing and evaluation of alternative energy systems included Ocean Thermal Energy Conversion (OTEC), grid-scale battery energy storage, and development of several microgrid test projects.

Under Task 1, Program Management and Outreach, HNEI provided overall program management and coordination, developed and monitored partner and subcontract agreements, and developed outreach materials for both technical and non-technical audiences. Additionally, HNEI continued to collaborate closely with ONR and NRL to identify high-priority areas requiring further detailed evaluation and analysis.

Under Task 2, Fuel Cell Systems, HNEI conducted testing and evaluation of single cells, stacks and balance of plant components to support NRL efforts to develop fuel cells for unmanned aerial vehicles (UAVs), identified contaminant mechanisms and developed mitigation techniques for organic contaminants present in air and hydrogen, validated a method to measure and separate mass transfer coefficients suitable for the design of low cost and high power density fuel cells, and evaluated the potential of anion exchange membrane fuel cells. Development and laboratory testing continued on fuel cell air purification materials and novel sensor devices. HNEI also developed and advanced battery diagnosis techniques and investigated key performance aspects of battery modules.

Efforts under Task 3, Alternative Fuels, focused on the development, testing and evaluation of alternative fuels and technologies, and included activities in the areas of Methane Hydrates,
Technology for Synthetic Fuels Production, Low-cost Material for Solar Fuels Production, and Hydrogen Fueling Support. Methane hydrate destabilization was examined using ionic salt compounds found in seawater, and calorimetric investigation focused on hydrate formation and dissociation in sand matrices. Hydrate desalination and removal of biological contaminants was also examined. Synthetic fuels processing focused on hydrogen production for fuel cell applications, second generation biofuel properties impacted by petroleum aromatics, solvent based extraction of fermentable sugars from biomass, development of a novel bioreactor for liquid fuels from synthesis gas, bio-contamination of blended fuels and biodiesel degradation, biofuel corrosion in diesel/renewable diesel/seawater mixtures, constant volume carbonization processing variables to convert waste biomass, and enhanced performance of hybrid biochar supports for high rate anaerobic digestion. For solar fuels production an environmentally friendly potentially low-cost thin film printing process was refined to fabricate copper-zinc-tin-sulfo-selenide solar cells with double the efficiency achieved during APRISES11. Hydrogen refueling support involved commissioning hydrogen production and compression equipment, procurement of a Power Export Unit for emergency backup power from a fuel cell electric bus, and the design of a hydrogen dispensing system.

Task 4, Ocean Energy included development of advanced heat exchangers for Ocean Thermal Energy Conversion (OTEC), Wave Energy Testing, and baseline water monitoring for Seawater Air Conditioning. To advance OTEC heat exchanger development, a subaward was made to Makai Ocean Engineering. Makai designed, built, and tested six configurations of Epoxy-Bonded Heat Exchangers. A new 100-kW test station was designed and constructed to support this testing. Results were promising and led to the design and fabrication of the Foil Fin Heat Exchanger. An autonomous control system for the OTEC test facility was also developed, and long term corrosion testing was continued. In support of the Navy’s Wave Energy Test Site (WETS) off Marine Corps Base Hawaii, and in collaboration with NAVFAC, HNEI subcontracted with Sea Engineering, Inc. to conduct a selection process, deploy and commission a remotely operated vehicle (ROV). This adds a critically important capability to support wave energy conversion device and mooring inspections, particularly for the deep-water sites at WETS. Seawater Air Conditioning (SWAC) pre-impact conditions were characterized with further deployments of long-term oceanographic mooring, water column profiling and sampling to assess the environmental impact of this new system on the ocean ecosystem near Honolulu.

Funding for the Geothermal Resource Assessment planned for task 5 was reallocated to other areas of the program as approved by ONR.

Task 6, Microgrids/Grid Integration included a range of projects to develop, test and integrate secure microgrid technology including distributed energy resources. An empirical model to characterize the DC performance of PV modules was expanded to evaluate AC performance of PV systems and power conditioning units, as well as the impact of shading. Development of a
low-cost, real-time power monitor with wireless communications for distribution system operations was continued. Advanced, real-time data analysis and controls were added to the power monitor system hardware and software, leading to a second provisional patent being filed, "Enabling Ubiquitous Distribution Grid Modeling for Enhanced Visibility and Controls". Hardware-in-the-loop equipment was purchased and initial setup completed in order to test distributed energy resources and devices in real-world grid operation scenarios. Additionally, the Conservation Voltage Reduction prototype was advanced towards being more cost effective by utilizing a small DC power supply to emulate a solar module and power an inverter. Initial tests were successfully conducted at the UH Marine Center. The Battery Energy Storage System (BESS) on Molokai was modified for faster response, enabling the BESS to respond to contingency events on the grid. Work continued on the Coconut Island DC microgrid including procurement of an electric boat (E-boat) and electric utility vehicle, along with a swappable battery system. HNEI completed the conversion of the E-boat to an all-electric vehicle, and installed the battery charging station for the swappable battery system in the Boat House on Coconut Island. To increase the amount of distributed PV that can be connected and utilized by the microgrid on the Island of Molokai, the impact of a Load Bank was analyzed and found to be an effective solution. Development was continued on solar forecasting methods and systems, including testing and evaluation in an operational framework, and validating the predictions generated using ground observations. Work continued on the Coconut Island DC microgrid including procurement of an electric boat (E-boat) and electric utility vehicle, along with a swappable battery system. HNEI completed the conversion of the E-boat to an all-electric vehicle, and installed the battery charging station for the swappable battery system in the Boat House on Coconut Island. The Maui College project integrated an additional 500 kW of PV and a 500 kW/500 kWh battery, and performance was assessed on the campus microgrid, along with charging of electric vehicles from renewable energy. Additionally, agreements executed with the utility for Power Purchase, Energy Performance, and Fast Demand Response. The Kauai College project assessed, procured, deployed and analyzed the performance and impact of Demand Side Management Load Controller technologies and protocols on the campus microgrid.

Under Task 7, Energy Efficiency, areas of focus included modeling air flows in naturally ventilated spaces, monitoring and performance comparison of building research platforms, the installation and analysis of small, vertical axis wind turbines, and support of the utility’s demand response demonstration projects.

This report describes the work that has been accomplished under each of these tasks, along with summaries of task efforts that are detailed in journal and other publications, including reports, conference proceedings, presentations and patent applications. Publications produced through these efforts are listed and available, or linked, on HNEI’s website at https://www.hnei.hawaii.edu/publications/project-reports#APRISES12.
TASK 1: PROGRAM MANAGEMENT AND OUTREACH

This program-wide task provided management and coordination of all research, test, development and evaluation efforts under APRISES1. Partner and subcontract agreements were developed and monitored, and outreach materials for both technical and non-technical audiences were developed. In close collaboration with ONR, high-priority needs requiring further detailed evaluation and analysis were identified for application of emerging energy technologies, with a focus on Hawaii and the Asia-Pacific region. Task-specific information and more detail are provided below for partner, subcontract and outreach activities.

TASK 2: ELECTROCHEMICAL POWER SYSTEMS

Under Task 2, fuel cell testing and evaluation was conducted on single cells, stacks and balance of plant components to support NRL efforts to develop fuel cell powered autonomous vehicles; to support development of mitigation techniques for organic contaminants present in air and hydrogen; to validate a method to measure and separate mass transfer coefficients suitable for the design of low cost and high power density fuel cells, and to evaluate the potential of anion exchange membrane fuel cells using commercial materials and mass production manufacturing methods.

Battery research under this task focused on automation of battery diagnosis to allow online monitoring and forecasting, investigation of the performance and durability of battery technology under large-scale grid support operations, and impact of vehicle to grid (V2G) usage on electric vehicle (EV) type batteries.

Contaminant Mitigation focused on development of advanced fuel cell air purification materials and novel sensor devices to allow the use of fuel cells to be expanded into harsh environmental conditions. These sorbent materials and devices were tested in controlled laboratory conditions under this effort.
2.1 Fuel Cell Development and Battery Testing

2.1a Fuel Cell Development

Testing and evaluation was conducted on single fuel cells, stacks and balance of plant components to support NRL efforts to develop fuel cell powered unmanned aerial vehicles (UAVs), develop contaminant mechanisms and mitigation techniques for organic contaminants present in air and hydrogen, validate a method to measure and separate mass transfer coefficients suitable for the design of low cost and high power density fuel cells, and evaluate the real potential of anion exchange membrane fuel cells using commercial materials and mass production manufacturing methods. HNEI also tested battery packs to support the development of the NRL battery state of health diagnostic.

Key accomplishments included characterization and design recommendations to NRL related to their fuel cell stack design based on metallic bipolar plates. Two HNEI developed hydrogen recovery units were sent to NRL which were integrated into a breadboard system and successfully operated and validated. The applicability range of the NRL battery pack state of health diagnostic was tested and extended to 0°C from 25°C. Recovery strategies were validated for fuel cells contaminated with acetylene (a welding fuel) and bromomethane (a product of biological activity in oceans). The use of the segmented cell was demonstrated as a diagnostic tool revealing different signatures for fuel cell contamination mechanisms. The impact of two fuel cell system contaminants on the oxygen reduction and hydrogen oxidation reaction mechanisms were established. Several impedance spectroscopy models for data interpretation and parameter extraction were developed and validated to validate results obtained with the HNEI method to measure and separate reactant mass transfer coefficients. The realistic performance of anion exchange membrane fuel cells were established using commercially available and mass production manufacturing methods.

Details of the work conducted in each of these areas are described below, and in the publications and presentations referenced at the end of this section.

Support to NRL

Under APRISES11 and 13, HNEI supported NRL by providing extensive diagnostic data for NRL stacks based on 3D printed bipolar plates to establish the limits and benefits of that manufacturing technology, co-developed with NRL a hydrogen recovery sub-system to increase efficiency, and extended a NRL battery state of health diagnostic based on impedance from a single cell to a short stack. Under APRISES12, these activities were continued with test data for NRL stacks based on metallic bipolar plates to verify their quality and improve their design, by providing advice for the
integration of the hydrogen recovery sub-system to the UAV breadboard system, and by verifying
the applicability of the NRL battery state of health diagnostic to a wider temperature range.

**Fuel cell for UAV systems**

Under APRISES 12, HNEI continued to support NRL efforts to develop fuel cell powered
unmanned aerial vehicles (UAVs). Work conducted under this activity focused on the issues
associated with fuel cell stack manufacturing and balance of plant development. Particular
attention was given to the tradeoff between weight, volume, and performance to meet flight
requirements and the manufacturability of system components. The potential of stamped metal
bipolar plates was explored as these components can be significantly thinner than those made of
composites or by 3D printing, as previously determined by NRL and HNEI, resulting in a lower
volume and a lighter weight per cell. Corrosion resistant metals are typically used in the production
of metal bipolar plates to prevent degradation under fuel cell conditions. Metals such as stainless
steel have protective layers that prevent degradation. However, these layers also exhibit a high
resistivity leading to unacceptable voltage losses. Specialized coating layers are thus applied to the
plates, post-formation, to alleviate the high resistance and increase conduction without sacrificing
the protective benefits. Manufacturing of metallic bipolar plates can be summarized into four
general steps; boss formation, removal of excess material, plate bonding or welding, and coating
application. A high dimensional accuracy is necessary in the final manufactured product to achieve
uniform distribution of reactants from plate to plate in the stack and channel to channel within each
cell. A low dimensional accuracy can result in issues such as gas leakage, reactant starvation, and
uneven plate compression leading to localized excessive stresses or hot spots. Engineers and
scientists at HNEI continue to consult with NRL on a weekly basis to address issues such as those
mentioned above in the design of NRL’s in-house developed stamped metal plate fuel cell system
and provide testing and evaluation services leveraging the full suite of advanced stack diagnostics
developed at HNEI.

In the reporting period for APRISES 2012, multiple fuel cell stacks built by NRL with metal
bipolar plates were tested and evaluated at HNEI for design conformity and performance
uniformity. Build issues, such as gas leakage due to improper sealing or plate to plate performance
non-uniformity, were identified and communicated to NRL for correction in subsequent builds.
Optimal operating conditions, stack orientation with respect to the aerial vehicle chassis, and
reactant configurations were determined and incorporated by NRL into their system designs. As
part of the balance of plant development, integration and validation of the HNEI developed
hydrogen recovery unit, reported under APRISES 2013, was performed and two units were sent
to NRL for breadboard system integration. Test results were disseminated to NRL through weekly
update meeting presentations and data files were transmitted to NRL using the ARMDEC Safe
Access File Exchange system. Intellectual property developed in this project has been submitted
for a full, non-provisional patent under Patent Application 15/932,050.¹ For more information and
specific details of the UAV fuel cell development program at NRL, contact Karen Swider-Lyons (karen.lyons@nrl.navy.mil).

Li-ion state of health monitoring

The utility of a single-point impedance-based technique to monitor the state-of-health of a pack of four 18650 lithium-ion cells wired in series was completed under APRlSES11 funds. The single-point state-of-health frequency is unique to each type of cell chemistry, manufacturer and form factor, and nearly invariant with state-of-charge making it an ideal probe for continuous online monitoring. The work reported here under APRlSES12 funding broadens the applicability of the single-point monitoring technique to identify temperature induced faults within packs at a lower temperature of 0 °C. Under such operating conditions, lithium-ion cells are prone to performance loss and a number of safety concerns. During cycling at a low temperature, impedance differences between cells in series can cause weaker cells to overcharge and overdischarge while the pack still maintains a perceived acceptable voltage within the normal operational boundaries.

The present study utilized commercial 18650 cylindrical lithium-ion cells of 2.6 Ampere-hour nominal capacity. Single cells and packs were tested in a thermal chamber at 25 or 0 °C. Discharge cycling in the serial pack configuration used two different modes of lower voltage cutoff: (i) when the first cell in the pack reached 2.75 V or (ii) when the pack voltage reached 11.0 V. Observations from the single-point impedance monitoring technique at 316 Hertz were validated against an exhaustive analysis of different cells degradation mechanisms using electrochemical voltage spectroscopy (incremental capacity analysis).

Data were utilized to develop a state of health map (Figure 2.1a.1), which shows the average impedance response of uncycled cells at 25 and 0 °C (yellow circles). The dashed line represents an empirical relationship established between impedance response and temperature. As temperature decreases, the acceptable impedance response shifts toward higher real and imaginary impedance due to slow kinetics for both cell reactions. The free form shapes represent arbitrary risk indexes where green envelopes 3x the impedance variance across 0 to 100 % state of charge, orange is 4x and red is 5x the impedance variance at the identified temperatures. The boundaries for the risk indexes are developed arbitrarily, but can be informed with future safety testing of cells cycled under the abusive low temperature condition. The small black dots indicate the actual impedance response of the pack when cycled at 25 °C for 1, 10, 30 and 50 cycles. There is little change in the impedance response over 50 charge/discharge cycles at this temperature. The pack level impedance response is much different for packs cycled at 0 °C. The pack level impedance is shown for the pack with a 2.75 V cell cutoff (light blue circles) and 11.0 V pack cutoff (dark blue circles) where the number inside the circle indicates the number of completed cycles prior to diagnostic testing. The low temperature cycling condition is abusive to the pack, particularly the pack discharged to pack voltage cutoff of 11.0 V, with a progressive translation outside of the
healthy zone. More details are provided in the published manuscript (item 1 in the Publications and Presentations Resulting from these Efforts section).

Figure 2.1a.1. State of health map generated from single-point impedance responses at 316 Hertz after 1, 10, 30, and 50 discharge cycles, where the cycle number is denoted inside the circles. The acceptable impedance variance range (<3x) is shown in green, 4x in orange and 5x in red. The empirical relationship between impedance response and temperature at 316 Hertz is shown by the black dashed line.

**PEM fuel cell contamination**

The effects of different contaminants on proton exchange membrane fuel cell operation was investigated using prior APRISES and other federal funds to ultimately identify and develop more effective prevention and mitigation strategies. Specifically with APRISES11 and 13 funds, the effects of air and fuel contaminants on incumbent platinum catalysts and platinum metal group free catalysts were characterized using different analytical techniques to support the development of mechanisms and recovery strategies. Activities also targeted aspects relevant to field operation (contaminant effects on stacks, contaminant mixtures, and long term exposure to contaminants). Under APRISES12 funds, these activities were continued for several organic contaminants in air and hydrogen. Acetylene (welding fuel), benzene (chemical intermediate, combustion product), naphthalene (chemical intermediate, fumigant) and bromomethane (fumigant, product of biological activity in oceans) are present in air. Caprolactam is released by polymer components of the fuel cell system and ethylene glycol is the preferred automotive coolant.
Acetylene in air

Acetylene, widely used as a welding fuel and as a precursor for chemical syntheses, is, among airborne contaminants, a representative alkyne. Acetylene in the atmosphere originates almost exclusively from anthropogenic sources, including manufacturing and end-use plant emissions, fossil and biofuel/biomass combustion. Acetylene concentrations up to 5.5 (1 h average) and 3 (24 h average) ppm by volume near an acetylene plant were predicted with a diffusion model. Acetylene adsorption as well as catalytic and electrochemical reactions on platinum (Pt) were extensively studied. Stable surface species were reported for acetylene chemically adsorbed (low coverage) on Pt surfaces under an ultra-high vacuum. Adsorbed acetylene species are electrochemically reduced to ethylene and ethane when the adsorption voltage is lower than 0.2 V versus a hydrogen electrode reference, or are electrochemically oxidized to carbon dioxide at a potential higher than 0.35 V versus a hydrogen reference. However, under specific operating conditions, the adsorption rate of acetylene is larger than the oxidation rate which favors acetylene accumulation and inhibits oxygen adsorption on the Pt surface. Initial accelerated tests with 300 ppm by volume acetylene led to an 88% cell performance loss. Ex situ rotating ring/disk electrode tests confirmed that acetylene adsorption severely inhibits the oxygen reduction reaction (ORR) and shifts the ORR mechanism in favor of a hydrogen peroxide product (rather than water), a strong oxidant that can damage the membrane. A more detailed study was needed to better understand acetylene contamination mechanisms to design mitigation measures. More specifically, intermediates and products resulting from acetylene exposed to an operating fuel cell environment have not previously been identified.

Generally, contaminant reactions in the cathode of an operating fuel cell include not only catalytic reactions but also electrochemical reactions. Under APRIVES12 work, the catalytic and electrochemical acetylene reactions were characterized by using conditions that either suppress electrochemical reactions or not. Furthermore, reaction intermediates and products were identified by gas chromatography. These tests were supplemented by two electroanalytical techniques (chronoamperometry, cyclic voltammetry) to facilitate and confirm species assignments.

Acetylene reactions and products in an operating proton exchange membrane fuel cell are summarized in Figure 2.1a.2. It is surmised that catalytic reactions predominantly occur on the bare Pt surface whereas electrochemical reactions occur on the ionomer-covered Pt surface because the latter reactions require the transport of ions. Carbon dioxide is produced by the electrochemical oxidation of acetylene at cathode potentials above 0.5 V versus a hydrogen electrode and the catalytic oxidation of acetylene by the oxygen in air. Above 0.65 V versus a hydrogen electrode, the acetylene adsorbates are rapidly oxidized into carbon dioxide by platinum oxides. The carbon dioxide product readily desorbs from the Pt surface and is entrained by the air flow. On the other hand, below 0.3 V versus a hydrogen electrode acetylene adsorbates are reduced to ethane, ethylene and methane electrochemically and catalytically by the hydrogen crossing over.
from the anode through the membrane. All these reduction products also readily desorb and are entrained by the air flow. Reduction and oxidation processes mentioned so far lead to a rapid cell performance recovery after the acetylene exposure is interrupted. However, the reduction intermediates vinylidene and ethylidyne formed between 0.3 and 0.5 V versus a hydrogen electrode are electrochemically stable even at potentials up to 0.83 V versus a hydrogen electrode. Additionally, the carbon monoxide oxidation intermediate (or a related oxygenated species) formed above 0.5 V versus a hydrogen electrode is also electrochemically stable below 0.69 V versus a hydrogen electrode. Therefore, a cell exposed to acetylene is particularly vulnerable when the cell is operated at cathode potentials within the 0.3 to 0.69 V versus a hydrogen electrode. These observations were useful to formulate an effective recovery strategy.\(^5\) If a fuel cell is poisoned and result in a cathode potential below 0.5 V versus a hydrogen electrode, an increase in current density to reach a cathode potential below 0.3 V versus a hydrogen electrode promotes a rapid cell performance recovery. Alternatively, if the fuel cell is poisoned above 0.5 V versus a hydrogen electrode, operation with a cathode potential higher than 0.69 V versus a hydrogen electrode accelerates the performance recovery. More details are provided in the published manuscript (item 6 in the Publications and Presentations Resulting from these Efforts section).

Figure 2.1a.2. Acetylene conversion rate and product distribution in proton exchange membrane fuel cells at different voltages (left). Acetylene reactions at different electrode potentials. PZC: potential of zero charge. Adsorbates with a subscript “ad” refer to catalytic reactions.
Aromatic hydrocarbons in air

Benzene is present in crude oil and gas wells. Benzene is a commodity chemical used to manufacture other organic compounds and polymers. Naphthalene is produced to manufacture chemical precursors, intermediates and chemicals. Benzene and naphthalene are released in air by several mechanisms including evaporation during processing operations and product use and as a combustion residue. It is known that benzene and naphthalene adsorb on platinum due to an interest in electrochemical syntheses and effluent treatment, resulting in a partially blocked active surface and leading to a poorer cell voltage (equivalent to a larger effective current density). However, only a few reports relate to benzene and/or naphthalene effects on proton exchange membrane fuel cell operation. None of these reports considered the relative importance of the successive contaminant processes (transport, adsorption/desorption, reaction, product adsorption/desorption) on cell behavior.

Contamination processes are contaminant concentration dependent and therefore expected to depend on the distance from the air inlet port because progressive adsorption and consumption by surface reactions locally decrease the flow channel concentration. Therefore and under APRISES12, a segmented cell was used to record the local cell performance. As already mentioned for acetylene, the contaminant concentration was higher than in atmospheric air to enhance and accelerate effects, thus limiting test durations to an acceptable level.

The observed performance drop with benzene was accompanied by a relatively rapid and small dimensionless current density redistribution of 8 to −9 % (Figure 2.1a.3, left). It is surmised that the relatively low adsorption energy of benzene on the platinum catalyst surface only consumes a small fraction of the benzene inventory contained in the air stream (the contaminant concentration is relatively constant across the cell). Furthermore, the segments near the cell outlet (those close to segment 10) are more largely impacted (the dimensionless local current is less than 1). It was not possible to identify a reasonable explanation for this observation. In contrast, the dimensionless current distribution resulting from naphthalene contamination (Figure 2.1a.3, right) is larger varying from 14 to −25 %, which is explained by a higher adsorption energy on platinum (higher coverage). The current distribution is also time dependent and correlates with the cell voltage drop. The cell voltage decreases due to the accumulation of naphthalene on the catalyst surface (naphthalene oxidation does not take at these cell voltages), which increases the current density redistribution. However, at a cell voltage of 0.26 to 0.28 V, the current density trend reverses because naphthalene is desorbed and/or reduced to less strongly adsorbed products such as decalin (an alkane). As a result, the cell voltage reaches a steady state near a cell voltage of 0.1 V with a small effect on current distribution because most of the naphthalene is reduced to a benign form.
These results indicate that the current distribution could be used as a signature to identify specific contamination mechanisms. More details are provided in the published manuscript (item 10 in the Publications and Presentations Resulting from these Efforts section).

Figure 2.1a.3. Segments’ voltage (top) and normalized current densities (bottom) for an exposure to 2 ppm benzene (left) and 2.3 ppm naphthalene (right).

_Bromomethane in air_

Bromomethane was used as a biocide in agriculture, fumigant, chemical intermediate and fire extinguishing agent. Bromomethane is also naturally formed by algae and kelp in ocean. Trace amounts of bromomethane have been detected in most places. Industrial areas, fumigated homes and fields have higher levels (ranging up to 1.2 ppb). The literature indicates that bromomethane and bromide ions are a threat to proton exchange membrane fuel cells. However, little information exists in relation to bromomethane adsorption and reactions on Pt either in contact with a gas phase or aqueous acidic environments. Fortunately, the adsorption and reactions of a related species, the bromide anion (Br\(^-\)), on a Pt electrode was extensively studied in aqueous electrolyte. Bromomethane slowly hydrolyses in water, yielding methanol and bromide ions. Methanol is readily oxidized to carbon dioxide in the air compartment, which easily desorbs from the Pt surface as indicated above in relation to acetylene contamination. The adsorption of bromide ion on a Pt surface occurs between 0.135 and 1.19 V versus a hydrogen electrode, which almost entirely covers the fuel cell accessible electrode potential range. Rotating ring/disk electrode results demonstrated that strongly adsorbed bromide ions suppress the adsorption of oxygen and hydrogen by blocking catalyst sites and altering the oxygen reduction path by promoting the formation of the hydrogen peroxide intermediate.
Under APRISES12 work, bromomethane contamination of proton exchange membrane fuel cells was investigated using both single cells and segmented cells. In addition to the usual characterization methods (impedance spectroscopy, cyclic voltammetry, linear scanning voltammetry, polarization), other analytical techniques were employed either in situ or ex situ (scanning electron microscopy, transmission electron microscopy, X-ray absorption spectroscopy, X-ray photoelectron spectroscopy) to gain additional structural and chemical information considering that a cell voltage loss persisted after contaminant exposure. X-ray spectroscopies were completed in collaboration with NRL, the Brookhaven National Laboratory and the University of New Mexico.

Experimental results indicated that trace amounts of bromomethane in the air stream caused a slowly evolving, significant and locally variable cell performance loss. As illustrated in Figure 2.1a.4, left, bromomethane is hydrolyzed to a bromide ion, which accumulates at the catalyst layer interface because its negative charge prevents it from entering the ionomer (Donnan exclusion) and inhibits both kinetic and mass transport processes. Methanol oxidation at high electrode potentials facilitates the hydrolyzation of bromomethane (Le Chatelier principle). The Pt catalyst surface is eventually covered with the bromide ions, which cannot be removed solely by changing the cell voltage. Also, the formation of stable complex ions $[^\text{PtBr}_4]^{2-}$ and $[^\text{PtBr}_6]^{2-}$ favors Pt dissolution and re-deposition resulting in larger Pt particles, a smaller catalyst surface and a permanent cell performance loss. The transport of these complex ions is favored by the presence of liquid water. Hence, segmented cell data show that the current density increases during contamination near the sub-saturated inlet. This observation was supported by spectroscopic analyses that showed a more deteriorated catalyst near the cell outlet. However, it was also found that less bromide was present on the catalyst in the same region. This inconsistency will require additional tests to resolve and improve the contamination mechanism.

A low electrode potential applied during operation (near the limiting current for example) induces bromide desorption from Pt sites (Figure 2.1a.4, right). The simultaneous presence of liquid water would favor the removal of desorbed bromide ions from the cell and restore its performance. However, the recovery is incomplete owing to the irreversible damage associated with Pt dissolution and re-deposition (up to 94 % in a single cell). More details are provided in the published manuscripts (items 7 and 9 in the Publications and Presentations Resulting from these Efforts section).
Caprolactam and ethylene glycol in air and hydrogen

Ethylene glycol is a relevant contaminant because it is widely used as a coolant, antifreeze agent, and de-icing solution. De-icing of airport runways and airplanes is the primary source of ethylene glycol in the environment. Ethylene glycol is also dispersed in the environment by the disposal of products that contain it. Caprolactam, which is an important monomer for Nylon 6 production, is another potential contaminant that the proton exchange membrane fuel cell system materials commonly release as a result of either degradation or leaching. These two contaminants may adsorb on the Pt catalyst, compete with the main reactions, or penetrate into the ionomer and membrane, which would increase cell voltage losses attributed to reaction kinetics, and ionic conductivity of the catalyst layer and membrane. However, the effects of ethylene glycol and caprolactam on the hydrogen peroxide production during oxygen reduction and on the hydrogen oxidation were not previously investigated. As mentioned above, hydrogen peroxide slowly damages the catalyst layer ionomer and membrane.

Under APRISES12 work, the ex situ rotating ring/disk electrode method was used to separate the kinetic effect from ohmic and mass transfer contributions, which is facilitated by a small electrode active surface, controlled hydrodynamics and a simple ohmic loss measurement and correction. In contrast, ohmic and mass transfer contributions are more difficult to compensate in a single fuel cell owing to a much larger active area and dependence on location along the flow (inlet to outlet). Both anode and cathode reactions were investigated because system contaminants can reach both reactant compartments and their different electrode potentials are expected to yield different results and tolerance limits. Furthermore, contaminant concentrations were varied to gain insight into the levels that would lead to measurable effects. This information is important for the design of mitigation strategies.
The activity of the platinum catalyst decreased for both oxygen reduction and hydrogen oxidation with the increase in ethylene glycol and caprolactam concentration (Figure 2.1a.5, left, concentration effect not shown). This observation is to a significant extent due to a large Pt surface coverage as confirmed by cyclic voltammetry. Furthermore, the oxygen reduction side reaction product hydrogen peroxide is also formed at a higher rate with the increase in ethylene glycol and caprolactam concentration (Figure 2.1a.5, right, concentration effect not shown). A decrease in Pt active surface area leads to a smaller number of contiguous Pt sites, which favors oxygen adsorption in an end-on configuration, decreases the likeliness of an oxygen-oxygen bond breakage and increases the hydrogen peroxide yield (H_2O_2) rather than water (H_2O). For both contaminants a low concentration of 0.001 mole per liter is sufficient to observe a significant effect on oxygen reduction. The concentration increases to 0.01 mole per liter for hydrogen oxidation, which expectedly indicates that the anode reaction is less sensitive to contamination because the reaction is more facile. These concentrations need to be translated for use with fuel cells (gas phase rather than liquid phase concentrations) to mitigate negative impacts on cell performance with the use of filters. More details are provided in the published manuscript (item 8 in the Publications and Presentations Resulting from these Efforts section).

Figure 2.1a.5. Polarization curves for oxygen reduction in the presence of ethylene glycol (EG) and caprolactam (left). Hydrogen peroxide (H_2O_2) yields with background correction during the oxygen reduction (right). I: current density, E: electrode potential versus a hydrogen electrode.

**Mass transfer analysis**

Fuel cells are still too expensive for mass commercialization. Material costs are reduced by increasing current densities, effectively decreasing stack size. Under these conditions, reactant mass transfer becomes significant. HNEI is currently developing a method to measure and separate mass transfer coefficients into elementary contributions to facilitate design optimization. However, the method needs to be validated by another method. HNEI is currently developing impedance spectroscopy models to meet this objective and this activity is conducted in collaboration with the
Institute of Energy and Climate Research, Jülich, Germany. This activity leverages other federal funds provided by the Army Research Office. Under APRISES11, an impedance model based on a physical representation of processes was validated using data obtained with oxygen (rather than air); a high stoichiometry and a low current density to minimize concentration gradients and match the 1D model (through the membrane/electrode assembly plane). Under APRISES 13, the model was extended for more practically relevant operating conditions leading to concentration gradients along the flow field channel thereby relaxing stoichiometry and current density limitations. For APRISES 2012, efforts were focused on aspects related to the catalyst layer design and data processing: ionomer loading uniformity in the catalyst layer, catalyst loading level, and a novel approach to analyze impedance spectra.

**Ionomer uniformity analysis**

Near the open circuit voltage and at high load signal frequencies, only cathode catalyst layer processes in a proton exchange membrane fuel cell are relevant. Under these conditions, impedance data form a straight line with a 45 degrees angle in a Nyquist representation from which the catalyst layer ionomer conductivity is obtained. However, the linear behavior is not always observed which was attributed to non-linear ionomer properties. Therefore, a more accurate interpretation of impedance data requires a model that includes these non-uniform ionomer properties.

Under APRISES12, impedance spectra were measured using a segmented fuel cell, for improved parameter statistics, and a power supply/load bank combined unit, considering measurements are completed at the open circuit potential. The excitation signal amplitude superimposed to the open circuit potential means that power is intermittently generated and consumed. The impedance model was derived with the objective to obtain an analytical solution and by assuming that the ionomer proton conductivity is an exponential function of the distance through the catalyst layer thickness.

Experimental data showed a good fit to the model (Figure 2.1a.6), which confirmed the hypothesis of a non-uniform ionomer proton conductivity. The proton conductivity at the membrane interface varies in the range from 0.09 to 0.23 ohm$^{-1}$ cm$^{-1}$. The mean proton conductivity is 0.13 ohm$^{-1}$ cm$^{-1}$, which agrees well with the value for humidified Nafion at the measurement temperature of 60 °C. This impedance model modification is integrated below to a more comprehensive version used to obtain parameters for validation of the HNEI method to measure mass transfer coefficients. More details are provided in the published manuscript (item 5 in the Publications and Presentations Resulting from these Efforts section).
Figure 2.1a.6. Experimental (points) and fitted model impedance (dashed lines) for the whole cell and for segments 1 to 3. The left panels show the Nyquist spectra in the coordinates with equal scales along the real and imaginary axis. The right panels show the same spectra with the stretched real coordinate, to represent the details. Arrows in the frame (a) indicate frequencies in Hertz. Im(Z): imaginary impedance, Re(Z): real impedance.
**Cathode catalyst loading**

A decrease in platinum loading to commercially relevant levels below 0.1 mg cm\(^{-2}\) causes a significant increase in mass transport losses. This observation is especially relevant for the development of the HNEI mass transfer coefficient measurement method and the concurrent development of impedance models for validation. However, characterization of such low loaded electrode with impedance spectroscopy has seldom been attempted. Furthermore, existing models have not been fitted to experimental data owing to a need for significant computational resources to avoid a slow convergence toward a solution.

Under APRISES12, a segmented cell was used to acquire impedance spectra for membrane/electrode assemblies with two different platinum loadings (0.1 and 0.4 mg cm\(^{-2}\) for both anode and cathode). High stoichiometries were used to minimize concentration gradients along the flow field length and fit overall cell spectra because local oxygen concentrations were unknown. The impedance model was derived by combining previous versions that includes the non-uniform conductivity of the catalyst layer ionomer (previous section) and the non-uniform concentration gradient along the flow field channel with the objective to use as many analytical solutions as possible to minimize computational resources to fit experimental data.

A good agreement was found between experimental and model impedance spectra (not shown). Mass transfer coefficients in the gas diffusion and cathode catalyst layers are given in Figure 2.1a.7). The smaller mass transfer coefficient in the catalyst layer for a lower catalyst loading is ascribed to a limiting oxygen adsorption on the catalyst surface. The linear increase of the mass transfer coefficient in the catalyst layer with current density is unclear and warrants further analysis. Additionally, the cathode catalyst layer mass transfer coefficient obtained by impedance spectroscopy is smaller by an order of magnitude in comparison to those derived using the HNEI method. This is due to the difference in operating conditions and a larger amount of liquid water for the present measurements with air rather than with diluted oxygen streams for the HNEI method. In contrast, the gas diffusion layer mass transfer coefficient is almost independent of current density, is different for both membrane/electrode assemblies (attributed to a membrane/electrode assembly preparation variation) and is much larger than for the cathode catalyst layer. Furthermore, the gas diffusion layer mass transfer coefficient for the high loaded membrane/electrode assembly is in agreement with the value measured with the HNEI method. Again, this impedance model modification is integrated below to a more comprehensive version used to obtain parameters for validation of the HNEI method to measure mass transfer coefficients. More details are provided in the published manuscript (item 4 in the Publications and Presentations Resulting from these Efforts section).
Figure 2.1a.7. Fitting parameters for the low platinum (open circles) and high platinum (filled circles) loaded cells. Mass transfer coefficient in the cathode catalyst layer (CCL, left) and in the gas diffusion layer (GDL, right).

**Novel analysis for impedance spectra**

Water management is important to optimize fuel cell performance. For example, the membrane requires water to maintain its ionic conductivity. However, if product water accumulates in the gas diffusion electrodes, oxygen transport is impeded. The water distribution is not uniform across the active area of a fuel cell because the air stoichiometry is generally low to minimize the energy required by a blower or compressor. For instance, an air stoichiometry of two leads to a 50 % decrease in oxygen concentration along the flow field length between the cell inlet and outlet with associated changes in local current density and transport parameters. Impedance spectra collected with a fuel cell contain this localized information. However, an impedance model derived on the basis of locally non-uniform parameters has not previously been available for data analysis.

Under APRIS12, an impedance model was first derived by separating the active area into a fixed number of virtual segments, each having a distinct set of five kinetic and transport parameters. All segments were interconnected via an oxygen mass balance in the flow field channel and represented by the latest impedance model (previous two sections). Subsequently, the overall impedance spectrum for a segmented cell operated at a low and practical air stoichiometry of two was used to fit the impedance model which contains 50 (10 virtual segments) or 100 (20 virtual segments) parameters.

The impedance model showed a good agreement with experimental impedance spectra (Figure 2.1a.8, left). The oxygen diffusivity in the cathode catalyst layer was not uniform across the cell active area and decreased from the inlet to the outlet for low current densities (Figure 2.1a.8, right). For current densities larger than 0.2 A cm$^{-2}$, the non-uniformity disappeared. This behavior is presumed to be due to the accumulation of product liquid water downstream of the flow field channel. However, with a constant air stoichiometry, the reactant stream flow velocity proportionally increases with the current density, which facilitates liquid water removal from the porous electrode layers. Also, the oxygen diffusivity near the cell inlet increased with current density. This observation is consistent with Figure 2.1a.7 data obtained with a higher air stoichiometry.
The development of the novel analysis approach is ongoing with a focus on its applicability to a set of local impedance spectra. More details are provided in the published manuscript (item 2 in the Publications and Presentations Resulting from these Efforts section).

Figure 2.1a.8. Experimental (filled points) and fitted model (open symbols) spectrum of the proton exchange membrane fuel cell (left) for 10 virtual segments. Experimental and fitted points are shown for the same frequencies. Oxygen diffusion coefficient in the cathode catalyst layer (CCL) along the air channel for a current density of 0.2 A cm$^{-2}$ (right). Im(Z): imaginary impedance, Re(Z): real impedance.

**Anion exchange membrane fuel cells**

The development of stable and highly ionically conductive anion exchange materials (membranes and ionomers) has attracted significant attention for application in fuel cells. The conductivity of these materials is due to hydroxyl anions rather than protons. The change in chemical environment enables the use of less costly catalysts than those based on platinum group metals for both fuel oxidation and oxygen reduction. The performance of anion exchange membrane fuel cells operated with oxygen (rather than air) and platinum catalysts is still significantly lower than for proton exchange membrane fuel cells. This situation was ascribed to slow reaction kinetics and ionic and mass transport limitations. The real potential of anion exchange membrane fuel cells is currently unknown because commercial materials and mass production manufacturing methods have not yet been used.

Under APRISES12 work, commercially available Pt catalysts, ionomer and membranes, and gas diffusion layers were used to assemble membrane/electrode assemblies. Catalyst loadings were also commercially relevant and close to the Department of Energy targets. Catalyst coated membranes were prepared using digital printing, a method consistent with mass production, which improves reproducibility. Key operating parameters, gas stream relative humidity and oxygen concentration, were also varied to identify relevant areas for future design iterations. The project was completed in collaboration with Pajarito Powder LLC and EWII Fuel Cell LLC.
The maximum power density was reproducible and reasonably high at approximately 260-280 mW cm\(^{-2}\) with saturated gas streams and oxygen (Figure 2.1a.9, left). Under these conditions, impedance spectra showed two capacitive loops at high and intermediate frequencies, which were respectively attributed to hydrogen oxidation and oxygen reduction (not shown). The presence of these loops suggest that both reactions are slow and would benefit from improved catalysts. Changes in reactant streams’ humidification revealed that the best performance was observed with a 50 % relative humidity leading to a peak power density of 330 mW cm\(^{-2}\). This observation suggests that water management can be improved by optimizing the hydrophobicity of anode and cathode gas diffusion layers. Operation with air led to a lower performance which was attributed to electrolyte poisoning by carbon dioxide with the creation of carbonate anions that exchange hydroxyl anions decreasing ionomer and membrane conductivities, and mass transfer losses at the cathode owing to the diluted stream (Figure 2.1a.9, right). Impedance spectra showed an additional inductive behavior at low frequencies (not shown). It is presumed that this feature originates from the oxygen reduction side reaction (2-electron pathway leading to hydrogen peroxide followed by its disproportionation), which occurs in parallel with the main reaction (4-electron pathway leading to water). This statement supports the need for improved cathode catalysts with a higher selectivity. More details are provided in the published manuscript (item 3 in the Publications and Presentations Resulting from these Efforts section).

Figure 2.1a.9. Polarization curves obtained with oxygen for three membrane/electrode assembly (MEA) samples (left). Polarization curves obtained with oxygen and air (right). HFR: high frequency resistance, iR: ohmic voltage loss.
Publications and Presentations

*Peer Reviewed Publications*


Conference Proceedings


Contributed Presentations


References


2.1b Battery Testing

APRISES12 battery research was focused on three areas; the automation of battery diagnosis to allow online monitoring and forecasting [1-6]; the investigation of the performance and durability of battery technology under large-scale grid support operations; and the impact of vehicle to grid (V2G) usage on electric vehicle (EV) type batteries.

In the area of battery diagnosis, we developed new strategies that are allowing increased understanding of Li-ion battery degradation automatically or semi-automatically. Significant progress was made in the understanding of how environmental and usage aspects affect batteries. Of particular interest was the investigation of intrinsic variabilities in battery packs made of thousands of single cells. We found that the pack capacity will be increasingly limited by the cell that degrades the fastest, and not necessarily by the cell with the lowest initial capacity. The journal publication for this study was selected as the cover article for the monthly issue of the peer reviewed open access journal Energies.

In the area of grid operations, focus was set on the lithium ion titanate batteries used in grid-scale deployed systems monitored by HNEI under other APRISES tasks and efforts [7-9]. We found that Lithium titanium oxide (LTO)-based Battery Energy Storage Systems (BESS) could be better suited than graphite-based batteries for reserve applications because of the limited capacity loss at high SOC. We also used the gathered knowledge to estimate the impact of different energy/power strategies. For these batteries, we found that increasing power at the expense of energy could possibly reduce capacity loss by 50%.

In the area of vehicle to grid, focus was set on the understanding of the additional degradation induced by V2G to assess the potential for grid storage [7, 10-13]. We clearly established a detrimental impact of V2G under aggressive conditions but we also established that, under certain conditions...
conditions, V2G could help increase the longevity of the battery pack by delaying the typical accelerated degradation at end of life. In practice however, such results will only be obtained with intelligent control algorithms that would require a coordinated policy effort.

All the battery testing was done in the battery-testing laboratory at HiSERF that was developed under APRISES13. All the results of APRISES12 research have been published in peer reviewed scientific literature [1-13], and are discussed in more detail below.

**Li-ion battery degradation**

In APRISES12 we focused on the automation of the analysis to allow online monitoring and forecasting. HNEI introduces the concept of features of interest (FOI) which correspond to small sections of the voltage curves that varied significantly only for one type of degradation and not for the others. FOIs can be selected on any representation of the cell electrochemical behavior. In this work, IC curves were chosen but, among others, voltage vs. capacity or differential voltage curves would have been equally viable choices. For IC curves, a FOI can be voltage based (peak position, front/back tail voltage, peak half-width, voltage variation, resistance increase …), intensity based (peak/arch intensity, intensity at front/back tail, intensity variation …), capacity based (area under IC curves) and derivative based (slope of peak/arch) as shown in Figure 2.1b.1.

![Figure 2.1b.1 Example of Features of Interest (FOI).](image)

The FOI technique for semi-automated analysis of battery cycling data (i.e. with human intervention to limit the number of cases to consider) was first tried on graphite intercalation compound (GIC) / Lithium iron phosphate (LFP) batteries [4, 6] cycled under fast charging and dynamic driving conditions, Figure 2.1b.2. For these studies, the chosen FOI were area based and
they allowed identifying and forecasting the ongoing aging modes acting on the cell in-operando, to detect and quantify the reversible and irreversible part of lithium plating, and to provide a unique tool towards early lithium plating detection. More detail can be found in [4, 6].

The technique was also validated on two other popular Li-ion battery chemistries, GIC/ Lithium Nickel Manganese Cobalt Oxide (NMC) [5] and GIC/ Lithium Nickel Cobalt Aluminum Oxide (NCA) [2] with FOIs based on voltage, area and IC intensity. In the latter study, we applied these techniques to investigate cell-to-cell variations at the initial stage and after aging and found no correlation between the two. A critical aspect of this study was that degradation between cells was identical but the pace at which the degradation took place varied from cell to cell. It highlighted that lithium-ion cells’ degradation exhibits a non-trivial amount of intrinsic variability. The practical consequence of this intrinsic variability in a battery pack is that the overall capacity will be increasingly limited by the cell degrading the fastest and not necessarily by the cell with the lowest initial capacity. This study was selected as the cover article for the monthly issue of the peer reviewed open access journal Energies. Finally, we also compared the results of our approach to a new impedance based technique [1] for low temperature cycling of battery packs. This was done in collaboration with Navy Research Laboratory.

Figure 2.1b.2: Diagnosis and prognosis of a graphite/LiFePO4 battery using HNEI techniques.
With the viability of the FOI approach demonstrated, we next focused on the complete automation of the analysis without the need for human intervention [3, 5]. A sensibility analysis showed that, without human input or complex pattern recognition techniques, no automated diagnosis is possible as no FOI is solely influenced by one degradation mechanism. To circumvent this issue, we developed a new multi-step approach where a final multidimensional look-up table is to be embedded in the automated process to enable a low computing but robust diagnosis of the battery degradation. The originality of this approach resides in the consideration of the variations of all FOIs concurrently by using detection in an n-D space for n-FOIs. This enables having accurate prediction even when each FOI taken separately cannot provide a conclusive diagnosis.

The methodology first consists in emulating the cell that is to be monitored from its half-cell data. This emulation approach creates a virtual representation of the cell from its individual electrode data. The virtual cell can then be degraded under different degradation modes to highlight the changes in voltage response. Battery degradation can be summarized in seven degradation modes, loss of lithium inventory (LLI), loss of active material (LAM) on the positive electrode (PE) and on the negative electrode (NE), lithiated (li) or not (de), and the kinetics limitations (RDF) of the PE and NE. Once the emulation is completed, FOIs can be identified from the voltage response of the cell and their sensibility towards capacity loss and degradation modes can be established. Finally, the variation of the most sensible FOIs upon different degradation paths can be compiled into a multidimensional look-up table. Only the final look-up table is to be embedded in to the battery management system (BMS), which renders this method appealing. The SOH diagnosis is performed by comparing the measured FOI values to the values stored in the look-up table.

Out of 5000 possible validation degradation scenarios, the average diagnosis error for the model was 1.3% for a GIC/LFP cell with up to 30% capacity loss, Figure 2.1b.3. Throughout the range of capacity loss, 90% of the diagnoses have an error of less than 4.0%, 6.0%, and 1.0% for LLI, LAM_{PE} and LAM_{NE}, respectively. The maximum error rose to 9.0%, 9.0%, and 4.5% for LLI, LAM_{PE} and LAM_{NE}, respectively when 95% of the data was considered. For a LTO//NMC cell, (the cell chemistry used in BESS monitored under APRises projects), the average diagnosis error was below 0.1%. Considering 90% of the data, the error on LLI and LAM_{PE} estimation was small, less than 1%, but the error for LAM_{NE} was increasing from 1% to 12% at 30% capacity loss. The errors increased up to 3.5%, 2.5% and 16% when 95% of the data are considered. The automated diagnosis was concluded to be accurate for at least 90% of the test data and the diagnosis errors were also found to be localized and thus easily manageable.
Figure 2.1b.3: Average diagnoses error for (a) the GIC/LFP cell and (b) the LTO/NMC. For each capacity loss, the left bar represents percentage of LLI, the middle bar the percentage of LAMPE and the right bar the percentage of LAMNE. The error bars represent the maximum diagnosis error. The error bars are enriched with quantile information: The spread between □, ○, <, and > accounts for 50%, 90%, 95%, and 99% of the data respectively.

**BESS system cell durability**

The purpose of this APRISES project is to understand aging of commercial cells used in large scale BESS based on single cell laboratory testing. The project had two objectives: First to test individual single cells in a laboratory setting to understand the cell aging patterns, reproduce the aging observed in real life and accelerate this degradation to enable the end of life prognosis of the installed BESS. Second, to monitor, quantify and analyze the battery degradation observed in the BESS systems installed on the power grid (under other APRISES efforts).

To reach the first objective, we investigated the cell degradation as a function of different aging conditions with both calendar and cycle aging. The calendar aging study used a design of experiment methodology to assess the effect of SOC and temperature on calendar degradation in eight experiments. The cycling aging study focused on understanding the degradation introduced by the BESS field usage throughout the three years of testing. This knowledge was used to test 3
single cells under nominal and harsher conditions. This approach is summarized in Figure 2.1b.4 and comprises three distinct steps: usage analysis, laboratory test and HNEI custom analysis. In the first step, we used three years’ worth of collected real-world BESS data to quantify the average usage of the system and defined representative metrics. In the second step, we generated a design of experiment that allowed us to test the impact of each of the selected metrics of degradation. Step 1 and 2 were completed under APRISES12. In the last step, we are planning to use HNEI’s unique battery degradation analysis capabilities such as incremental capacity analysis with FOIs and pack modeling to analyze cell degradation and diagnose the impact of the selected metrics individually. This will be conducted under APRISES16 funding and reported at a later time.

Figure 2.1b.4: Schematic test plan of the laboratory testing for the BESS single cells.

The results of the first and second steps are summarized in Figure 2.1b.5. First, we investigated the usage over three years of a BESS operating at the distribution level of the Hawaii Island grid. The BESS was in use for more than 90% of the time and stored 1.5 GWh of energy, which amounts to close to 2 MWh per day for a system rated at 250 kWh. This implies an intensive usage of the cells with an average of 5 equivalent full cycles per day (>5000 total cycles in 3 years). Our study of the maintenance cycles showcased that these 5000 equivalent cycles induced an estimated 5-10% degradation on the single cells. Our analysis of the duty cycle suggests that the usage of the cells can be described by five parameters: The representative usage consists of several 9 s, alternating C/2 charge and discharge pulses causing 5% SOC swings with a 0.75% SOC/min ramp rate at 35 ºC. However, extreme values with currents up to more than 4 C, 100% SOC swings and temperatures above 50 ºC were also observed.

Second, we investigated the battery degradation associated with the representative usage of the BESS. The research entailed the impact of different stress factors such as the C-rate, the temperature, and the SOC swing range on the battery degradation. The results showed that the accelerated laboratory testing forecasted a capacity loss similar to the values observed in the field. Temperature increase and C-rate increases were found to have a detrimental effect on capacity
retention. In addition, it was found that capacity faded faster when smaller SOC swings were applied. Moreover, no significant compounding interactions were identified between the three stress factors. Initial modeling showcased that the modules are not all losing capacity at the same pace because of slight temperature gradients. The forecast for up to 10 years indicates capacity loss for the hottest cells in the order of 30% vs. 15% for the coolest cells. In this work, we assumed a perfect battery pack with identical perfectly balanced modules fading at the same pace. This assumption might not be verified in the field and might explain the larger observed spread of fading. Therefore, more comprehensive modeling taking into account cell-to-cell variations, inhomogeneous aging conditions will be performed under APRlSES16 to improve the accuracy of the simulations.

Regarding calendar aging, the cells did not degrade significantly when kept below 35 °C, but deteriorated from exposure to temperatures above 45 °C especially if left at low SOC. This result was counterintuitive based on common understanding of the calendar aging of Li-ion cells that suggests more degradation at high temperature and high SOCs. This was likely induced by the presence of a titanate NE in lieu of the graphite NE. Calendar aging is well known to be associated with loss of lithium inventory induced by the growth of a passivation layer. This parasitic reaction is fueled by the voltage of the battery, above 4V, that is enough to decompose the electrolyte. In LTO-based cells, this is inhibited because the voltage is lower, 2.5V, and thus the electrolyte stable.

In order to compare our calendar aging results and the behavior of these titanate cells to the state of the art, we performed a literature review [7] on the topic and found that LTO based cells are indeed less affected than graphite cells. Losing little capacity from calendar aging could be a significant advantage for BESS reserve applications. Such systems must spend most of their time resting at high SOCs to be ready to be used at any time. Therefore, LTO-based BESS could be better suited than graphite-based BESS for this application. Moreover, the limited loss at room temperature or below allows for easy and prolonged storage of cells without performance fade.

Although it cannot be concluded yet that the testing acceleration protocol simulated actual long-term battery usage, this dataset elucidated the influence of certain factors such as the impact of cooling and of sizing on the BESS longevity. There was an undeniable deleterious effect of temperature on the cells. Temperatures above ambient need to be avoided both during usage and during idling and offline periods, especially if the BESS is at low SOC. When identifying an adequate sizing of the BESS, this study can be used to roughly estimate the impact of different energy/power strategies. The SOC swing range is a proxy for the BESS energy. Decreasing the SOC swing is equivalent to deploying a BESS with higher capacity performing the same task. The C-rate corresponds to the power rating. Since power is voltage multiplied by the current, decreasing current emulates a BESS that is required to deliver more power given the same voltage.
and energy. Table 2.1b.1 compiles the difference in capacity loss associated with dividing or multiplying the available energy or power by a factor of two while performing the same usage. In this case, since small SOC swings induced more capacity loss and low currents induced less loss, it was most advantageous to increase power (−48% capacity loss) at the expense of energy. More work is needed to investigate sizing issues further, but the proposed test matrix shows great promise. The gathering of information in 6 months of testing should enable the determination of which topology is most efficient based on the predicted usage.

Further detail can be found in [8, 9].

Figure 2.1b.5: Graphical summary of the laboratory experiments performed on the LTO/Lithium Cobalt Nickel Aluminum Oxide Altairnano Generation 1 cells.
Table 2.1b.1: Impact of different Power-to-Energy combinations on capacity loss after the same overall usage (lower is better).

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<th>Energy</th>
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<tr>
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<td>+39%</td>
<td>+9%</td>
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**V2G impact assessment**

Battery degradation is extremely important to EV technologies and is a function of several factors, such as electrode chemistries, operating temperatures, and usage profiles (i.e. driving vs. driving + vehicle-to-grid applications). The goal of this research was to assess such impact. The battery test plan used two separate experiments: a cycling experiment to assess the impact of both V2G and grid-to-vehicle (G2V) charging strategies and a calendar aging experiment to assess the impact of temperature and SOC, Figure 2.1b.6.

The effect of constant power V2G and G2V protocols on single cells was investigated. Since V2G and G2V protocols might have a combined effect with other variables such as the charging schedule, and the charging level, it was essential to study a matrix of tests encompassing the different combinations. Four different duty cycles were selected to occur during @Home and @Work periods: A V2G discharge followed by a charge and rest (DCR), a charge then a rest (CR, standard usage), a rest then a charge (RC, G2V delayed charging), and just a rest (R). The pace of calendar aging is known to be dependent on the cells' SOC and on the environmental temperature [7]. For EV applications, the SOC could be anywhere from 100% to 0% and the temperature, dependent on the location and climate (from -27°C to 55°C in this study). Since calendar aging on GIC//NCA cells occurs for the most part at high temperature and SOC, the density of measurement was increased in this area. More detail on the experimental protocol can be found in the full publication [12].

For this study, 100 GIC/NCA cells were purchased. They are representative of the cells used by Tesla in their EVs. Preliminary testing, Figure 2.1b.7, consisted in assessing the cell-to-cell variations and in the emulation of the cell enabling a sensibility analysis and proper FOI selection. More detail can be found in [13]. The cell-to-cell variation analysis revealed that the test cells were of high quality with similar thermodynamic properties as well as less than 0.5% variation in rate capability and maximum capacity, and less than 3% variation in resistance. Thus, the selected cells
were found suited for long term studies of cells tested under a range of aging scenarios such as V2G and G2V. As a result, 36 cells were selected for the cycle aging experiment and 16 cells for the calendar aging experiment.

Figure 2.1b.6: Test plan for the V2G/G2V study.
With 52 cells in testing, and to accelerate the analysis of the degradation data and perform advanced diagnosis without resorting to post-mortem analysis, the FOI approach was used. In order to select the most appropriate FOIs, a sensibility analysis was performed from an emulated version of the cells. The impact of the degradation modes is different enough to enable accurate diagnosis of cell degradation and permit comparison of cells following different degradation paths. Selected FOIs were the intensity of the peak at 4.1V and the intensity and position of the minimum in voltage between 3.7 and 3.9V.

Next, the effect of V2G and G2V on battery durability was investigated. In addition, the effects of calendar aging on capacity loss, resistance increase, and rate capability were identified. Results were reported in [12] and are summarized in Figure 2.1b.8.

This study focused on testing the impact of V2G discharging the battery twice a day to the power grid for a total of 2 hours per day at the maximum possible power to maximize potential electricity savings or revenues for the EV owner. Results showed that such a V2G step twice a day increased the capacity loss by 75% and the resistance by 10%. Reducing the V2G usage by half (to one discharge cycle lasting 1 hour per day) degraded the cell less but the result was still found to
accelerate the capacity loss by 33% and the resistance increase by 5% over no V2G at all. Thus, a detrimental impact of V2G under these aggressive conditions was clearly established for these cells. Translating these results to the entire life of the cells using the model developed for this project showed that participating in V2G programs could decrease the lifetime of the battery packs below 4 years because of a capacity loss of more than 20%. In contrast, delaying the G2V charge rather than charging immediately after driving (to help the grid to spread the load) had no significant effect (<1%) on capacity retention and was found to limit the resistance growth (5% less increase). It was noted that this experiment was performed at room temperature where the SOC exercised very little influence on calendar aging.

The calendar aging experiment showed that the storage SOC has a much higher impact at higher temperature. This suggests that delayed G2V should induce less degradation and be beneficial in warmer climates. Looking more closely at calendar aging, aging was found to influence the cells and that, at room temperature, charging the cells twice a day instead of once lowered the rate of capacity loss by 5%. However, since the capacity loss increases with temperature and SOC, this will not be the case in warmer climates. The capacity loss associated with time, temperature and SOC was modeled with a double-quadratic equation. This modeling allowed for the prediction of the capacity loss induced by time, temperature and SOC. Looking at the individual effect analysis, storage temperature was found to have the biggest impact on capacity loss and rate capability. However, the SOC had more influence on the resistance increase.
From the analysis of the FOI, published in [11] and summarized in Figure 2.1b.9, the modes causing the degradation of these commercial graphite//NCA cells subjected to 20 different duty cycles, including cycle and calendar aging, were investigated. It was found that, in general, the cells did not degrade in the same way, and that the degradation was path dependent. Cycle aging, with or without an extra discharge step to determine the effect of V2G strategies on battery life, resulted in greater loss of active material and more kinetic limitations on the negative electrode than calendar aging. Temperature induced additional loss of lithium inventory and loss of active material at the positive electrode. SOC, on top of catalyzing the temperature effect, caused kinetic limitations and loss of negative electrode material. Most noteworthy, the loss of active material at the negative electrode was faster than the loss of lithium inventory in the cycle-aging experiment. This finding was a clear sign that the cycled cells will enter a stage of advanced aging characterized by the onset of lithium plating. This result led to a revision of the lifetime prognosis for the usage of these cells for EV application. However, the manifestation of the second stage could be delayed or suppressed with intelligent control algorithms.
Following up on the concept of intelligent control algorithms to reduce the impact of V2G on the cells, we teamed up with the University of Warwick [16] for a collaborative publication on the policy impact of our respective findings [10]. We concluded that the simplistic approach adopted by current V2G pilot studies, namely that an EV is discharged and charged without consideration of battery degradation is not economically viable because of the impact additional V2G cycling has on battery life. However, a smart control algorithm with an objective of maximizing battery longevity can reverse this. In such an approach, the control algorithm only allows access to the battery's stored energy if there are no adverse effects on battery longevity; therefore, the worst case is that a battery degrades as if there was no V2G. This approach relies upon the development of accurate battery prognostic models and further advances in understanding the causes, mechanisms and impacts of battery degradation.

From a policy perspective, anticipated EV growth offers great potential for V2G to play a significant role as a grid service. When coupled with jurisdictions that have committed to renewable energy, V2G can be an enabler for carbon reduction. Installing the grid improvements and platform is an essential first step, but establishing the appropriate compensation model will be challenging and necessary for V2G to expand. Ultimately, establishing a new, free market to aggregate and trade grid services combined with the methodology envisioned by us and others could lead to unbridled growth of V2G as a future grid service.

Figure 2.1b.9: Graphical summary of the FOI analysis of the cycle and calendar aging studies.
In summary, much was accomplished under APRISES12 battery efforts. Significant progress was made in the understanding of how different key environmental and usage aspects affect the single cells and how these cells can be characterized. These studies pave the way to develop a complete BESS model under APRISES16 funding.

Publications and Presentations

Peer Reviewed Publications


Contributed Presentations and Posters


3. EV cell degradation under electric utility grid operations: Impact of calendar aging & vehicle to grid strategies, A. Devie and M. Dubarry, EV Summit and Transportation Summit, Cocoa Beach, FL, USA, October 2016. (Poster)


5. Laboratory testing of Lithium Titanate based cells for BESS applications, A. Devie and M. Dubarry, EV Summit and Transportation Summit, Cocoa Beach, FL, USA, October 2016. (Poster)


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12. Hawai’i Energy and the Role for Storage, M. Dubarry and K. McKenzie, American Chemical Society Hawai’i Local Section Election Luncheon, Honolulu, HI, USA, November 2017


References


2.2. Contaminant Mitigation and Field Testing

Task 2.2 focused on the development of advanced fuel cell air purification materials and novel sensor devices to allow the use of fuel cells to be expanded into harsh environmental conditions. These sorbent materials and devices were tested in controlled laboratory conditions under this effort. Under other APRISES funding, field testing is planned onboard a fuel cell electric bus in Hawaii Volcanoes National Park (HAVO), where the environment contains detrimental gas contaminants such as the acidic gases SO$_2$, NO$_2$ and H$_2$S.

The key accomplishments of this APRISES12 subtask were as follows: comparative studies of low concentration SO$_2$ and NO$_2$ sorption by activated carbon supported 1-ethyl-3-methylimidazolium acetate and potassium hydroxide sorbents, quantum chemical modeling of gas contaminant (SO$_2$ and NO$_2$) and 1-ethyl-3-methylimidazolium acetate sorbent binding interactions; fabrication and installation of a small scale test stand for testing HNEI synthesized materials; preliminary testing of a novel sensor system and refinement of operational protocols which are designed to expand operational capability of fuel cell vehicles; the characterization of
commercially available air filtration materials under HAVO conditions to predict field performance and lifetime; the renovation of HNEI’s HIG 412 laboratory on the UH Manoa campus to allow future materials development work to be performed.

**Air Filtration: Materials Development**

Under APRISES12 we expanded our experimental investigations of activated carbon supported ionic liquid sorbents as advanced high performance sorbent materials for air purification to include simultaneous acid gas (SO\(_2\) and NO\(_2\)) contaminant sorption. Furthermore, theoretical modelling studies of gas contaminants (SO\(_2\), SO\(_3\), CO\(_2\) and NO\(_2\)) and ionic liquid binding interactions were performed to gain an understanding of the thermodynamic properties and the favored binding interactions occurring during SO\(_2\) and NO\(_2\) sorption. Ionic liquids are a class of “green compounds” which have recently received considerable attention in numerous applications due to their negligible volatility, large liquidus range, and tunable chemical properties [1-8]. Ionic liquids have recently been shown to be capable to partially regeneratively absorb a variety of contaminants through physisorption and chemisorption processes [9].

In APRISES 12 we evaluated single and mixed acid gas contaminant sorption performance of activated carbon supported 1-ethyl-3-methylimidazolium acetate and activated carbon supported potassium hydroxide (KOH) sorbents under simulated atmospheric conditions containing 2-10 ppm SO\(_2\) and NO\(_2\) in air at 25°C and 50% relative humidity. In order to mitigate the effects of high viscosity of the ionic liquids, we prepared activated carbon sorbents loaded with 10 and 30 wt% 1-ethyl-3-methylimidazolium acetate ionic liquid using methods developed under APRISES 13. Thus thin films of the ionic liquid were supported on a coconut based granulated activated carbon. We focused on activated carbon supported 1-ethyl-3-methylimidazolium acetate ([C\(_2\)mim][Ac] sorbent) as it was previously determined to have superior performance compared to other activated carbon supported ionic liquid sorbents, under practical conditions [8].

The single contaminant studies showed that the [C\(_2\)mim][Ac] sorbent, has superior sorption performance for SO\(_2\), with breakthrough times greater than pure activated carbon, pelletized KOH activated carbon and granulated KOH activated carbon. The granulated KOH activated carbon and pure activated carbon had highest NO\(_2\) break through times compared to the ionic liquid sorbents. Generally, the pelletized KOH activated carbon had the lowest SO\(_2\) or NO\(_2\) absorption performance indicating pelletized sorbents may not be ideal for use in high flow rate applications such as fuel cells.

The mixed gas contaminant sorption behavior was studied at 5 ppm SO\(_2\) and 5 ppm NO\(_2\), 25°C, and 50 % RH with a flow rate of 30 LPM. The 30 wt% [C\(_2\)mim][Ac] sorbent maintained its superior performance in SO\(_2\) capture even in the presence of NO\(_2\), Figure 2.2.1. The trend in SO\(_2\) or NO\(_2\) uptake in the mixed gas contaminant studies was similar to that of the single gas
contaminants. Overall, the breakthrough times were lower than in the single gas contaminant sorption testing suggesting no cooperative sorption effects in mixed gas contaminants.

Figure 2.2.1. Simultaneous sorption of SO₂ and NO₂ at 5 ppm and 30 LPM for sorbents, (a) pure activated carbon, GCN30; (b) 10 wt % KOH impregnated activated carbon, (c) 30 wt% [C₂mim][Ac] sorbent and (d) 10 wt % [C₂mim][Ac] sorbent.

The mixed gas contaminant sorption behavior of 30 wt% [C₂mim][Ac] sorbent is shown in Figure 2.2.1c. The greater SO₂ selectivity of the 30 wt% [C₂mim][Ac] sorbent and its ability to displace absorbed NO₂ suggest potential use of the sorbent in the separation of SO₂ and NO₂ in mixtures. The high SO₂ selectivity exhibited by 30 wt% [C₂mim][Ac] sorbent is preferable in fuel cell applications, where SO₂ has the greater detrimental impact compared to NO₂. This supported ionic liquid sorbent has potential for use in integrated filtration systems composed of multiple segments in which each sorbent segment is optimized for the effective selective removal of individual/multiple gas pollutants. The superior performance of the 30 wt% [C₂mim][Ac] sorbent suggests that impregnation of ionic liquid onto nanoporous support has the potential to significantly enhance their use as practical sorbents for low concentration gas contaminant capture due to the increased gas diffusion through the ionic liquid thin films compared to sorption in pure bulky ionic liquids. Furthermore, the high viscosity of ionic liquids which is an impediment in gas sorption in bulky ionic liquids, has beneficial effects in supported ionic liquids as it reduces the forward flow and stripping of the ionic liquids from the support due to the continuous flow of the challenge gas.
Theoretical Density Functional Theory (DFT) calculations using dispersion corrected B3LYPd functional [11-14] and a 6-311(d,p) basis set [15, 16] were performed with the GAMESS [10] software package to gain insight into the types of interactions taking place between a single contaminant XO₂ (X = N, S), SO₂ and NO₂, and the 1-ethyl-3-methylimidazolium acetate ionic liquid.

The experimentally observed greater selectivity for SO₂ than NO₂ using the [C₂mim][Ac] sorbent was confirmed by DFT calculations which indicated larger binding energies for SO₂ compared to NO₂ by the ionic liquid. The studies indicated that the gas contaminants preferentially interact with the oxygen atoms of the acetate anion of the ionic liquid compared to the imidazole cation, Figure 2.2.2.

![Figure 2.2.2. Lowest energy [C₂mim][Ac]·XO₂·YO₂ structures where XO₂·YO₂ is (a) NO₂·NO₂, (b) NO₂·SO₂, (c) SO₂·NO₂, and (d) SO₂·SO₂. The atom colors are: black (C), blue (N), red (O), yellow (S) and white (H).](image-url)
For detailed information on Methods, Results and Discussion of work performed under the air filtration materials development effort, see the paper listed below under Publications Resulting from these Efforts, “Severa, G., Head, J., Bethune, K., Higgins, S., Fujise, A., Comparative studies of low concentration SO$_2$ and NO$_2$ sorption by activated carbon supported [C2mim][Ac] and KOH sorbents. Journal of Environmental Chemical Engineering, 2018, 6 (1), 718-727.

Furthermore, under APRISES12, an air filtration test stand was fabricated and installed for testing small sized samples of HNEI synthesized materials. General laboratory equipment associated with syntheses and characterization of gas contaminant sorbent materials was set up in the lab.

Under APRISES14 syntheses and characterization of metallo ionic liquids for SO$_2$ mitigation will be begun. This effort will be guided by theoretical calculations and our previous experimental findings.

**FCEV Operation in Contaminated Air Environments**

HNEI has continued previous APRISES13 efforts to develop the Environmental Sensor System (ESS) to allow fuel cell vehicles to operate safely and reliably in environments with contaminated air. The addition of the ESS turns a fuel cell vehicle into a ‘smart’ vehicle capable of sensing and reacting to the environment in which it is operating in order to protect the fuel cell from air contaminants. The development of the ESS included device design, fabrication, installation and troubleshooting along with programming the interface with the vehicle control system to allow communication.

Under APRISES 12 funding, the ESS was tested onboard a fuel cell electric bus and integrated into the vehicle control software. The control software integration allows the user to set the air contaminant thresholds at which the ESS performs the protection protocols. These protection protocols consist of shutting down the fuel cell and relying on the battery power should a threshold of any monitored air contaminant be met, either in the environment or after the air filter. The result of the ESS installation and testing can be seen in Figure 2.2.3, where a simulated high air contaminant environment is repeatedly introduced to the ESS and the resulting reaction from the vehicle can be seen protecting the fuel cell by shutting it down.
Figure 2.2.3. Fuel cell current response to simulated high air contaminant environments displaying the ability of the ESS to control the fuel cell for protecting from high air contamination (Box B represents one half of the ESS unit)

For more detail, see the paper “Environmental Sensor System for Expanded Capability of PEM Fuel Cell Use in High Air Contaminant Conditions” that was submitted to the International Journal of Hydrogen and is listed below and available on the HNEI website. This work is currently under review at the US Patent and Trademark office for a full utility patent. HNEI is currently in discussions with several fuel cell companies who are interested in licensing the technology.

In support of the HAVO bus project, two of the major fuel cell air filters manufactures were tested at HNEI’s air filtration test stand in preparation for use at HAVO. Both company’s filters were tested under simulated HAVO conditions and compared for performance, see Table 2.2.1.
Table 2.2.1 Detailed breakthrough times showing performance characteristics of two commercial air filter suppliers

<table>
<thead>
<tr>
<th>Filter Manufacturer</th>
<th>Breakthrough (hrs)</th>
<th>SO₂ Captured by filter (mg)</th>
<th>Areal Density (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>137.3</td>
<td>14806.5</td>
<td>8.9</td>
</tr>
<tr>
<td>A</td>
<td>134.0</td>
<td>14449.5</td>
<td>8.6</td>
</tr>
<tr>
<td>A</td>
<td>50.0</td>
<td>8021.2</td>
<td>4.8</td>
</tr>
<tr>
<td>A</td>
<td>50.0</td>
<td>8021.2</td>
<td>4.8</td>
</tr>
<tr>
<td>A</td>
<td>29.8</td>
<td>6297.5</td>
<td>3.8</td>
</tr>
<tr>
<td>A</td>
<td>29.8</td>
<td>6298.5</td>
<td>3.8</td>
</tr>
<tr>
<td>B</td>
<td>179.2</td>
<td>4653.5</td>
<td>10.6</td>
</tr>
<tr>
<td>B</td>
<td>8.0</td>
<td>797.2</td>
<td>1.8</td>
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<td>B</td>
<td>8.0</td>
<td>798.2</td>
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<tr>
<td>B</td>
<td>0.7</td>
<td>122.9</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The characterization of commercially available air filtration materials in the HNEI air filtration test stand allows a commercial filter to be chosen for use in HAVO, and performance can be predicted and incorporated into the ESS control software. This is an integral part of the technology which will allow the control software to accurately predict filter lifetime in the conditions tested. Further, the development of the protocols for testing can be applied to any environment ONR intends to use fuel cells in to accurately predict performance in that environment. The above data is proprietary and therefore not published or disclosed.

Under this task, HNEI has renovated a laboratory on the UH Manoa campus (HIG 412). The renovated laboratory will be utilized for materials development work related to fuel cells and fuel cell performance and be available to HNEI staff for other projects requiring a materials lab.

Publications and Presentations

Peer Reviewed Publications


Contributed Presentations


Patents

U.S. Patent Application No.: 15/269,390, Title: ENVIRONMENTAL SENSOR ARRAY FOR FUEL CELL AIR FILTRATION SYSTEMS, Filed: September 19, 2016, Inventor: Scott Robert Higgins and James Ewan

References


**TASK 3: ALTERNATIVE FUELS**

This effort focused on the development, testing and evaluation of alternative fuels and technologies, and included activities in the areas: Methane Hydrates Technology for Synthetic Fuels Production including Hydrogen Production for Fuel Cell Applications, Evaluation of Second Generation Biofuels, Novel Solvent Based Extraction from Biomass, Liquid fuels from Synthesis Gas, Bio-contamination of Fuels, Biofuel Corrosion Control, Waste Management, and High Rate Anaerobic Digestion, and Low-cost Material for Solar Fuels Production, and Hydrogen Refueling Support.”

**3.1 Methane Hydrates**

The APRISES12 Methane Hydrates activities comprised four areas of focus: Hydrate Energy, Environmental Impacts of Methane Release from Hydrates, Hydrate Engineering Applications, and International Collaborative R&D.
National R&D programs on methane hydrates were initiated in Japan and India in the mid-1990’s with the goal of commercial gas production within a 20 year time horizon. The U.S. established its own program in May 2000. The Methane Hydrate Research and Development Act of 2000 (Public Law 106-193) included seven technical areas of focus: (1) identification, exploration, assessment, and development of methane hydrate as a source of energy; (2) technology development for efficient and environmentally sound recovery of methane from hydrates; (3) transport and storage of methane produced from methane hydrates; (4) education and training related to methane hydrate resource R&D; (5) assessment and mitigation of environmental impacts of natural and purposeful hydrate degassing; (6) development of technologies to reduce the risks of drilling through methane hydrates; and (7) support of exploratory drilling projects. The objectives of the Methane Hydrates Task of the APRISES initiative reflect most of the priorities of P.L. 106-193, but emphasize those areas of particular relevance to the ONR and which are consistent with the overall goals of APRISES. Specifically, the development of hydrates and related sources of seafloor methane as logistical fuels for Naval applications, and related marine environmental issues, have been the principal areas of interest; exploratory drilling projects and seafloor stability/safety have received limited attention. Work also was performed to explore engineering applications of hydrates such as hydrogen fuel storage. Task objectives were devised to leverage fully the hydrate R&D expertise and infrastructure that had been developed at HNEI during previous research programs on CO₂ ocean sequestration and deep oil spills.

During the present reporting period, the goals of the APRISES Methane Hydrates Task were to:

- Pursue development of methods to recover methane gas from hydrates.
- Investigate environmental impacts of methane hydrates on the marine environment.
- Explore engineering applications for hydrates such as desalination and biofiltration.
- Promote international collaborative research on methane hydrates.

Specific technical initiatives that were pursued to attain the above goals included:

- Continue laboratory experiments on hydrate destabilization by chemical inhibitors, focusing on ferric chloride (FeCl₃) and related ionic salt compounds found in seawater.
- Complete an experimental calorimetric investigation on hydrate formation and dissociation in sand matrices.
- Collect and analyze samples from methane hydrate reservoirs on the Chatham Rise offshore of New Zealand to investigate the mechanisms of microbial methane metabolism in ocean sediment.
- Mentor and provide technical support to an undergraduate student conducting experiments to assess the feasibility of utilizing hydrates for desalination and biofiltration.
- Organize the 9th International Workshop of Methane Hydrate R&D.
Work on the Methane Hydrates Task focused on the four primary areas and is described below.

Hydrate Energy

Practicable and environmentally acceptable methods to destabilize hydrate reservoirs in seafloor sediments and arctic permafrost must be developed in order to release and collect the methane gas for energy applications. Hydrate destabilization strategies also are of critical importance to the operation of natural gas transport pipelines, which are vulnerable to blockage by solid hydrate plugs. Under prior ONR awards, significant progress was made by HNEI in elucidating the mechanisms by which various chemical reagents destabilize pure methane hydrate.

For APRISES12, we continued our experimental studies of hydrate destabilization by reagent injection, focusing on FeCl₃ and related transition metal salt compounds present in seawater. Based on our prior preliminary calorimetry results, FeCl₃ appears consistently and significantly to outperform alcohols currently employed by the natural gas industry for pipeline flow assurance (i.e., to prevent the formation of hydrate plugs). Consequently, a series of experiments were conducted to clarify the mechanism of action by which FeCl₃ destabilizes methane hydrate and to explore other inhibitors with similar chemical features.

There is general consensus that seafloor hydrate reservoirs that occur in sandy sediments are the low-hanging fruit that will be the first to be developed commercially. In consideration of this, we previously initiated experiments to investigate hydrate formation and dissociation in sand matrices. For APRISES12, these experiments were completed and the results constitute the basis of the M.S. thesis of a graduate student in ocean engineering.

The primary accomplishments under this activity were: (1) completed an experimental study to determine the effectiveness and mechanism of action by which FeCl₃ and other transition metal salts destabilize methane hydrate and published these results in a peer review journal; and (2) completed a study on the effects of porous media (sand) on phase equilibrium of methane hydrate.

Destabilization by Transition Metal Salts

Clathrate hydrates can be induced to dissociate (melt) or prevented from forming by application of thermodynamic inhibitors such as alcohols and salts. These inhibitors shift the equilibrium between the three phases, hydrate (H), liquid water (Lw), and guest molecular vapor (V) to lower temperature or higher pressure (Sloan & Koh, 2008). It has been posited that dissolved inhibitors tie up water molecules needed for hydrate formation via hydrogen bonding, as in the case of alcohols and glycols (Nihous et al., 2009), or via Coulombic forces, as in the case of salt ions (Sloan & Koh, 2008).

The behavior of clathrate hydrates in the presence of transition metal salts was investigated using a Differential Scanning Calorimeter (DSC). Specifically, a DSC was employed to determine the onset temperature for methane hydrate decomposition in the presence of ferric chloride
hexahydrate, \([\text{FeCl}_2(\text{H}_2\text{O})_4]\)\(\cdot\)2\(\text{H}_2\text{O}\), anhydrous ferric chloride, FeCl₃, MnSO₄, FeSO₄, CuSO₄, and AgNO₃, and to compare the inhibiting properties of these transition metal salts with NaCl and CaCl₂, two well-known salt inhibitors.

Most of the transition metal salts investigated in the present study inhibited methane hydrate formation at high concentrations but none to the extent of sodium chloride except for FeCl₃. 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 (FeCl₃, FeSO₄, and MnSO₄), appeared to promote hydrate formation, i.e., dissociation temperature increased slightly as indicated by negative \(\Delta T\) (defined as the reduction in dissociation temperature induced by the inhibitor) in Table 3.1.1. This effect has not been observed with other chloride salts, but has been observed with other water soluble compounds such as alcohols (Abay and Svartaas, 2010).

The present results appear to confirm Sabil et al.’s (2010) assertion that the inhibitor effect increases with increasing charge on the cation. The chloride salt of the higher charged Fe\(^{3+}\) exhibits greater inhibition of methane hydrate formation in comparison to Na\(^{+}\); but the iron salt of the larger polyatomic anion, sulfate, exhibits less inhibition than the FeCl₃ salt. One possible explanation for the behavior observed in this and previous studies is that, when salts dissolve, the ions interact with the dipoles of the water molecules. The stronger interaction between water with salt ions (versus hydrate guest molecules) interferes with the organization of the water lattice around the clathrate hydrate guest molecule, and thus inhibits hydrate formation. The strength of the salt ion-dipole bond between the metal ion and water molecules may correlate with the degree of inhibition of hydrate formation. The strength of the ion-dipole bond in the primary solvation shell is expected to increase with the electrical charge, \(z\), on the metal ion and decrease as its radius, \(r\), increases (Petrucci et al., 2007). Therefore, higher charged metal ions, such as Ca\(^{2+}\) and Fe\(^{3+}\) would be expected to have a greater attraction to the water molecules and thus more effectively impede hydrate formation. Furthermore, larger polyatomic anions, such as SO\(_4^{2-}\) would have a weaker attraction to the water molecules and would be less effective inhibitors. Table 3.1.2 summarizes the ionic radii for the monoatomic cations and anions for the salts included in this study.
<table>
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<th>Inhibitor</th>
<th>CH$_4$ Pressure (MPa)</th>
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<td></td>
<td>3.94</td>
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<td>4.9</td>
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<td>FeCl$_3$</td>
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<td>282.8</td>
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</table>

Table 3.1.1. Temperature of Dissociation of Methane Hydrate in the Presence of Metal Salts.
The degree of methane hydrate inhibition induced by the salts that were studied (as indicated by the reduction in dissociation temperature at a given pressure), when compared between mixtures with the same mole percentages of the salt, increases in the following order: FeSO₄ ≈ CuSO₄ < MnSO₄ ≈ AgNO₃ ≈ CaCl₂ < NaCl < FeCl₃. A smaller decrease in the dissociation temperature was observed with salts that contained the larger sulfate anion when compared to salts that contained the smaller chloride anion. A smaller decrease in the dissociation temperature was observed with salts that contained smaller cations like Fe²⁺ when compared to salts that contained larger cations such as Ag⁺ and Mn²⁺. Therefore, consideration of the charge and size characteristics of the anion and cation components of the tested salts appears to support the mechanism based on the ion-dipole interaction between the ions and water posited above to explain this behavior (Table 3.1.2). Several other water soluble metal salts are available and additional inhibitor activity on methane hydrates provided by these salts should be investigated to confirm this trend.

Table 3.1.2. Ionic Radii.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radii (Å)</th>
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<tr>
<td>Mg²⁺</td>
<td>0.72</td>
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<tr>
<td>Ca²⁺</td>
<td>1.0</td>
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<tr>
<td>Cu²⁺</td>
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</tr>
<tr>
<td>Mn²⁺</td>
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</tr>
<tr>
<td>Fe²⁺</td>
<td>0.63</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.49</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>1.15</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.81</td>
</tr>
</tbody>
</table>

Complete details can be found in a publication by Sylva et al. (2016) which is posted on the HNEI website.

Phase Equilibrium of Methane Hydrates in Porous Media

Calorimetric experiments were performed to test the hypothesis that the pressure-temperature phase boundaries of methane hydrate change when formation and dissociation occur in porous media. Two “standard” sands (designated as Toyoura and Ottawa) selected by the national methane hydrate R&D programs in Japan and the U.S. were employed in these experiments. The data suggest that a small shift in the phase boundary of hydrates might occur in porous media. The measured change is of the order of scatter in the experimental data but is consistent. Figure 3.1.1 shows an example of the measured change in the dissociation temperature of methane hydrate in Toyoura sand. For both tested sands, and over a range of pressures relevant to deep ocean
sediments, the phase boundary for a simple water-methane binary system tends to over-predict hydrate melting temperature.

Figure 3.1.1. Measured dissociation temperatures (DT) of methane hydrate formed in a Toyoura sand matrix. The blue solid line represents the phase boundary of pure methane hydrate (no sand).

Lower melting temperatures imply 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.

Complete details of these experiments can be found in the M.S. Plan B thesis report by Miyakita (2014) which is posted on the HNEI website.
Environmental Impacts of Methane Release from Hydrates

The goal of this focus area is to elucidate the mechanisms by which microbes control free methane gas levels in, and methane leakage from, the seafloor sediment and arctic permafrost; and generate and produce methane in the water column. While this goal is directly relevant to methane fuel production from naturally-occurring accumulations of hydrates, the results are also important to assessments of the environmental impacts of deep ocean oil spills--like the 2010 Deepwater Horizon incident--and marine and terrestrial waste disposal (e.g., near-shore organic runoff and deposition; dumping of dredged material; landfills).

In cooperation with the marine biogeochemistry group at NRL, we have collected sediment, pore water, and water column samples during research cruises in the Gulf of Mexico, off the North Slope of Alaska, and New Zealand. Molecular biology analyses have characterized the microbial assemblages in these samples and correlated these populations with methane levels and fluxes but, to date, isolation, incubation and culturing of the key benthic organisms (i.e., methanogens and methanotrophs) have been very difficult. As an alternative, a novel approach was devised to investigate critical microbial metabolic pathways using single cell techniques that comprise the following steps: first, identify Archaea within methane hydrate sediment samples collected during past research cruises using fluorescence and/or confocal microscopy. Using a laser tweezers, single cells are isolated for DNA amplification. Analysis of an ensemble of experiments could yield populations and metabolic mechanisms. Unfortunately, sediment pore water samples from previous oceanographic expeditions were not viable for this approach, so fresh samples were collected during a research cruise by NRL to the Chatham Rise offshore New Zealand.

Technical accomplishments included collecting microbiological samples from the Chatham Rise offshore New Zealand, and testing a novel approach to investigate the critical microbial metabolic pathways of methane production and consumption in the ocean sediment using single cell DNA amplification techniques.

Molecular biology analyses have characterized the microbial assemblages collected during previous oceanographic research cruises with NRL to various offshore sites, and correlated these populations with methane levels and fluxes. To date, however, isolation, incubation and culturing of the key benthic organisms (i.e., methanogens and methanotrophs) have been very difficult. As an alternative, we pursued a novel approach to investigate the critical microbial metabolic pathways using single cell DNA amplification techniques that comprises the following steps: first, Archaea was identified within methane hydrate sediment samples collected during past research cruises using fluorescence and/or confocal microscopy. Next, using laser tweezers, single cells are isolated for DNA amplification.

Analysis of the samples collected from the Chatham Rise exploration offshore New Zealand did not yield biologically rich sediments (Naval Research Laboratory, 2013). It was initially speculated that a previously massive release of methane had caused a benthic depression resulting
in a bathymetric “pockmark.” Sixteen samples that had been collected from this exploration were analyzed at the University of Hawaii Biological Electron Microscopy Facility (http://www5.pbrc.hawaii.edu/bemf/) using SEM and EDS. From this analysis, it was determined that the majority of the samples had a mostly inorganic composition with little to no carbon as seen in Figure 3.1.2.

A limitation of the single cell isolation technique is that random cells are selected, and identification can only occur after sequencing is performed. To determine if the targeted microorganisms are minimally present within the samples, Fluorescent In-Situ Hybridization (FISH) was attempted. As a control, nearshore brackish water sediments was used with a Marker Gene Technologies Cy3 fluorescent in-situ hybridization kit and Archaea and methanotroph specific oligonucleotide probes applied (Bourne et al. 2000; Jupraputtasri et al. 2005). An Olympus BX-43 microscope with fluorescence capability having Cy3 filters was used for visualization. Weak fluorescence was observed using this methodology, suggesting its utility prior to single cell isolation. An observed limitation that was the presence of background fluorescence due to non-specific adsorption onto micrometer sized sediment.

Although the sediments had a low organic composition, single cell isolation was performed using a Zeiss PALM laser and optical tweezer system. Many cells were isolated and amplified using 16rDNA targets or Archaea primers, dependent upon the depth of the sediment sample, and an illustra Single Cell GenomiPhi DNA Amplification Kit. Target microorganisms that include Archaea and methanotrophic bacteria were not identified.
Figure 3.1.2. SEM (a) and EDS (b) analysis of a Chatham Rise sample; piston core #9, sample 496, 175cm below sea floor surface. Replicate analysis across the sample yields either an absence or low carbon presence.

Hydrate Engineering Applications

Numerous attempts to develop practicable hydrate desalination systems have been pursued in the past with limited success. Hydrate desalination takes advantage of the exclusion of dissolved salts during the crystallization process. This same property can be exploited to selectively filter mixtures of gases (comprising both hydrate formers and non-formers) or to remove chemical and biological contaminants from aqueous solutions. As part of an undergraduate research project, we have provided mentoring, technical support, and access to our facilities to a student investigating hydrate desalination. An additional component of his study is to assess the degree of removal of biological contaminants from a water sample. For APRISES FY12, we completed this ongoing study and the results constitute the basis of the student’s senior Honors Thesis in Global Environmental Science.

As part of an undergraduate research project, we provided mentoring, technical support, and access
to our facilities to a student investigating hydrate desalination. An additional component of his study was to assess the degree of removal of biological contaminants from a water sample.

Experiments were performed to assess the feasibility and effectiveness of using hydrates as a method to purify water. While these experiments demonstrated that hydrates will remove a portion of the dissolved salts in seawater and, to a much lesser extent, certain biocontaminants from fresh water, the effectiveness of the process could not be accurately quantified due to a lack of repeatability in the measured data.

Key accomplishments and conclusions of the student’s research included:

- An experimental facility and test protocols were developed to investigate hydrate desalinization and removal of biological contaminants.
- Hydrates were successfully formed from water contaminated with salt and bovine serum albumin (which was used as a benign proxy for biological pathogens).
- Hydrates were more effective at purifying a saline solution than a solution that contained albumin.
- Trapping of contaminants within the non-uniform, collected hydrate samples significantly impacts the effectiveness of using hydrates to purify the solution.
- Based on the demonstrated potential for hydrates to reduce the level of salt in a solution, hydrates could be used as a first step process for integrated desalination systems based on reverse osmosis or multi-stage flash distillation. This will allow the subsequent steps to reduce their energy requirements.
- Suggested future work includes an investigation which clarifies why the hydrate was more effective at purifying the saline solution than the solution that contained albumin. This may help to determine if hydrates can be used to purify biologically-contaminated water. Another experiment to consider is whether the temperature and pressure conditions affect the rate of hydrate formation, and consequently, the amount of contaminants included in the hydrate lattice.

Complete details of these experiments can be found in the Senior Honors Thesis in Global Environmental Science at the University of Hawaii by Chinaka (2013). A copy of this thesis is posted on the HNEI website. (See Theses Resulting from these Efforts at the end of this subtask.)

**International Collaborative Research and Development**

Pursuant to the goal of promoting international R&D cooperation on methane hydrates, that was a cornerstone of the methane hydrate task of the previous HEET program proposal, HNEI provided support for and served as a member of the International Organizing Committee of the 9th
International Fiery Ice Workshop on methane hydrates in 2014. The 9th International Workshop on Methane Hydrate R&D was held in Hyderabad, India on 9-12 November 2014. HNEI served on the organizing committee and as a sponsor for this (and previous) workshops. The 9th Workshop was attended by 106 scientists, engineers, and other stakeholders. The workshop comprised two keynote lectures, 10 national reports, six breakout sessions and 46 individual research presentations consisting of 16 oral and 30 poster presentations. The Final Workshop Report is available online at http://www.igu.in/19-3/12report.pdf and is also posted on the HNEI website.

Publications and Presentations


Theses Resulting from these Efforts


References


3.2 Technology for Synthetic Fuels Production


3.2a Hydrogen Production for Fuel Cell Applications

Under previous phases of APRises, waste materials representative of streams generated at contingency bases were characterized for reactivity in steam and inert environments to inform design of appropriate-scale, hydrogen production systems [1]. These data reflect the reactivity of the organic fraction of the waste stream, but the inorganic fraction (i.e. ash) may play an important role in determining maintenance requirements and associated costs. Under the current phase, components of the contingency base waste streams with high ash contents as identified in Table 5 of Cui and Turn [1] were prepared and analyzed for elemental composition using x-ray fluorescence. These components included cardboard, white paper, food trays, food waste (dog food), high density polyethylene, polyvinyl chloride, low density polyethylene, wood, rubber, and textiles. Results of the analysis are reported. Under other funding, future analysis will report the potential impacts of the composite ash fraction under temperatures typical of hydrogen production systems.

Samples of the materials identified in Tables 3.2a.1 and 3.2a.2 were air dried to <10 wt% moisture and ground until the entire sample passed through a 200 µm sieve. Two particle size reduction techniques were used. A Retsch Ultra Centrifugal Mill ZM200 was used for materials with structural integrity and resistance to moderate heating. For materials that were heat sensitive or lacked structural integrity, a Retsch Cryogenic mill was employed. Pellets were made using 8.0 g (±0.1 g) of sample mixed with 2.0 g (±0.1 g) of Hoechst Wax C powder (Bruker AXS, bis-stearoyl-ethylendiamin, C_{38}H_{76}N_{2}O_{2}, grain size approximately <10 µm) as binder. The mixture was pressed in a 40 mm bore steel die in a manually operated hydraulic press (Herzog, TP20). Pressure was applied until the reading was stable at 20 ton, and then held for 10 s. At least two pellets were made from each sample for analysis by x-ray fluorescence (XRF). Each pellet was analyzed twice, once on each side.

During previous studies of the XRF instrument it was found that for routine analysis of biomass it is sufficient to analyze each sample twice (once on each side of the pellet) [2, 3]. This approach typically results in relative systematic error (bias or trueness) less than ±20% for elements in the range 25 to 100 ppm, less than ±15% for the range 100 to 1000 ppm and less than ±10% for
concentrations above 1000 ppm. The relative precision (measured as the relative standard error) was often less than ±5%, typically ±1–2% for concentrations >25 ppm.

The XRF analysis was done on a wavelength-dispersive (WD) XRF spectrometer (S8 Tiger from Bruker AXS) with a 4 kW water-cooled X-ray tube with Rh anode, 75 μm Be window, and 60 kV maximum acceleration voltage. Spectrum recording and evaluation was performed with the precalibrated / standardless software Quant-Express (Bruker AXS, delivered with the XRF instrument) intended for analysis of approximately 70 elements from F to U. The instrument and method have been described in detail elsewhere [2, 3]. Blank runs of pellets produced of 10 g Hoechst Wax C showed the following concentrations: Cl, 81 ppm; Ru, 34 ppm; Cu, 9 ppm; Fe, Zn, 6 ppm; and Ni, 5 ppm.

XRF detection and quantification limits vary by element [2, 3], and values are provided in the results section. Elements present at concentration of less than 25 ppm can have significant bias when examined by XRF as shown previously [2, 3]. For example, Cu is known to be overestimated by ~9 ppm or as CuO by ~12 ppm, whereas chlorine is typically underestimated by ~30%. In general, results for elements with concentrations less than 25 ppm (or ~40 ppm as oxides), or levels which are close to the detection limit, should be interpreted with caution.

In this study, quantitative results are reported for: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, and Sr. These elements can be measured quantitatively via XRF as demonstrated in previous calibration studies [2, 3]. The results presented herein also include Zr, Mo, Ru, Pd, and Ag, however, it has not been demonstrated that these elements can be reliably quantified by XRF due to a lack of certified values for these element in the CSRM's used in our previous studies [2, 3].

The method used to analyze the pellets automatically corrects for the 20% wax binder present. However, the composition of the organic part of the sample is not calculated in the iterative process. Instead, the method requires that the empirical chemical formula \((\text{C}_x\text{H}_y\text{O}_z\text{N}_q)\) of the organic matrix is specified by the user based on estimates or actual data from organic elemental analysis of the sample. The specified fixed formula for the organic matrix is incorporated, and the mass fraction of the organic matrix is then calculated in the iterative process. As demonstrated elsewhere, pure cellulose \((\text{C}_6\text{H}_{10}\text{O}_5)\) can be used as the default composition of the organic matrix for biomass which gives results essentially indifferent from using the empirical formula of the actual biomass samples [2, 3].

Results of the analysis of contingency base waste samples are presented in Tables 3.2a.1 and 3.2a.2. Elements present at concentrations greater than 0.1% in at least one of the parent materials include Ca, Ti, Mg, Si, Al, S, Na, P, Cl, and K. The inorganic elemental analysis presented here coupled with the composition of C, H, O, and N in the organic matrix reported by Cui and Turn [1] and the waste stream recipes described by Margolin et al. [4] and Ruppert et al. [5] will provide
the data necessary to conduct thermochemical equilibrium analysis of contingency base waste across a range of operating conditions representative of hydrogen production systems. These analyses will inform system design and waste sorting strategies to improve system performance. Results of the thermochemical equilibrium analysis of contingency base waste will be conducted under future phases of APRISES.
Table 3.2a.1. X-ray fluorescence (XRF) analysis of plastics. Labeling corresponds to Table 3 in Hong and Cui [1], polyvinyl chloride (PVC), high density polyethylene (HDPE), low density polyethylene (LDPE), polystyrene (PS), and other (compact disc).

<table>
<thead>
<tr>
<th>Properties</th>
<th># 4-3 PVC</th>
<th># 4-2 HDPE</th>
<th>#4-4 LDPE</th>
<th>#4-6-1 PS</th>
<th>#4-7 Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (12) /ppm</td>
<td>28.2 ± 69.0</td>
<td>0.0 ± 0.0</td>
<td>1,250.0 ± 67.8</td>
<td>0.0 ± 0.0</td>
<td>396.0 ± 69.5</td>
</tr>
<tr>
<td>Al (13) /ppm</td>
<td>54.5 ± 59.8</td>
<td>0.0 ± 0.0</td>
<td>310.8 ± 49.5</td>
<td>14.0 ± 28.0</td>
<td>7.3 ± 17.8</td>
</tr>
<tr>
<td>Si (14) /ppm</td>
<td>104.3 ± 51.2</td>
<td>84.1 ± 67.3</td>
<td>1,740.0 ± 61.6</td>
<td>7.4 ± 14.7</td>
<td>536.5 ± 85.3</td>
</tr>
<tr>
<td>S (16) /ppm</td>
<td>891.67 ± 42.38</td>
<td>0.0 ± 0.0</td>
<td>225.0 ± 8.83</td>
<td>10.5 ± 7.1</td>
<td>25.3 ± 13.1</td>
</tr>
<tr>
<td>Cl (17) /ppm</td>
<td>N/A a</td>
<td>0.0 ± 0.0</td>
<td>113.3 ± 76.7</td>
<td>11.4 ± 22.8</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>K (19) /ppm</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>105.1 ± 13.4</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Ca (20) /ppm</td>
<td>24,916.7 ± 1,130.3</td>
<td>14.0 ± 16.9</td>
<td>65,650.0 ± 1,396.4</td>
<td>948.5 ± 45.6</td>
<td>317.7 ± 30.9</td>
</tr>
<tr>
<td>Ti (22) /ppm</td>
<td>7,121.7 ± 278.4</td>
<td>0.0 ± 0.0</td>
<td>2,585.0 ± 44.4</td>
<td>2,050.0 ± 87.2</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Fe (26) /ppm</td>
<td>391.5 ± 55.8</td>
<td>20.8 ± 4.8</td>
<td>179.8 ± 8.6</td>
<td>22.3 ± 2.6</td>
<td>36.2 ± 2.7</td>
</tr>
<tr>
<td>Zn (30) /ppm</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>154.5 ± 1.3</td>
<td>84.1 ± 2.1</td>
<td>1.6 ± 3.9</td>
</tr>
<tr>
<td>Ru (44) /ppm</td>
<td>0.0 ± 0.0</td>
<td>88.8 ± 8.9</td>
<td>60.4 ± 40.8</td>
<td>24.3 ± 17.0</td>
<td>30.3 ± 33.6</td>
</tr>
<tr>
<td>Ag (47) /ppm</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>98.8 ± 50.0</td>
</tr>
<tr>
<td>XRF Ash% wt</td>
<td>4.95 ± 0.27</td>
<td>0.04 ± 0.02</td>
<td>10.69 ± 0.29</td>
<td>0.50 ± 0.04</td>
<td>0.15 ± 0.04</td>
</tr>
<tr>
<td>Ash % wt (Ref [1])</td>
<td>8.7</td>
<td>0.9</td>
<td>13.4</td>
<td>0.3</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Note: a. PVC matrix used is C2H3Cl and the element in the table doesn’t include chlorine


Table 3.2a.2. XRF analysis of other waste materials.

<table>
<thead>
<tr>
<th>Properties</th>
<th>White paper</th>
<th>Food tray</th>
<th>Cardboard</th>
<th>Dog food</th>
<th>Wood</th>
<th>Textile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (11) /ppm</td>
<td>755.3 ± 54.5</td>
<td>326.2 ± 87.3</td>
<td>960.5 ± 97.9</td>
<td>2,035.0 ± 241.6</td>
<td>0.0 ± 0.0</td>
<td>381.8 ± 73.6</td>
</tr>
<tr>
<td>Mg (12) /ppm</td>
<td>1,258.3 ± 46.2</td>
<td>194.2 ± 17.2</td>
<td>753.0 ± 69.3</td>
<td>725.3 ± 56.6</td>
<td>124.0 ± 20.1</td>
<td>58.9 ± 40.9</td>
</tr>
<tr>
<td>Al (13) /ppm</td>
<td>219.2 ± 31.9</td>
<td>820.7 ± 75.5</td>
<td>4,075.0 ± 176.0</td>
<td>25.7 ± 41.8</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Si (14) /ppm</td>
<td>1426.7 ± 52.8</td>
<td>901.3 ± 139.0</td>
<td>4,785.0 ± 177.5</td>
<td>260.5 ± 41.3</td>
<td>10.3 ± 20.1</td>
<td>100.5 ± 67.0</td>
</tr>
<tr>
<td>P (15) /ppm</td>
<td>38.18 ± 21.78</td>
<td>61.5 ± 13.7</td>
<td>69.4 ± 47.1</td>
<td>3,486.7 ± 100.5</td>
<td>85.5 ± 6.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>S (16) /ppm</td>
<td>1,181.7 ± 41.7</td>
<td>733.2 ± 31.3</td>
<td>1,277.5 ± 32.0</td>
<td>1,500.0 ± 71.6</td>
<td>42.7 ± 5.5</td>
<td>14.7 ± 17.0</td>
</tr>
<tr>
<td>K (19) /ppm</td>
<td>0.0 ± 0.0</td>
<td>10.5 ± 16.2</td>
<td>193.3 ± 10.8</td>
<td>7,220.0 ± 100.6</td>
<td>940.3 ± 42.2</td>
<td>163.0 ± 14.3</td>
</tr>
<tr>
<td>Ca (20) /ppm</td>
<td>59,266.7 ± 1,838.1</td>
<td>7,481.7 ± 53.1</td>
<td>10,375.0 ± 150.0</td>
<td>3,930.0 ± 122.0</td>
<td>440.5 ± 18.1</td>
<td>172.0 ± 10.5</td>
</tr>
<tr>
<td>Ti (22) /ppm</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>389.5 ± 37.5</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Mn (25) /ppm</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>36.9 ± 3.1</td>
<td>73.93 ± 4.45</td>
<td>48.0 ± 2.5</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Fe (26) /ppm</td>
<td>119.8 ± 7.2</td>
<td>41.4 ± 2.8</td>
<td>521.8 ± 113.6</td>
<td>222.2 ± 79.1</td>
<td>13.9 ± 9.3</td>
<td>37.5 ± 2.4</td>
</tr>
<tr>
<td>Cu (29) /ppm</td>
<td>0.0 ± 0.0</td>
<td>11.6 ± 1.6</td>
<td>21.5 ± 3.8</td>
<td>28.8 ± 1.9</td>
<td>4.1 ± 4.8</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Zn (30) /ppm</td>
<td>0.0 ± 0.0</td>
<td>2.8 ± 4.3</td>
<td>31.5 ± 2.9</td>
<td>136.0 ± 4.9</td>
<td>3.9 ± 4.5</td>
<td>4.6 ± 5.4</td>
</tr>
<tr>
<td>Sr (38) /ppm</td>
<td>41.1 ± 1.8</td>
<td>3.9 ± 4.3</td>
<td>15.3 ± 2.6</td>
<td>3.50 ± 3.85</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Zr (40) /ppm</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>3.2 ± 3.7</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Mo (42) /ppm</td>
<td>0.0 ± 0.0</td>
<td>7.7 ± 11.9</td>
<td>11.1 ± 13.0</td>
<td>3.6 ± 8.8</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Ru (44) /ppm</td>
<td>34.78 ± 19.9</td>
<td>39.2 ± 20.2</td>
<td>56.4 ± 4.1</td>
<td>24.0 ± 26.4</td>
<td>53.7 ± 12.9</td>
<td>15.2 ± 12.9</td>
</tr>
<tr>
<td>Pd (46) /ppm</td>
<td>0.0 ± 0.0</td>
<td>21.5 ± 34.7</td>
<td>13.5 ± 27.1</td>
<td>38.6 ± 30.4</td>
<td>18.5 ± 37.1</td>
<td>12.2 ± 24.3</td>
</tr>
<tr>
<td>XRF Ash% wt</td>
<td>6.44 ± 0.22</td>
<td>1.60 ± 0.08</td>
<td>4.07 ± 0.17</td>
<td>3.74 ± 0.15</td>
<td>0.25 ± 0.03</td>
<td>0.15 ± 0.04</td>
</tr>
<tr>
<td>Ash % wt (Ref [1])</td>
<td>11.0</td>
<td>3.7</td>
<td>4.7</td>
<td>7.2</td>
<td>0.3</td>
<td>2.2</td>
</tr>
</tbody>
</table>
References


3.2b Evaluation of Second Generation Biofuels

Hydroprocessed renewable diesel (HRD-76) and synthesized isoparaffin (SIP-76) have been produced in sufficient quantity for testing by the US Navy, and demonstrated as compatible replacements or blend stock with marine diesel (NATO F-76). Operational limitations with respect to the lubricity, seal swell and cold-flow properties, however, need to be addressed before operational use of 100% HRD-76 or SIP-76. Aromatics are known to improve seal swell and low-temperature characteristics. In this study, three commercial aromatic fluids (Aromatic 100, 150 and 200) produced from petroleum refining were added to HRD-76 and SIP-76 at various concentrations to investigate their impacts on the properties of the biofuel blend. The composition, hydrogen content and physicochemical properties of these aromatic fluids were determined according to ASTM methods and compared with that of HRD-76, SIP-76, and F-76. The seal-swell capability of the aromatic fluids and biofuel blends was investigated using nitrile O-rings, while the effects of aromatic fluids on fuel low-temperature quality were evaluated using differential scanning calorimetry. In addition, ASTM D5304 and D2274 tests were conducted to
investigate the impacts of adding aromatics to biofuels on long-term storage and oxidative stabilities. Although the composition and characteristics of these three aromatics fluids varied, all were capable of inducing o-ring seal swell and adjusting the density of biofuels without significantly affecting the biofuels’ stabilities. HRD-76 and aromatic fluid blends also exhibited liquid to solid phase transitions at lower temperatures and greater hydrophilicity than neat HRD-76.

Complete details can be found in the publication listed below.

**Publications**


**3.2c Novel Solvent Based Extraction from Biomass**

Under this subtask, HNEI completed an assessment of a bio-oil derived from a yeast process that utilizes sugar rich yeast extract to significantly improve the energy balance.

Growth on the recycled mixed glucose/xylose carbon substrate was successfully demonstrated with glucose consumed before xylose and overall cell mass to lipid yields (YP/X) between 57% and 61% was achieved (w/w relative to whole dried cell mass). Enzymatic hydrolysis of the delipified carbohydrate fraction recovered approximately 9%–11% (w/w) of the whole dried cell mass as fermentable sugars, which were successfully recycled as carbon sources without further purification. In total, up to 70% (w/w) of the whole dried cell mass was recovered as lipids and fermentable sugars, and the substrate to lipid yields (YP/S) was increased from 0.12 to 0.16 g lipid/g carbohydrate consumed.

In a prior funding year it was demonstrated that the application of ionic liquid based co-solvents to simultaneously extract lipids and pretreat the carbohydrate fraction of oil seed biomass (*jatropha* and *safflower* seeds) also successfully pretreated the biomass for further enzymatic hydrolysis of the carbohydrate fraction to fermentable sugars (Severa et al, 2014). As the spent (i.e. delipified) yeast cell mass contains glucose, mannose and other sugars that have been previously shown to be efficiently utilized by oleaginous yeast, the extraction system of Severa et al (2014) was applied to the lipid bearing red yeast *R. toruloides* to investigate whether fermentable sugars could be recovered and recycled. If successful the process could be used to reduce the total amount of fermentable sugars required for each new fermentation, thus creating an indirect route to increase the substrate to lipid yield (YP/S). The general concept is provided below in Figure 3.2c.1. The
use of recovered sugars should improve the yield of bio-oil recovered per amount of substrate (sugars) required to support growth. This has the effect of increasing the energy yield (i.e. energy out versus energy in).

![Diagram of biological processes](image)

Figure 3.2c.1. Pathways for the recovery of waste carbohydrate (A) and recycled fermentable sugars (B).

Since the growth media for batch two was dissolved in the recycled hydrolysis solution plus “make-up” deionized water, it was unclear if there were any background chemicals in the hydrolysis solution that would inhibit cell growth. To test this batch, fermentations were executed wherein recycle was and was not used. Figure 3.2c.2 below presents the biomass production and carbohydrate consumption by *R. toruloides* in two such batch fermentation studies. In batch one no recycle was used and the culture was grown entirely on defined media containing carbon in the form of glucose and xylose at a carbon to nitrogen ratio of 108. In batch two, the same defined media was used except that the sugars recovered from the delipified biomass (after bio-oil had been extracted using the novel extraction system) were used as a supplement to the defined media. Batch one (without recycle) reached a maximum cell mass density of approximately 9.1 (±0.2) gdw/L, a value comparable to previous reports performed under similar conditions using simple carbohydrate feeds such as glucose. As expected, *R. toruloides* consumed xylose only after glucose depletion, Figure 3.2c.1. The substrate to lipid yield (*Y_{PS}* ) for batch one was 0.12 ±0.07 (g lipid/g fermentable sugars consumed), Table 3.2c.1. This value is similar to those obtained for the growth of the oleaginous yeast *Lipomyces starkeyi* grown on glucose and mannose. Batch two produced qualitatively similar results. Both batch one (no recycle) and batch two (with recycle) achieved similar final cell mass densities (9.1 (±0.2) gdw/L for batch one versus 9.4 (±0.2) gdw/L for batch two) that are in line with previous reports. The biomass to lipid yields (*Y_{PX}* ) for batch one and two were also similar at approximately 60.5 (±1.5) and 57.4 (±0.3) % (% w/w, whole dried cell mass), respectively, and equivalent to those reported by others. For batch culture under similar conditions (∼ 56 % w/w, whole yeast), indicating that the batch culture conditions were appropriate for lipid
production. The substrate to lipid yield (Y_{PS}) in batch two significantly improved to 0.16 ± 0.07 (g lipid/g fermentable sugars consumed), verifying the use of delipified yeast hydrolysate as a source of recycled carbon to increase the substrate to lipid yield (Y_{PS}).

Figure 3.2c.2. Biomass production and carbohydrate consumption by *R. toruloides*: batch one (open symbols) and batch two (closed symbols). Circles: xylose; Squares: glucose; triangles: cell mass.

Table 3.2c.1: Batch fermentation data.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Cell mass</th>
<th>Cell mass fermentable sugars</th>
<th>Cell mass to lipid yield (Y_{PX})</th>
<th>Substrate to lipid yield (Y_{PS})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(gdw/L)</td>
<td>Glucose % (w/w)(^1)</td>
<td>Mannose % (w/w)(^1)</td>
<td>% (w/w)(^1)</td>
</tr>
<tr>
<td>1</td>
<td>9.1 (±0.2)</td>
<td>8.6 (±0.2)</td>
<td>0.9 (±0.1)</td>
<td>60.5 (±1.5)</td>
</tr>
<tr>
<td>2</td>
<td>9.4 (±0.2)</td>
<td>9.8 (±0.2)</td>
<td>1.4 (±0.1)</td>
<td>57.4 (±0.3)</td>
</tr>
</tbody>
</table>

\(^1\)Fermentable sugars are those recovered from hydrolysation reaction. Weight percent values are relative to freeze dried whole yeast.

\(^2\)The calculation of grams carbohydrate (i.e. fermentable sugars) consumed was made using the total amount of make-up sugars added as the starting concentration.

Estimating the cost savings associated with recycling is challenging given that bulk pricing for fermentable sugars (mixtures of glucose and xylose) derived from woody biomass are not currently available. Alternatively, the potential cost savings was approximated using glucose as the sole carbon source, Figure 3.2c.2. For a process producing 10,000 kg of lipids, 83,333 kg are consumed
without recycle ($Y_{PS} = 0.12 \text{ g/g}$, Table 3.2c.1). With recycle ($Y_{PS} = 0.16 \text{ g/g}$, Table 3.2c.1) only 62,500 kg are consumed. Using a bulk price of glucose between $1,100-1,200 per metric ton yields a feedstock cost savings of $25,000 (or $2.50 per kg of lipid). Clearly, the benefit of these savings must be levied against costs to process the carbohydrate fraction into fermentable sugars using ionic liquid pretreatment followed by enzymatic hydrolysis. While these costs are significant, one potential scenario is to integrate this into a production process that already applies ionic liquids to pretreat woody biomass to recover fermentable sugars. In this scenario the technology to treat and recover fermentable sugars from high cell density cultures of lipid bearing microorganisms would already be in place.

### Table 3.2c.2: Scale up analysis using recycle of carbohydrate fermentable sugars.

<table>
<thead>
<tr>
<th>Mass feed carbohydrate (kg)</th>
<th>X (gdw/L$^1$)</th>
<th>Volume (L)</th>
<th>Lipid Yield (g/g)$^2$</th>
<th>Mass biomass produced (kg)</th>
<th>Mass lipid recovered (kg)</th>
<th>Mass carbohydrate recovered (kg)</th>
<th>Mass carbohydrate in makeup (kg)</th>
<th>Savings ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fed-Batch w/o recycle</td>
<td>2.145</td>
<td>80</td>
<td>10,000</td>
<td>0.22</td>
<td>800</td>
<td>472</td>
<td>0</td>
<td>2.145</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Fed-Batch with recycle</td>
<td>2.145</td>
<td>80</td>
<td>10,000</td>
<td>0.24$^3$</td>
<td>800</td>
<td>472</td>
<td>192</td>
<td>1,953</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$1,632^4$</td>
</tr>
</tbody>
</table>

$^1$Optimized biomass density and lipid to carbohydrate consumed yield on from the literature were used [3].

$^2$Lipid Yield (g lipid/ g carbohydrate consumed) of fed batch w/o recycle was taken from literature and the yield of fed batch with recycle was calculated based on the amount of carbohydrate in make-up.

$^3$The R. toruloides yeast was assumed to be composed of 60 % lipids, 24 % carbohydrates, 3 % ash and 14 % proteins.

$^4$The savings are calculated based on difference in quantity of processed carbohydrate used in fed batch w/o recycle and fed batch with recycle multiplied by the cost of processed carbohydrates. The cost of processed carbohydrates (glucose or mannose) was assumed to be $8.50/ kg based on market price for 25 kg of glucose.

Results were published as listed below, and are available on the HNEI website.

### Publications and Presentations

**Peer Reviewed Publications**


*Presentations*


### 3.2d Liquid Fuels from Synthesis Gas

The aim of this task was to develop a new technology to produce liquid fuels from syngas (H\(_2\), CO, and CO\(_2\)). The process consists of two steps: (1) formation of polyhydroxybutyrate (PHB) by a chemoautotrophic bacterium from the gas substrates, and (2) conversion of PHB into liquid fuels. Because of very low solubility of the gas substrates in an aqueous mineral solution, the microbial cell density and productivity of gas fermentation depend on the gas mass transfer rate. In this work, a novel bioreactor was designed, built and operated for gas fermentation enhancement under a raised gas pressure. In previous research, a liquid oil was formed via PHB methanolysis, but the energy content was relatively low because of a high oxygen content of the oil. In this work, catalytic deoxygenation of PHB was investigated to make a hydrocarbon oil of low oxygen content.

The **novel bioreactor** was built with a stainless steel vessel (10 cm diameter, 4 liters, 20 atm work pressure) as shown in Figure 3.2d.1. An external liquid circulation loop was connected with stainless steel tubing, including a stainless steel magnetic drive pump (13.8 atm maximum pressure) and an in-line pH probe (10 atm maximum pressure). The parts were purchased from Cole Parmer (Vernon Hills, IL).
An aqueous mineral solution was circulated via the loop and sprayed into full cone plumes (90°) through three nozzles (BETE Fog Nozzle, Greenfield, MA) with a total open area of 0.1 cm². The mineral solution composition and other experimental conditions can be found in reference [1]. At a circulation rate of 3 L min⁻¹, the liquid in the bioreactor was mixed very well and the tiny liquid droplets provided good gas/liquid contact. The gas volumetric mass transfer coefficient reached ca. 250 h⁻¹. The water droplets also prevented the gas mixture from possible ignition when the gas composition was in the flammable range of H₂. The solution pH was controlled by an integrated pH controller (Etatron DLX/B series, 15 atm, Cole-Parmer, IL) with a base solution (5 wt% ammonium). The fermentation was conducted in an air-conditioned room (ca. 25 °C). The flow rates of individual gases from the cylinders were controlled with mass flow meters at predetermined standard cm⁻³ min⁻¹ (sccm at 0 °C, 1 atm), from which the total gas flow rate and inlet gas composition were determined. The operation pressure in the bioreactor was kept at a predetermined level by using a backpressure regulator (BPR) that was controlled with nitrogen pressure. When the gas pressure in the bioreactor was higher than the preset (nitrogen) pressure,
gas was discharged and the exhaust gas was sampled with a plastic bag for composition analysis. The discharged gas flow rate was measured with a soap film meter under ambient conditions (ca. 25 °C, 1 atm). The H₂-rich exhaust gas went to fume hood through vent tubing and was immediately diluted below its lower flammable level (4 % vol). The tightness of the bioreactor system was tested by using air up to 6 atm and the gas fermentation was conducted below 5 atm absolute.

A gas fermentation was started by adding an inoculum of *Cupriavidus necator* into 1.5 L mineral solution. Figure 3.2d.2 is the time courses of cell density (dry cell mass concentration) under 1 atm absolute pressure (Run A) and 4 atm absolute pressure (Run B), respectively. The specific growth rates were calculated by using a linear correlation of natural logarithm of cell density versus time and listed in Table 3.2d.1. Specifically, two growth stages and rates were observed during fermentation as indicated by a critical cell density (X<sub>cr</sub>). Under 1 atm gas pressure, the critical cell density was ca. 4.5 g L⁻¹, where the specific growth rate dropped from 0.094 h⁻¹ to 0.011 h⁻¹. Under 4 atm gas pressure, the critical cell density was ca. 6.3 g L⁻¹, where the specific growth rate declined from 0.12 h⁻¹ to 0.01 h⁻¹. The linear correlations in each stage exhibited quite high coefficients of determination (R²) as shown in Table 3.2d.1. The two growth stages can be recognized easily under 4 atm (Figure 3.2d.2). In about 100 hours, the dry cell mass concentration under 4 atm reached 18 g L⁻¹ and started to decline, probably because of depletion of growth nutrients. This was confirmed by Run C in which the cell mass at the end of Run B was recovered with centrifugation and re-suspended in a fresh medium solution containing doubled amounts of ferric ammonium citrate (0.2 g L⁻¹) and MgSO₄·7H₂O (1 g L⁻¹). As shown in Figure 3.2d.2, the cell density was 11.7 g L⁻¹ at the beginning and increased almost linearly with time. Because of the high initial cell density, only one low growth rate (0.0074 h⁻¹) was observed throughout the gas fermentation (Table 3.2d.1, Run C).

The high operation pressure in the bioreactor significantly enhanced gas fermentation. The growth rate was increased from 0.094 h⁻¹ to 0.12 h⁻¹ when the operation pressure was raised from 1 atm to 4 atm. The numbers imply that the chemolithotrophic growth under 1 atm was to some extent restricted by gas substrates. When the cell density reached a critical level (X<sub>cr</sub> 4.5 g L⁻¹), the dissolved concentration of one gas such as O₂ first declined below a critical level and the gas became the limiting substrate. After that, the cell growth rate was reduced to and maintained at a quite low level (0.01 h⁻¹) because of the limitation of the gas substrate. Under a high pressure (4 atm), the solubility of gas was increased to support a higher critical cell density (X<sub>cr</sub> 6.3 g L⁻¹). The result shows that about 40% more cell mass was formed under the conditions of sufficient gas substrates because of the raised pressure. Once the critical cell density was reached, however, the specific growth rates dropped to the same low level (0.01 h⁻¹). The slow chemolithotrophic growth was attributed to gas limitation as well as the energy consumption for cell maintenance. This was confirmed by using an inoculum of very high cell density under which the gas became limited right at the beginning and no high growth rate was observed throughout the gas fermentation.
Table 3.2d.1. Effect of gas pressure on cell growth rate.

<table>
<thead>
<tr>
<th>Run</th>
<th>( P_a ) (atm)</th>
<th>FeMg</th>
<th>( X_0 ) ( \text{c} )</th>
<th>( X_{cr} ) ( \text{d} )</th>
<th>High rate</th>
<th>Low rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(g L(^{-1}))</td>
<td>(g L(^{-1}))</td>
<td>( \mu ) ( \text{e} )</td>
<td>( \mu ) ( \text{e} )</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>4.5</td>
<td>0.094</td>
<td>0.960</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.011</td>
<td>0.975</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>1</td>
<td>0.45</td>
<td>6.3</td>
<td>0.12</td>
<td>0.976</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.010</td>
<td>0.954</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>2</td>
<td>11.7</td>
<td>None</td>
<td></td>
<td>0.0074</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.969</td>
<td></td>
</tr>
</tbody>
</table>

a. The absolute gas pressure in bioreactor; b. Concentrations of Fe and Mg: (1) ferric ammonium citrate 0.1 g L\(^{-1}\), MgSO\(_4\) \( \cdot \) 7H\(_2\)O 0.5 g L\(^{-1}\), and (2) ferric ammonium citrate 0.2 g L\(^{-1}\), MgSO\(_4\) \( \cdot \) 7H\(_2\)O 1 g L\(^{-1}\); c. The initial cell density or dry cell mass concentration; d. A critical cell density between a high growth stage and a slow growth stage; e. The specific growth rate \( \mu \) is the slope of linear correlation: \( \ln (X/X_0) = \mu t \). \( R^2 \) value is a statistical measure of how close the data are to the regression model.
In the gas fermentations above (Table 3.2d.1), 1.5 L of mineral solution was gassed by a constant gas stream at 140 sccm or 0.093 vvm (gas volume per liquid volume per min). In contrast to a high gassing rate (1-2 vvm) used in conventional bioreactors, a low gassing rate (<0.1 vvm) resulted in a low gas discharge rate, and hence low H₂ waste. The exhaust gas flow rate was measured under room conditions (25 °C, 1 atm) and converted into sccm under the standard conditions (0 °C, 1 atm). Figure 3.2d.3 shows the gas uptake rates, i.e. the difference between the inlet and outlet gas flow rates, by the microbes in 1 L medium solution. Under 1 atm gas pressure, the gas uptake rate increased with time (i.e. cell density), and reached a plateau around 50 sccm L⁻¹. The number indicates that about 54 vol% of the inlet gas was absorbed and utilized by the microbes. Under 4 atm gas pressure, the gas uptake rate increased with time much faster, approaching a higher plateau around 70 sccm L⁻¹. The number indicates that about 75 vol% of the inlet gas was absorbed and utilized by the microbes. With an inoculum of very high cell density, the gas uptake rate under 4 atm gas pressure started at ca. 55 sccm L⁻¹ and increased to a plateau around 80 sccm L⁻¹. It indicates that about 86 vol% of the inlet gas was absorbed and utilized by the microbes. Table 3.2d.2 gives the gas uptake rates and gas compositions at the end of fermentations, from which the uptake rates of individual gases at the quasi steady state are calculated.

![Figure 3.2d.3. Gas uptake rates by C. necator under different gas pressures (1 atm and 4 atm). See Table 3.2d.1 for the fermentation conditions and the concentrations of Fe and Mg. The amounts of Fe and Mg were doubled in one fermentation (4atm_FeMg).](image-url)
Table 3.2d.2. The inlet and outlet gas flow rates and gas compositions at the end of fermentations.

<table>
<thead>
<tr>
<th>Run</th>
<th>Inlet Gas</th>
<th>Outlet Gas</th>
<th>Uptake Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$F_{in}^a$</td>
<td>$H_2 (^v %)$</td>
<td>$O_2 (^v %)$</td>
</tr>
<tr>
<td>A</td>
<td>140</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>140</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>140</td>
<td>70</td>
<td>20</td>
</tr>
</tbody>
</table>

*a. See Table 3.2d.1 for the operation conditions; b. Gas flow rate (cm³ min⁻¹) under standard conditions (273 K, 1 atm) and gas composition in volume % (= mole %).

Obviously, the microbial gas uptake rate was increased under the high pressure because of the enhanced gas mass transfer rate. At the end of gas fermentations, ca. 80 vol % of inlet gas was taken up by microbes under 4 atm while about 50% of the inlet gas was consumed under 1 atm (Table 3.2d.2). Interestingly, the same CO₂ uptake rate (11.4–11.9 sccm or ca. 0.5 mmole min⁻¹) was observed at the quasi-steady state under both low and high pressures. This was in line with the same low specific growth rate under the gas limitation as shown above.

Crotonic acid is a possible key intermediate in the catalytic deoxygenation of PHB. In one experiment, 0.5 g PHB or crotonic acid and 10 mL of H₃PO₄ solution were put into a 20 mL polytetrafluoroethylene (PTFE) reactor (Par Instrument, IL). The reactor was purged with N₂ gas and then heated in a thermostat oven that was preheated and maintained at 220 °C. After a predetermined time, the reactor was quickly cooled down in tap water. The reaction solution consisted of a top layer of oily products and a bottom layer of aqueous phosphoric acid solution. The oil was recovered by extraction with methylene chloride and the water moisture of solvent solution was removed with anhydrous magnesium sulfate. After evaporation of methylene chloride at 40 °C, the oil was weighted to calculate the yield based on the initial amount of PHB or crotonic acid. More information on materials and methods can be found in reference [2]. The oils produced under typical reaction conditions (100 wt% H₃PO₄, 220 °C, 3 hours) were analyzed with ¹³C-NMR (Figure 3.2d.4), FTIR (Figure 3.2d.5) and GC-MS (Figures 3.2d.6, 3.2d.7), respectively. The results show that almost same oil products were produced from crotonic acid or PHB.
Figure 3.2d. (A) $^{13}$C-NMR spectra of PHB (black) and PHB-derived oil (blue), and (B) $^{13}$C-NMR spectra of crotonic acid (black) and crotonic acid-derived oil (blue). The structural formula of PHB and crotonic acid are also presented.
Figure 3.2d.5. FTIR spectra of crotonic acid (black), PHB (red), crotonic acid-derived oil (blue) and PHB derived oil (pink).

Figure 3.2d.6. GC-MS chromatograms of PHB-derived oil (A) and crotonic acid-derived oil (B).
The chemical formula of PHB and crotonic acid are $[-\text{OCH(CH}_3\text{)CH}_2\text{CO-}]_n$ and CH$_3$CH=CHCOOH, respectively. The carbonyl (C=O) and carboxyl (COO) groups are the major oxygen-containing groups. Comparing the $^{13}$C-NMR spectra of PHB and crotonic acid with the spectra of the oil products reveals that the oxygen-containing groups were almost completely removed (Figure 3.2d.4), and aromatic, alkene and alkane groups were formed in the oily compounds. This was confirmed with FTIR analysis (Figure 3.2d.5). The huge absorption peak of carbonyl group (C=O) at 1700 cm$^{-1}$ of crotonic acid and 1720 cm$^{-1}$ of PHB disappeared in the oil products. The absorption peaks (3100 to 2800 cm$^{-1}$, 1458 cm$^{-1}$, 1380 cm$^{-1}$, and 870 cm$^{-1}$) of oil compounds indicate the presence of methyl, methylene, and aromatic groups as the major groups. Similar composition of the oils was also confirmed with GC-MS analysis (Figure 3.2d.6). All the facts above indicate that crotonic acid is the key intermediate formed in the first step of PHB deoxygenation. The reaction routes and mechanisms will be further investigated under
The chemical compounds in the oils were identified with a NIST11 mass spectral data library as shown in Figure 3.2d.7. In addition to the main compounds of alkenes and aromatics, a few aldehydes and ketones (retention times of 28.318, 30.614, 33.245, 33.710 and 40.909 in Figure 3.2d.7) were also detected by GC-MS analysis. All the analytical results consistently indicate that PHB was deoxygenated at a low temperature (220 °C) to form a hydrocarbon oil in one pot reaction.

In addition to the liquid oil, byproducts in the gas phase were also investigated. In one experiment, 3.6 g of PHB or crotonic acid and 72 mL of H₃PO₄ solution in a glass beaker was put in a 600 mL reactor (Parr Instrument, IL). The reactor was then purged with nitrogen to remove air (using at least ten times the reactor volume’s worth of nitrogen). The reactor was heated to a pre-determined temperature. After the reaction, the reactor was cooled down in ambient conditions and gas samples were taken with a FT-IR gas cell for qualitative analysis. The quantitative determination of gas byproducts was performed by using gas chromatography equipped with a thermal conductivity detector (GC-TCD, Varian Bruker 450-GC, FL) [2]. Figure 3.2d.8 is the FTIR spectra of gas products formed from crotonic acid and PHB, respectively. By comparing with the spectra of pure CO₂, CO and propylene C₃H₆, we found that the major gaseous product was CO₂ followed by propylene, with a negligible amount of CO. Therefore, PHB was deoxygenated primarily via decarboxylation (formation of CO₂), instead of decarbonylation (formation of CO). It should be pointed out that more oxygen was removed through decarboxylation than decarbonylation at the expense of one carbon. Decarboxylation has a higher efficiency than decarbonylation for PHB deoxygenation.
According to the complete decarboxylation of a PHB monomer or crotonic acid ($\text{C}_4\text{H}_6\text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{CO}_2$), the theoretical yield of $\text{CO}_2$ is 51.2 wt% of initial PHB. The detected $\text{CO}_2$ in gas phase accounted for 35.3 wt%, or 68.9 % of maximum yield. It implies that at least 68.9 % of oxygen in PHB was removed by decarboxylation. Some oxygen in PHB might also be removed by formation of water [2]. With crotonic acid, 70.8 wt% of oxygen was removed as $\text{CO}_2$ via decarboxylation. In deoxygenation of PHB or crotonic acid, propylene $\text{C}_3\text{H}_6$ was the major gaseous hydrocarbon [2]. As shown in Figure 3.2d.8, almost the same gas byproducts were produced from crotonic acid and PHA, respectively, providing additional evidence that crotonic acid is the key intermediate formed in the first step of PHB deoxygenation.
Phosphoric acid was the catalyst in PHB decarboxylation, and its concentration had a significant effect on oil yield under typical reaction conditions (220 °C, 3 hours) as shown in Figure 3.2d.9. In a solution of 50 wt% H₃PO₄, oil yield was only 5.4 wt% of PHB and crotonic acid was a major product [2]. With increase of H₃PO₄ concentration, the residual crotonic acid content decreased, and little crotonic acid was left in the 100 wt% H₃PO₄ or polyphosphoric acid. The PHB-derived oil yield increased from 5.4 wt% to 37.3 wt% corresponding to the increase of H₃PO₄ concentration from 50 wt% to 100 wt%. Little char (<2 wt%) was formed in these H₃PO₄ solutions. In polyphosphoric acid solution (115 wt% H₃PO₄), however, a substantial amount of char (55.5 wt%) was formed, and the oil yield declined to 5.2 wt% of initial PHB. Carbonization of PHB became the predominant reaction in polyphosphoric acid solution. A similar effect of phosphoric acid on crotonic acid was also observed (Figure 3.2d.9). We suspect that PHB carbonization occurred after its thermal degradation into crotonic acid based on our previous observation that crotonic acid was the key intermediate of PHB deoxygenation.

The concentration of H₃PO₄ also affected the composition of the PHB-derived oils as revealed by GC-MS analysis. Table 3.2d.3 gives the relative peak area (%) of the compounds identified by GC-MS analysis (Figures 3.2d.6 and 3.2d.7). Specifically, aromatics (benzene and naphthalene derivatives) were the main oil compounds in 100 wt% H₃PO₄, probably formed via ring condensation [3]. They became predominate in polyphosphoric acid solution. Formation of high C/H ratio hydrocarbons in high concentration of phosphoric acid was in agreement with our
previous observation on char formation in polyphosphoric acid. A few unsaturated ketones and aldehydes were detected by GC-MS, which might be produced together with CO₂ and water with phosphoric acid catalysis as reported in other studies [4]. The existence of unsaturated ketones and aldehydes implies a possible way of aromatics formation, which may involve some transient ketones and aldehydes via aldol condensation, dehydration and aromatization reactions [3-4]. In diluted phosphoric acid solutions (70-85 wt%), however, acyclic alkenes and alkanes or cycloalkenes and alkanes became the important compounds, indicating that aromatization reactions were to some extent inhibited by water, low phosphoric acid concentration or both. In 50 wt% H₃PO₄, the O-containing compounds were the main products, revealing that PHB deoxygenation was not completed in the presence of water.

Table 3.2d.3. Chemical profile of PHB-derived oil in different phosphoric acid solutions at 220 °C for 3 hours.

<table>
<thead>
<tr>
<th>H₃PO₄ (wt%)</th>
<th>O-containing compounds</th>
<th>Relative peak area (%) a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acyclic alkanes</td>
<td>Cycloalkanes</td>
</tr>
<tr>
<td>50</td>
<td>66.3</td>
<td>3.7</td>
</tr>
<tr>
<td>70</td>
<td>27.5</td>
<td>1.7</td>
</tr>
<tr>
<td>85</td>
<td>16.2</td>
<td>3.2</td>
</tr>
<tr>
<td>100</td>
<td>15.2</td>
<td>0.7</td>
</tr>
<tr>
<td>115</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

a. The chemical structures were identified with GC-MS and their relative peak areas were compared.

Table 3.2d.4 shows the effect of phosphoric acid concentration on the distribution of hydrocarbons according to their carbon numbers. In a general trend, high H₃PO₄ concentration favored formation of hydrocarbons with high carbon numbers. Specifically, the C4-C9 compounds were the main compounds in 50% H₃PO₄ solution while C10-C15 became the main compounds in 100% H₃PO₄ solution. Based on carbon numbers, the oil produced in 100% H₃PO₄ could be a ‘drop in’ diesel, which usually has the carbon numbers ranging from C10 to C22, with an average carbon number of 14 or 15. As shown in Table 3.2d.4, phosphoric acid concentration is an important process parameter in controlling oil yield, the extent of deoxygenation, and the composition of hydrocarbons. As a result, this new knowledge may be used to find a type of new solid phosphoric acid catalysts that are widely used in oil refining industry.
Table 3.2d.4. Carbon distribution of PHB-derived oil in different phosphoric acid solutions at 220 °C for 3 hours.

<table>
<thead>
<tr>
<th>H₃PO₄ (wt%)</th>
<th>Relative peak area (%) (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C4</td>
</tr>
<tr>
<td>50</td>
<td>12.1</td>
</tr>
<tr>
<td>70</td>
<td>5.5</td>
</tr>
<tr>
<td>85</td>
<td>0.8</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>115</td>
<td>0</td>
</tr>
</tbody>
</table>

a. The carbon numbers were identified with GC-MS analysis and their relative peak areas were compared.

More detail on the study can be found in the publications listed below, including those partially supported by the APRISES12 program. These publications are available on the HNEI website.
Publications and Presentations

Peer Reviewed Publications


Contributed Presentations


Patents and Technology Licensing

A Novel Bioreactor for High Efficiency Gas Utilization by Microbes

Inventor: P. Munasinghe and J. Yu

Invention disclosure UH ID No. 00958, October 23, 2013

US Provisional patent 62433748, December 13, 2016


PCT application 107502, December 2017.

References


### 3.2e Bio-contamination of Fuels

Metabolic processes and interactions that can be limited to decrease the impacts of bio-contamination in blended fuels were investigated, using a genomic and proteomic approach.

Blended diesel fuels contain trace amounts of glycerol, an undesirable byproduct associated with biodiesel production, and also sulfur compounds typically found in diesel. During APRISES 2011, it was determined that a *Burkholderia sp.*, in the presence of glycerol can enhance the metabolism of dibenzothiophene (DBT), a stable organosulfur compound found in diesel. This co-metabolic activity results in the favorable reduction of undesirable chemical components that are typically found within blended diesel. It was also observed that along with the enhanced metabolism the secretion of a rhamnolipid (RL), a biosurfactant, was significantly increased. The literature suggests that RL could be involved in cell transport and may increase the biodegradation of hydrophobic chemicals (Bai et al. 1997) such as petroleum or biodiesels.

During APRISES 2012 the role that the secreted RL have on DBT metabolism was further investigated. This information could provide insights into what metabolic processes can be limited to decrease the impacts from bio-contamination.

*Burkholderia sp.* C3 grown using glycerol and DBT was found to cometabolically degrade DBT, and also exhibited higher growth rates when compared with glycerol alone. The cometabolism results show up to an 18-fold increase in DBT biodegradation and a tripling in RL secretion. Inhibiting RL biosynthesis using 2-Bromohexanoic Acid (HEX) or 2-Bromoocatanoic Acid (OC) significantly reduced both the growth rate of C3 and also the biodegradation of DBT, up to 8 times. A multifactorial analysis showed RLs are a statistically significant factor (p-value < 0.01) for DBT degradation. Addition of RLs into cultures grown after removing glycerol resulted in a 1.8-fold increase of DBT biodegradation.

Due to their amphipathic chemistry, biosurfactants can interact with polycyclic aromatic hydrocarbons and at water-oil interfaces. By inhibiting metabolic processes that influence cellular uptake mechanisms, bio-inhibition methods could be developed for application with blended...
biofuels. In conclusion, it is clear that RLs have an important influence on the metabolic functions involved with the cellular uptake of polycyclic aromatic hydrocarbons during co-metabolism with glycerol.

_Moniliella wahieum_ Y12 genome sequencing and investigation of proteins that are expressed during biodiesel degradation was investigated. Determination of the metabolic pathways that are involved with biodiesel degradation is necessary for the development of inhibitors. The degradation of fatty acids in yeast is a complex pathway requiring an assortment of β-oxidation enzyme activities (Hiltunen _et al._ 2006). During APRISES 2012 a genomic and proteomic approach using the biodiesel contaminant, _Moniliella wahieum_ Y12, is used for these investigations.

For elucidation of the genes involved with fatty acid metabolism, a shot-gun sequencing approach was applied. The genome coverage from the sequence analysis was analyzed using BlastX for the determination of potential genes related with fatty acid metabolism. The limited annotation performed have already revealed numerous enzymatic esterase and lipase orthologs that are associated with β-oxidation.

A comparative proteomic investigation was also performed for the determination of gene expression associated with the metabolism of biodiesel. When compared with _M. wahieum_ Y12 grown on glucose 150 proteins were uniquely expressed. Under other funding, further investigations that show the relationship between genetic composition and the proteomic expression results will be performed, after more comprehensive genomic data is obtained. This will allow for a better understanding of the metabolic processes involved with the degradation of biodiesel. In conclusion, _M. wahieum_ Y12 was found to express 150 unique proteins when grown on biodiesel as the sole carbon source.

**References**


3.2f Biofuel Corrosion Control

The US Navy successfully [1] demonstrated the use of a 50 vol. % - 50 vol. % blend (50v:50v blend) of a traditional, petroleum-based F-76 diesel and an algae-derived hydrotreated renewable diesel (algal HRD-76) in warships. Renewable biodiesel is an alternative fuel produced from renewable resources, such as vegetable oils and animal fats. The conventional biodiesel is produced using a transesterification process and consists of fatty acid methyl esters (FAME), while the HRD is chemically not esters but consists mainly of paraffins, a composition similar to the conventional petroleum diesel.[2] The HRD has advantages over the FAME biodiesel in three major aspects. First, HRD has been hydrotreated to remove oxygen and is free of aromatics, leaving predominantly linear and branched chain hydrocarbons in the fuel. Second, the hydrop processing includes desulphurization reactions which result in a low-sulfur fuel (< 10 ppm wt) with very low greenhouse gas emissions.[3] Third, the hyd roprocessing technology produces no byproducts and can be used in existing refineries without any new investments.[4] One difference, however, is that the HRD-76 has a higher diffusion coefficient for oxygen than F-76 due to a lower dynamic viscosity.[5] The ranking from the highest to lowest diffusion coefficient for oxygen is HRD-76, HRD-76/F-76 (50v:50v blend), and F-76. During the operation of the warships, seawater is drawn into the carbon-steel fuel tanks to maintain balance as the fuel is consumed. Therefore, there is interest to determine if the HRD-76 fuel and its blends can cause unexpected corrosion damage in fuel-seawater mixtures. APRISES 11 focused on the measurement of corrosion rates and the identification of microbiological species in the seawater/fuel mixtures. APRISES 12 (this work) focuses on the identification of corrosion products formed on the corrosion coupons exposed in the seawater/fuel mixtures. APRISES 13 focused on the utilization of corrosion inhibitors to attenuate corrosion.

In the present work (APRIS E12), an in-depth analyses was conducted on the identification of corrosion products that formed on plain-carbon 1018 steel (UNS G10180) exposed in natural seawater/fuel mixtures of HRD-76, HRD-76/F-76 50v:50v blend, and F-76 for various time durations (i.e., 3 days, 10 days, 1 month, 6 months, and 1 year). The 1018 coupons were immersed in bottles with the bottom half of the sample in the seawater layer and the top half in the fuel layer. The 1018 steel has a composition which is within specifications for steels typically used for pipelines and storage vessels and tanks. Energy dispersive X-ray analyses (EDXA), X-ray diffraction (XRD), Raman spectroscopy, and FTIR spectroscopy were used to identify the corrosion products. To differentiate between abiotic electrochemical corrosion and
microbiologically influenced corrosion (MIC), various permutations of filtered and unfiltered fuel and seawater combinations were used as exposure medium. A 0.22 micron filter was used to filter the seawater and fuel. Both aerobic and anaerobic conditions were examined. There were two aerobic conditions: Filtered aerobic where a 0.22 micron filter prevented larger air-borne contaminants into the test bottles, and an open aerobic where airborne contaminants were allowed to enter the test bottles. The seawater was either natural, off-shore, surface water or synthetic according to ASTM International (ASTM) specifications. Hence, the test conditions were filtered-aerobic, aerobic, or anaerobic of the following seawater-fuel mixtures: 1) filtered seawater/filtered fuel, 2) filtered seawater/non-filtered fuel, 3) non-filtered seawater/filtered fuel, and 4) non-filtered seawater/non-filtered fuel conditions. The results on molecular identification of bacteria and fungi performed via 16S ribosomal ribonucleic acid (rRNA) and 18S rRNA sequencing was reported in APRISES 11.

Also reported in APRISES 11 was that corrosion rates of 1018 carbon steel were primarily driven by oxygen reduction and were highest in HRD-76, followed by the HRD-76/F-76 50v:50v blend, and then F-76, which corresponded to the similar ranking of oxygen diffusion coefficients (from highest to lowest): HRD-76, HRD-76/F-76 50v:50v blend, and F-76. On the 1018 corrosion coupons, the region of steel in the seawater layer was most severely corroded due to the high corrosivity induced by chlorides. The corrosion-rate results showed that abiotic corrosion dominated the corrosion damage and overshadowed any effects of MIC. In the fuel/water interface and water zones, rust formation showed an inner layer (black) identified as magnetite and an outer layer (red/yellow) identified as lepidocrocite and goethite. The amount of magnetite in the inner layer increased with increasing content of HRD-76 in the fuels. Hence, the highest amount of magnetite was observed for the coupons exposed to the HRD-76 followed by those in the HRD-76/F-76 50v:50v blend and least in the F-76. White precipitates identified as Mg(OH)$_2$ (magnesium hydroxide), MgO (magnesium oxide), Na$_2$CO$_3$ (sodium carbonate), Na$_2$CO$_3$.H$_2$O (thermonatrite), Na$_3$H(CO$_3$)$_2$(H$_2$O)$_2$ (trona), CaCO$_3$ (calcite and aragonite) formed in the fuel zone and were shown to be a consistent visual indicator for a high corrosion rate of steel. Precipitation was likely induced by a high amount of oxygen reduction (in the fuel layer) that generated OH$^-$, which precipitated the carbonates and hydroxides. The presence of the white precipitates was most abundant on the coupons exposed to the HRD-76 and to a lesser degree on those exposed to the HRD-76/F-76 50v:50v blend, which is consistent with higher rates of oxygen diffusion and hence corrosion in the HRD-76 fuel.

Hence, higher rates of corrosion and the precipitation of carbonates and hydroxides are likely to be expected with the utilization of algal HRD-76 fuel as a replacement for traditional petroleum-based F-76. For more information, see the conference paper listed below, (which also includes results from APRISES13).
Publications and Presentations


References


3.2g Waste Management

Research under other phases of APRISES developed constant volume carbonization (CVC) techniques to convert biomass materials into carbon-rich materials. With the ultimate goal of manufacturing charcoals with physical and chemical properties tailored to their end use, the present study provides a deeper understanding of the CVC process by elucidating the effect of various processing variables on char yields and properties.

In recent work under earlier phases of APRISES, constant volume carbonization product yields were determined together with charcoal proximate analysis and in some instances with higher heating values (HHV) and elemental analyses [1,2,3]. CVC experiments consistently approached theoretical fixed-carbon yields across a variety of processing conditions [1,2,3]. Although charcoals maintained fixed-carbon yields near theoretical values, chars suffered a more intense devolatilization and therefore presented improved fixed-carbon contents from (1) higher heat treatment temperatures (HTTs) (in a 300-400°C range) [2,3], (2) prolonged soaking times at carbonization temperature (from less than 30 minutes to almost 3 hours) [3], (3) smaller particle sizes (from <2 mm to <0.2 mm in tests at HTT of 300°C) [3] or (4) higher mass loadings (from
129 to 165 g/L in spruce CVC tests at 300°C) [3]. Among these factors, char devolatilization was especially sensitive to the carbonization temperature, while the mass loading had a lesser effect. An intriguing phenomenon was also observed on the char morphology when testing charcoals produced at higher temperatures and pressures. As conditions became more severe in the CVC reactor, the charcoal solid structure transformed from a particulate solid retaining the original biomass morphology to a coke-looking piece that had undergone a transient plastic phase (TPP) and had adopted the shape of the reaction vessel [2,3].

Additionally, a single charcoal derived from a pyrolysis experiment in a reactor with a valve slightly opened to the atmosphere was also produced for comparison to the charcoals manufactured in the constant-volume reactor. Results from proximate, elemental, and bomb calorimetry analysis of the chars are also presented.

A detailed description for the reactor—named the Wall Heated Tubing Bomb (WHTB)—and the experimental procedure employed for the CVC experiments is given elsewhere [3]. Different versions of the WHTB reactor are presented in reference [3] going from its original version to an upgraded version with roughly double the loading capacity of the original. All reactor designs conserved the fundamentals of the CVC process permitting carbonization in a sealed reactor at elevated temperatures and pressures. Evolution of the reactor design mainly relied on improvements in loading capacities, in safety equipment and in data measuring techniques. The present study made use of the original reactor for the earlier runs on oak pyrolysis (see reference [3] for reactor details) plus an upgraded (current) reactor for the later experiments on birch pyrolysis. The current WHTB design has an internal volume of ~0.22 L and permits CVC of ~30 g of spruce grains sized below 2 mm. The amount of biomass loaded in the reactor can be further increased by the use of feedstocks with higher packing density, for example ~50 g could be loaded when using the same-sized birch grains (<2 mm), or by the use of finer powder.

The current WHTB introduced slight modifications to the safety system compared to the one presented in reference [3]. One of the safety apparatus, the burst diaphragm, was replaced for a lighter and smaller model (LaMot) with a superior pressure rating of 21.3 MPa at 22 °C (vs. 16.20 MPa at 22°C) [3] which allowed the testing of more severe experimental conditions. The new burst diaphragm is within the allowable working pressure of the weakest part of the WHTB reactor, i.e. the reactor body rated at 16.24 MPa at 537°C, [3] plus pressure allowances permitted by the ASME B31.3 piping code. Under certain conditions, one is allowed to operate at 33% over the allowable working pressure for events that are not longer than 10 hours at any one time, nor more than 100 hours per year [4]. In a couple of experiments that tested the influence of the biomass loading, the WHTB was additionally modified by extending the amount of dead-volume in the reactor tubing –i.e. additional tubing was added to the top part of the reactor system.
The biomass feedstocks pyrolyzed in the present study consisted of oak, spruce, birch and cellulose. Each biomass specimen was subject to the following characterization in HNEI laboratories: moisture and proximate analysis by standards ASTM E872-82(2013) [5] and ASTM E830-87(1996) [6] on three samples per specimen, ultimate analysis by ASTM E777-17 [7], E775-15 [8] and E778-15 [9] on two samples per specimen and bomb calorimetry on one sample per specimen. See reference [3] for a detailed study on the uncertainties of each analytical technique.

Table 3.2g.1 displays the data collected from the HNEI characterization (moisture content, proximate analysis, ultimate analysis, and higher heating value) of the biomass feedstocks along with compositional data (cellulose, hemicellulose and lignin) taken from literature [10].
Table 3.2g.1. Moisture content, ultimate and proximate analysis, higher heating value, and structural composition (cellulose, hemicellulose and lignin) of spruce, birch, cellulose and oak feedstocks. Spruce and birch analytical results are replicated from reference [3].

<table>
<thead>
<tr>
<th></th>
<th>Spruce</th>
<th>Birch</th>
<th>Cellulose</th>
<th>Oak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>7.8</td>
<td>7.9</td>
<td>5.9</td>
<td>7.5</td>
</tr>
<tr>
<td>[wt.%, wet basis]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>46.93±0.05</td>
<td>47.4±0.3</td>
<td>41.9±0.1</td>
<td>45.4±0.1</td>
</tr>
<tr>
<td>H</td>
<td>6.26±0.02</td>
<td>6.32±0.03</td>
<td>6.3±0.1</td>
<td>6.1±0.1</td>
</tr>
<tr>
<td>O&lt;sup&gt;d&lt;/sup&gt;</td>
<td>46.3</td>
<td>45.43</td>
<td>51.7</td>
<td>47.1</td>
</tr>
<tr>
<td>N</td>
<td>0.20±0.02</td>
<td>0.20±0.02</td>
<td>0.08±0.04</td>
<td>0.215±0.002</td>
</tr>
<tr>
<td>S</td>
<td>0.011±0.001</td>
<td>0.0158±0.001</td>
<td>0.00</td>
<td>0.017±0.001</td>
</tr>
<tr>
<td>Ash&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.36±0.17</td>
<td>0.67±0.02</td>
<td>0.00</td>
<td>1.18±0.05</td>
</tr>
<tr>
<td>Ultimate Analysis&lt;sup&gt;a&lt;/sup&gt; [wt.%, dry basis]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fCC&lt;sup&gt;f&lt;/sup&gt;</td>
<td>14.8±0.1</td>
<td>13.1±0.2</td>
<td>6.0±0.2</td>
<td>14.0±0.7</td>
</tr>
<tr>
<td>VM&lt;sup&gt;g&lt;/sup&gt;</td>
<td>84.9±0.1</td>
<td>86.2±0.2</td>
<td>94.0±0.2</td>
<td>84.8±0.8</td>
</tr>
<tr>
<td>Ash</td>
<td>0.36±0.17</td>
<td>0.67±0.02</td>
<td>0.00</td>
<td>1.18±0.05</td>
</tr>
<tr>
<td>Proximate analysis&lt;sup&gt;b&lt;/sup&gt; [wt.%, dry basis]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Higher heating value [MJ/kg]</td>
<td>18.00</td>
<td>18.50</td>
<td>16.15</td>
<td>17.67</td>
</tr>
<tr>
<td>Contents of structural components&lt;sup&gt;c&lt;/sup&gt; [wt.%, dry-ash free basis]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>43.6, 47</td>
<td>50.2, 49.1</td>
<td>100</td>
<td>58.4</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>27.4, 25.3</td>
<td>32.8, 31.6</td>
<td>0.0</td>
<td>31.4</td>
</tr>
<tr>
<td>Lignin</td>
<td>29.0, 27.7</td>
<td>17.0, 19.3</td>
<td>0.0</td>
<td>10.2</td>
</tr>
<tr>
<td>Extractives</td>
<td>1.8, 2.5</td>
<td>3.0</td>
<td>0.0</td>
<td>NA&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Average of two analysis, uncertainty indicates range of values. Elemental analysis of cellulose closely resembles C 44.4%, H 6.2% and O 49.4% given by its formula (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>.

<sup>b</sup> Average of three analyses, uncertainty indicates standard deviation.

<sup>c</sup> Composition of structural components taken from [10].

<sup>d</sup> Oxygen by difference.

<sup>e</sup> Ash content determined by proximate analysis.

<sup>f</sup> Fixed-carbon content (fCC).

<sup>g</sup> Volatile matter content (VM).

<sup>h</sup> Not Available (NA).

Regarding characterization of the final pyrolytic products, non-condensable gases were subject to gas chromatography and volume evaluation. Solid charcoals were subject to ultimate and proximate analysis, SEM, bomb calorimetry and weight measurement. Details of the standards followed for each measuring technique are given presented elsewhere [3]. Additionally, gaseous, liquid and solid yields were subjected to a mass balance.

After the CVC tests on oak, the proximate analysis method for the characterization of the solid char was modified from a method that followed ASTM -D1762-84 [11] to a method that followed...
ASTMs E872-82(2013) [5] and E830-87(1996) [6] for respective determination of volatile matter and ash content. The accuracies of both proximate analysis methods were evaluated as follows: proximate analysis of cellulose samples following both methods (three samples per method) were deliberately interrupted after the volatile matter removal step. Since cellulose contains negligible ash, the remaining product would be fixed-carbon. The carbon purity of this fixed-carbon fraction can be used as an indicator of the accuracy of the reported values. The original proximate analysis technique revealed a “fixed-carbon” of just 94.54 wt% carbon with the balance comprising O and H in decreasing amounts, whereas the updated technique showed an improved “fixed-carbon” composed of 95.5 wt% carbon. The results indicated that the measured experimental fixed-carbon contents are likely to represent slight overestimates of the actual values.

A reproducibility study of the CVC process revealed good repeatability of char and gas yields (<±1.5 wt% absolute), and of the fractions determined by char proximate analysis (<±2 wt% absolute), and poor repeatability of the measured liquid yields [3]. The greater uncertainties of the liquid yields were a result of the difficulty recovering the final products from the reactor system. To gain a better understanding of the carbon fate, carbon mass balances revealed that >97 wt% of the elemental carbon present in the virgin biomass was recovered in the form of solid charcoal and in the form of gas, mainly as CO₂ and CO. The results confirmed that negligible free-tars were produced in the CVC process and that the final liquid product mainly represented water evolved during the carbonization process plus moisture inherent to the original feedstock.

This section presents experimental CVC conditions and results. The CVC results and trends at distinct processing conditions are evaluated against trends reported in literature from other carbonization processes and against theoretical trends predicted by thermodynamics.

Table 3.2g.2 displays the experimental conditions and results from the 23 experiments conducted in this study. A single carbonization experiment was performed in a reactor with one of the valves slightly opened to the atmosphere (experiment # 1). The final char was analyzed and compared to a char derived from CVC, i.e. performed in a sealed reactor, under analogous experimental conditions (temperature, pressure, particle size...). In the additional 22 experiments, CVC was performed and the influences of a number of processing conditions on product yields and properties were investigated.
Table 3.2g.2. Conditions and results for Wall Heated Tubing Bomb experiments. Superscripts are defined in footnotes at the bottom of the table.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>1*</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tbody>
<tr>
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<td>151125</td>
<td>150121</td>
<td>141121</td>
<td>150115</td>
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<td>160126</td>
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<tr>
<td><strong>Conditions</strong></td>
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<td></td>
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<tr>
<td>Reactor Type</td>
<td>Original</td>
<td>Original</td>
<td>Original</td>
<td>Original</td>
<td>Original</td>
<td>Original</td>
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<tr>
<td>Feedstock</td>
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<td>Oak</td>
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<td>Oak</td>
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<tr>
<td>Heat Treatment Temperature [°C]</td>
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<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300-350</td>
<td>300-370</td>
<td>300-400</td>
</tr>
<tr>
<td>Pretest Nitrogen Pressure [MPa]</td>
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<td>0.1</td>
<td>1.48</td>
<td>2.69</td>
<td>4.79</td>
<td>4.79</td>
<td>4.79</td>
<td>4.79</td>
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<tr>
<td>Immersion Time [min] *</td>
<td>34</td>
<td>134</td>
<td>24</td>
<td>38</td>
<td>21</td>
<td>37</td>
<td>181</td>
<td>63</td>
</tr>
<tr>
<td>Mass Loading [g biomass/L reactor]</td>
<td>~100</td>
<td>~100</td>
<td>~120</td>
<td>~160</td>
<td>~120</td>
<td>~145</td>
<td>~145</td>
<td>~155</td>
</tr>
<tr>
<td>Particle size [mm]</td>
<td>0.149-</td>
<td>0.149-</td>
<td>0.149-</td>
<td>0.149-</td>
<td>0.149-</td>
<td>0.149-</td>
<td>0.149-</td>
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<tr>
<td><strong>Reactants</strong></td>
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<tr>
<td>Moisture Content [% wb]</td>
<td>7.68</td>
<td>7.65</td>
<td>7.62</td>
<td>7.49</td>
<td>7.73</td>
<td>7.58</td>
<td>7.70</td>
<td>7.60</td>
</tr>
<tr>
<td><strong>Pyrolysis Reaction</strong></td>
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<td></td>
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<tr>
<td>Axis Peak Temperature [°C]</td>
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<td>233*</td>
<td>294*</td>
<td>311*</td>
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<td>347*</td>
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<td>NA</td>
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<td>0.104</td>
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<td>Methane [mg/g (Dry Feed)]</td>
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<td>Carbon Dioxide [mg/g (Dry Feed)]</td>
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<td>Gas Products [% db]</td>
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<td>62.09</td>
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<td>17.12</td>
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<td>Total [% db]</td>
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<td>NA</td>
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\* \* Superscripts are defined in footnotes at the bottom of the table.
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**Conditions**

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<td>Dual-current</td>
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<td>Heat Treatment Temperature [°C]</td>
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<td>400</td>
<td>500</td>
<td>550</td>
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<tr>
<td>Pretest Nitrogen Pressure [MPa]</td>
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<td>2.17</td>
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<td>0.1</td>
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<td>Immersion Time [min]</td>
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<td>Mass Loading [g biomass/L reactor]</td>
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**Reactants**

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**Pyrolysis Reaction**

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<tr>
<td>Axis Peak Temperature [°C]</td>
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<td>320</td>
<td>405</td>
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**Solid Products**

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<tr>
<td>Char Moist Mass [g]</td>
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<td>10.29</td>
<td>10.18</td>
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<td>2.1</td>
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**Gas Products**

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**Mass Balance**

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<td>Final Gas in V(_{\text{bomb}}) [mol]</td>
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<td>Nitrogen [mol %]</td>
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<td>NA</td>
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<td>NA</td>
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<tr>
<td>Carbon Dioxide [mg/g (Dry Feed)]</td>
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<td>NA</td>
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<tr>
<td>Gas Products [% db]</td>
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<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Char Yield [% db]</td>
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<td>65.21</td>
<td>53.36</td>
<td>41.16</td>
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<tr>
<td>Liquid [% db]</td>
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<td>26.33</td>
<td>29.98</td>
<td>25.43</td>
<td>17.54</td>
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<td>Solid not recovered [% db]</td>
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<td>2.14</td>
<td>1.92</td>
<td>1.82</td>
<td>3.22</td>
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In line with previous observations, [3] the tabulated results from the total mass balance showed that a considerable amount of the final products (around 20 wt%) was sometimes not recovered from the CVC experiments. The carbon mass balance of the CVC experiments revealed that nearly all the carbon present in the original feedstock (>92 wt%) was recovered in the final products in the form of solid or gas. The results confirmed the near absence of free-tars in CVC and supported the conjecture that liquid moisture was the main unrecovered product.

Experimental fixed-carbon yields were calculated on a dry basis as: $y_{fC} = y_{char} \cdot \%fC/100$. Literature values of fixed-carbon yields are typically calculated on a dry ash-free basis and ensuring common base units are important for valid comparison. In case of pyrolyzing feedstocks with minor ash contents such as the ones employed in this study, the required adjustments are nearly unnoticeable. A dry basis, rather than a dry-ash free basis, for the fixed-carbon yields was intentionally selected in this work with the goal of depicting experimental fixed-carbon yields along with yields of products (solid, gas, liquid), all given on a dry basis. Theoretical values were also calculated on a dry basis. The accuracy of the experimental fixed-carbon yields relied on the accuracy of the proximate analysis method.

Theoretical fixed-carbon yields were predicted by FactSage 5.4.1 [12] via Gibbs energy minimization modules that simulated a state of chemical equilibrium. Possible components of the products were selected from a large thermodynamic database based on the elements present in the reactants. "Solution" databases can also be selected based on the inorganic elements present in the reactants but were not included. A parity plot (Figure 3.2g.1) compares the theoretical values against experimental data. In consideration of the fact that theoretical fixed-carbon yields represent the limiting maximum values attainable by a carbonization process, the figure, in agreement with
earlier publications, [2,3] reconfirmed that CVC was able to approach its maximum possible efficiency, especially when higher temperatures (400-500°C) were used. The parity plot only displays results from CVC experiments that pyrolyzed birch feedstock.

Figure 3.2g.1. Parity plot displaying the experimental fixed-carbon yields from birch CVC vs theoretical fixed-carbon yields. Colors represent heat treatment temperature: ■300°C, □400°C, ▲500°C, ◆550°C. Symbol size represents immersion time: small symbols represent short experiments (~30 min) and the rest of the symbols represent long experiments (190 min). Symbol fillings represent special experimental conditions: ◆ small biomass particles, ◆ use of volume compensation, ◆ under initial nitrogen pressure, ◆ low heating rate, star symbol ◆ on top of a symbol indicates high loading.

Figure 3.2g.2 compares experimental data of fixed-carbon, volatile matter and ash yields derived from different carbonization methods: CVC, carbonization in a conventional furnace, hydrothermal carbonization and flash carbonization. The highest efficiency was reported by the CVC of birch at a HTT of 500°C which attained an experimental fixed-carbon yield of 34.2 wt%, with a remarkable fixed-carbon content of 86.5 wt%.
Figure 3.2g.2. Comparison of product yields from different carbonization techniques. CVC: Data from constant volume carbonization experiments at an initial (pretest) pressure of 0.1 MPa. FC: Data calculated from Flash Carbonization experiments [14]. FAO: Data calculated from the Food and Agriculture Organization (FAO) [21]. FAO provided theoretical reference values, but method and biomass species were not specified. Fuwape: Data calculated from carbonization in a conventional furnace [22]. HTC: Data calculated from hydrothermal carbonization [23].

In addition to approaching maximum efficiency, CVC is a simple process that requires minimal technical equipment and can be easily controlled. The main issue faced when considering the CVC scale up is the elevated pressures experienced by the reactor and consequently the need for costly high-pressure equipment. This will be further explored in future work under other funding.

In comparison, the flash carbonization process, developed and patented by Dr. Antal, presents a higher complexity [13]. In this process, a fire is ignited at the bottom of a deep packed bed of biomass in a pressurized reactor (~1-2 MPa). A continuous air flow is introduced from the top of the carbonizer and the pyrolysis gas is evacuated from the bottom. An inlet and outlet valve serve to regulate the gas flow to keep the reactor at constant pressure. A pyrolyzing reaction zone moves from the bottom to the top of the bed countercurrent to the downward air flow as the biomass is
thermochemically converted into a solid charcoal. The process revealed high efficiencies, and also achieved near-theoretical fixed-carbon yields.

Note that flash carbonization fixed-carbon yields in Figure 3.2g.2 were transformed from values on a dry-ash free basis given in reference [13] to values on a dry basis for consistency. Charcoal from one flash carbonization test on birch in Figure 3.2g.2 showed an almost complete volatile extraction. The char was characterized by a fixed-carbon content value of 91.4 wt% and a fixed-carbon yield of 21.8 wt%. As observed from carbonization processes in “open” reactors, the profound devolatilization was accompanied by a loss in process efficiency.

Compared to CVC, flash carbonization requires regulating the reactor pressure, recovering and handling of condensed tarry vapors and the handling of the continuous and variable composition exhaust gas to comply with environmental regulations. Additionally, flash carbonization processes require equipment capable of withstanding elevated pressures and temperatures. Temperatures as high as ~900°C and working pressures of around 1-2 MPa have been reported [14]. The temperatures are considerably higher than the ones reported in CVC processes.

The pressures in flash carbonization are not autogenerated as in CVC but are maintained by a back pressure regulator at a process setpoint, and a pressure relief valve avoids exceeding the maximum allowable working pressure of the reactor. Typically, flash carbonization operates at a pressure below those achieved in CVC processes. Nonetheless, recent CVC tests have successfully reduced CVC peak pressures while maintaining final fixed-carbon yields and fixed-carbon contents of the charcoals. Thus, pressures required in CVC processes could also change.

Sealed batch reactors are typical of both hydrothermal carbonization (HTC) and CVC processes (there are HTC processes that operate in continuous mode [15] but they are exceptions, the vast majority operate in batch mode). The main difference between HTC and CVC is the pyrolyzing medium. In HTC, the biomass is submerged in a liquid medium while in CVC, biomass is pyrolyzed in a low humidity gas atmosphere. As temperature increases, so does the pressure. Above a critical temperature value, HTC operating pressure is expected to dramatically surpass that of CVC due to the exponential pressure rise of saturated water with temperature. This critical temperature value is estimated to be ~200-250°C but could considerably change depending on the mass loading employed. Due to these high pressures, typical HTC operating temperatures are limited to a lower range of 180-250°C. The lower temperatures of HTC processes restrict the profound char devolatilization achieved by the pyrolytic processes in dry atmospheres. Consequently, HTC processes become impractical for the manufacture of charcoals intended for metallurgical applications. Hydrochars (chars from HTC), nonetheless, can be valuable products for soil amending and novel research has given hope to applications such as adsorption, catalysis, ion-exchange or energy storage [16-20]. Notice that Figure 3.2g.2 presents HTC yields
for a run that operated at a high temperature for a HTC process (280°C) which resulted in higher fixed-carbon yields and lower volatiles than typical, lower temperature HTC.

Finally, carbonization in a conventional furnace presented the lowest efficiencies (see Fuwape in Figure 3.2g.2). The Food and Agriculture Organization (FAO) of the United Nations also provided rough values for carbonization processes at various temperatures [21]. The values indicate high efficiencies and at a temperature of 500°C, intense devolatilization. Details about the carbonization process (other than the temperature) and biomass species were not specified.

**Plastic behavior of chars from CVC**

Under certain CVC conditions, the char morphology appeared to undergo a transient plastic phase that converted the original grainy biomass structure into a single piece that took on the shape of the reactor vessel interior and with the appearance of coke. Figure 3.2g.3 shows the contrasting appearances of some CVC charcoals with panels (b), (c), and (d) exhibiting characteristics associated with a transient plastic phase.

![Figure 3.2g.3](image_url)

Figure 3.2g.3. (a) Birch charcoal produced in a CVC test under a HTT of 550°C, an initial nitrogen pressure of 0.1 MPa, biomass particle size <2 mm, biomass loading of 130 g/L and an immersion time of 190 minutes. (b) Birch charcoal produced in a CVC test under a HTT of 300°C, an initial nitrogen pressure of 0.1 MPa, particle size <0.2 mm, biomass loading of 240 g/L and an immersion time of 190 minutes. (c) Oak charcoal produced in a CVC test under a HTT of 300-400°C, an initial nitrogen pressure of 2.69 MPa, a coarse particle size, biomass loading of ~120 g/L and an immersion time of 55 minutes. (d) Cellulose charcoal produced in a CVC test under a HTT of 300-400°C, an initial nitrogen pressure of 2.4 MPa, a particle size of 50-180 µm, biomass loading of ~200 g/L and an immersion time of 85 minutes.
Signs of a molten phase were evident in chars derived from CVC of birch particles of size <2 mm at a pretest pressure of 0.1 MPa N\textsubscript{2}, a HTT of 400 °C and a heating rate of ~1°C/s [3], and in chars from the CVC of cellulose grains in a size range from 0.050-0.18 mm, at a pretest pressure of 2.40 MPa N\textsubscript{2}, a HTT of 260 °C and a similar heating rate [2]. To our knowledge, this is the first time molten charcoal has been observed in pyrolysis processes operating at moderate conditions of temperature and slow heating rates.

These temperatures and heating rates contrast with those reported in “open” reactor configurations. In “open” reactors, the morphological transformation of the char into a plastic state have been studied by a limited number of authors using fast pyrolysis processes operating at temperatures >550°C [24-26], heating rates of ~500°C/s [24] to ~10^4°C/s [24,25,27], small particles and small amounts of sample. If the heating rates typical of slow pyrolysis (or carbonization) processes were employed, the transient plastic phase vanished and the structure of the charcoals resembled skeletons of the virgin biomasses [25].

In conclusion, it appears that volatiles act as plastifying agents. CVC processes foster the prolonged retention of a high concentration of volatiles within the char matrix. The result is the shift of the char softening point to lower temperatures and heating rates. Conditions employed in the CVC process such as temperature, pressure, heating rate, particle size or biomass loading played key roles in the evolution of the char morphology. Details of the influence of each variable are given in the following sections.

**Figures 3.2g.4 and 3.2g.5 illustrate the effect of sealing the WHTB reactor** on the product yields and proximate analysis of chars from oak pyrolysis at a HTT of 300°C and an initial pretest pressure of 0.1 MPa N\textsubscript{2} (Experiments # 1 and 2 in Table 3.2g.2). Notice that proximate analysis values in Figure 3.2g.5 represents the normalization to 100% of the solid fractions from Figure 3.2g.4. Carbonization in the sealed WHTB (i.e. CVC) and carbonization in a reactor slightly opened to the atmosphere resulted in charcoal yields of 58.6 wt% and 69.8 wt%, respectively but the CVC char product was characterized by a dramatically improved fixed-carbon content (55 vs 34 wt%, respectively) and fixed-carbon yield. Yields of free tars constituted a considerable fraction (not quantified) of the final products of the pyrolysis in the open reactor but became a negligible fraction in the CVC process. The liquid yield of the CVC test shown in Figure 3.2g.4 represents the char moisture content. Notice that the prolonged immersion time employed with the closed reactor (134 min) versus the “open” reactor (34 min) can partially account for the differences in the final products from both processes. Nonetheless, the higher extent of secondary char formation observed in the CVC process is mainly explained by the retention of volatiles in the reaction zone and consequent prevention of carbon losses in the outflow of gases and tars. In the CVC process, released volatiles are in contact with the solid at a higher partial pressure and for longer periods of time than in the “open” reactor. These effects promote secondary reactions between volatiles and
the solid char that produce secondary char and lead to higher fixed-carbon contents and fixed-carbon yields.

Figure 3.2g.4. Effect of sealing the reactor on the yields of char, condensate and gas from oak carbonization at a HTT of 300°C, initial atmospheric pressure, feedstock particle size of 0.149-0.425 mm and mass loading of ~100 g/L. Negligible free tars are recovered from the closed reactor experiments (CVC). Liquid yield mainly represents water content of the final moist charcoal.

Figure 3.2g.5. Effect of sealing the WHTB reactor on the proximate analysis of chars from oak carbonization at a HTT of 300°C, initial atmospheric pressure, feedstock particle size of 0.149-0.425 mm and mass loading of ~100 g/L.
In conclusion, the results demonstrate that the CVC process and appropriate processing conditions can produce charcoals with properties tailored for their end use. For example, lower rank charcoals can be produced at moderate temperature (300°C) and short reaction time (<60 mins) in greater yield (50-60 wt%) than any other known process; these charcoals are suitable for combustion applications. At the other end of the spectrum, high rank and value biocarbons with low volatiles and high fixed carbon content (>85 wt%) can be produced by using higher temperature (500-550°C) and longer soaking times at carbonization temperature (~3 hours). This opens up the opportunity for the production of metallurgical grade chars in a single step process, which is of great interest to this industry.

In addition, the morphological characteristics of charcoals can also be tuned. Higher HTT, pretest pressures, heating rates and possibly smaller particle sizes resulted in a change from a particulate charcoal that retained the structure of the virgin feedstock to a solidified single piece of coke-like material that had undergone a TPP transition and formed to the shape of the reactor vessel interior.

The main findings from the research are listed below:

1. Experimental fixed-carbon yields provide meaningful measurements of the carbonization efficiencies. Efficiencies obtained in the CVC process compare favorably with other carbonization processes such as flash carbonization, conventional carbonization or HTC. Confirming previous findings [2,3], CVC was able to consistently approach the maximum theoretical efficiencies predicted by thermodynamic equilibrium calculations, and produce negligible free tars and a gaseous product mainly composed of CO₂. CVC products consequently present minimum disposal issues and environmental impacts (i.e. due to the lack of tar products).

2. When the carbonization reactor was left slightly open to permit a constant atmospheric-pressure and provide an escape path for the released volatiles, the gaseous residence time and partial pressure were reduced. Under these conditions, volatiles have fewer opportunities for secondary char-forming reactions. Consequently, in comparison to chars derived from CVC, carbonization in the open reactor generates a notable fraction of free tar and a char with a lower fixed-carbon content and a lower fixed-carbon yield.

3. Based on CVC tests performed with different feedstocks, it appears that smaller particle sizes favor the formation of the TPP. Nonetheless, robust conclusions regarding the effect of particle size, as well as the mass loading, on char morphologies cannot be stated based on the CVC experiments presented herein. Increasing the particle size or mass loading can have opposing effects. Higher mass loadings or larger particles may raise intraparticle volatile pressure which would favor the TPP development. Conversely, both can slow down the intraparticle heat transfer which may prevent the TPP from occurring.
References


**3.2h High Rate Anaerobic Digestion**

An extensive amount of work was executed to develop biofilm supports that would cultivate growth of thin film biofilms possessing active methanogenic microbial communities. Specifically, biochar-based supports that stimulated the formation of island microbial communities in thin-film biofilms were envisioned and fabricated. Such biofilm supports were postulated to possess surface properties that would limit growth of biofilms to thin-films possessing highly efficient populations of active methanogenic microbial communities. Our approach under this effort was to entrap evenly distributed biochar granules within thin films of deacylated chitosan that can be molded/cut into preferred geometries (see, for example Figure 3.2h.1). Deacylated chitosan is a model polymer with surface functional groups (amines) that have been postulated to limit growth of biofilms. Biochar, by contrast, is a material shown (in this lab) to support growth of thick active methanogenic biofilm communities. Figure 3.2h.1 shows a representative example of this concept.

![Biochar granules in deacylated chitosan thin film.](image)

The casting process of these hybrid materials was the subject of long trials of various formulations and curing techniques, all of which were dedicated to finding the best and industrially relevant methods to systematically entrap biochar surfaces, equally distant from each other, within chitosan thin films. Factors such as starting deacylated chitosan concentration, the degree of deacylation, if and the degree to which plasticizers should be added, how to prepare and pour the deacylated chitosan film into molds, how to cure the film such that the biochar pieces were firmly held in place, as well as methods to restrict the biochar movement within the film during the drying process, were all exhaustively considered.

Ultimately, a process methodology was settled upon. Specifically, deacetylated chitosan (>85% degree of deacetylation) and sorbitol (plasticizer) were dissolved in 0.2 M acetic acid to final concentrations of 2.34 and 1.43 wt%, respectively. The stock solution was mixed using a stand-up mixer (Cole Parmer, 50006-01) at 200 rpm for 20 minutes before being left to stand until all entrained bubbles were fully dissipate. The stock deacetylated chitosan solution was then kept well
mixed under magnetic stirring until use. When ready for use, 9.31 ml of 0.05 vol% glutaraldehyde (GTA crosslinker) solution was added to each 100 ml of stock deacylated chitosan solution. After the addition of GTA, the solution was stirred for 30 to 60 minutes to permit the crosslinking reaction to occur. The solution was then heated by microwave (Panasonic NN-5560A or equivalent on low setting) until a solution viscosity resembling a thick hydrogel (20000 ≥ μ ≥ 70000 cP) was achieved. The microwaving process was periodically interrupted to permit stirring to prevent the formation of a surface skin.

Portions (approximately 26.31 ± 2.35 g of the resulting viscous hydrogel) were poured into molds with anti-stick coatings and allowed to settle undisturbed for a period of 1 hour until a level film approximately 5 mm thick was achieved. A desired mesh of sifted biochar (Charcoal Green Pure Black, Charcoal House) was then hand pressed into the viscous hydrogel to form the desired pattern (see, for example, Figure 3.2h.2). The biochar impregnated hydrogel was then dried in a convection oven at 50°C for 4 hours prior to being left overnight at room temperature. The dried film was then immersed in a 10 wt% sodium hydroxide (NaOH) bath for 20 minutes followed by 1 minute submersion in deionized water. The water rinse was repeated five additional times until the film dried to a constant weight at 50°C in a convection oven. These films were then stored at room temperature for an additional 2 days before being heat treated (cured) at 110°C for 2 hours in a convection oven (Figure 3.2h.3). In an industrial setting, these features could easily be accomplished on rolling beds and standing convection ovens through which the films are rolled. All aspects of this manufacturing approach could be accommodated with existing equipment in food or plastic film processing plants.

To test durability upon resuspension, the dried films were re-suspended in deionized water for a minimum of 6 weeks at room temperature, after which they were visually inspected for signs of disintegration. Although the fabricated films formed strong, hard disks when dried (Figure 3.2h.2B) they softened and greatly swelled upon re-submersion in aqueous solution (Figure 3.2h.2C). The biochar pieces remained well attached and within the original pattern through multiple shrink/swell cycles of the hybrid support material. Although the swelling process introduced water molecules that ultimately could have contributed to the dissolution of the internal hydrogen bonds of the chitosan polymer strands, the use of an internal crosslinking agent and post processing application of NaOH rinses afforded, as hypothesized, long film lifetimes (one to two years) at room temperature in standing water. Results also showed only minor fractions of the chitosan dissolved while the great majority of the core film remained intact (Figure 3.2h.2C). Small fragments of biochar would occasionally break off with handling but this is also a function of the source material from which the biochar is made. Some wood derived biochar are splintery while others are much harder and durable. Also, wood biochar, for example, is likely to break or chip than biochar derived from coal. Finally, preferred results were found with chitosan films that were smaller rather than thicker.
The biofilm supports were then tested continuously in anaerobic reactors for a period of six months followed by visual inspection of material integrity (Figure 3.2h.3). The reactor system comprised an initial mixing tank followed by anaerobic column reactors filled with either the hybrid chitosan-biochar support material or bulk biochar. The operating conditions were equivalent for both biofilm supports to permit cross comparison of performance. The feed wastewater was comprised of grease trap waste (GTW) wastewater collected from a local GTW processing facility possessing a chemical oxygen demand (COD) of approximately 18 to 20 g COD/L. The biochar packed reactors were inoculated with 250 mL of anaerobic sludge collected from a local wastewater treatment plant. Immediately following inoculation, the system HRT was set to 10.5 days (organic loading rate (OLR) of ~ 1.98 kg/m$^3$/d). After the start-up period, the HRT was lowered to 6.94 days (OLR was raised to 2.64 kg/m$^3$/d) and measurements started after steady state (as identified by steady gas production rates) was achieved. All other operating variables (temperature, pH control...etc.) were kept equivalent between the two systems. All monitored values were recorded daily. Liquid phase samples were collected every 1-2 days from reactors and analyzed for pH and dissolved oxygen (DO), when applicable. Weekly COD measurements were used to gauge performance.
The performance of the hybrid chitosan-biochar supports exceeded those achieved with bulk biochar in nearly all categories. Specifically, the reactors filled with bulk biochar achieved COD reductions of 94%, total suspended solids (TSS) reductions of 72%, and total biogas production of 343.5 l/kg COD degraded and 66% methane composition in the headspace biogas. By contrast, at equivalent organic loading rates (OLRs), the hybrid chitosan-biochar supports yielded a higher COD reduction of 95.8%, TSS reduction of 86% and total biogas production rates of 367.12 l/kg COD degraded with approximately 62.61% methane composition in the reactor headspace gas. Similar to the bulk biochar system, more than 98% of the total volatile organic compounds (TVOAs) were consumed in the reactor with the hybrid supports. More importantly, bulk biochar provided a COD reduction of 0.87% per gram biochar, while the biochar of the hybrid support material provided a COD reduction of 4.6% per gram biochar, equivalent to a greater than 5-fold increase in performance on a biochar weight basis. Table 3.2h.1 presents a comparison of key parameters for both systems.
Table 3.2h.1. Key performance parameters for the bulk biochar packed system and hybrid support packed system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bulk biochar</th>
<th>Hybrid support</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD reduction (%)</td>
<td>94</td>
<td>95.8</td>
</tr>
<tr>
<td>Specific COD reduction (%/g biochar)</td>
<td>0.87</td>
<td>4.6</td>
</tr>
<tr>
<td>TSS reduction (%)</td>
<td>72</td>
<td>86</td>
</tr>
<tr>
<td>Biogas production rate (L/kg COD degraded)</td>
<td>343.5</td>
<td>367.1</td>
</tr>
<tr>
<td>Headspace methane composition (%)</td>
<td>66</td>
<td>62.61</td>
</tr>
<tr>
<td>Methane production rate (L/kg COD degraded)</td>
<td>226.7</td>
<td>219.61</td>
</tr>
<tr>
<td>% maximum theoretical CH4 production rate</td>
<td>64.7</td>
<td>63.75</td>
</tr>
<tr>
<td>TN reduction (%)</td>
<td>52</td>
<td>32</td>
</tr>
<tr>
<td>TP reduction (%)</td>
<td>29</td>
<td>42</td>
</tr>
</tbody>
</table>

There was one category where the hybrid supports performed non-optimally and no better than the bulk biochar. Specifically, methane production yields remained well below the theoretical maximums. The methane production yield for the hybrid system reached 219.61 l/kg COD degraded which is 65.7% of the theoretical maximum methane production (350 L/kg COD degraded). Comparatively, the bulk biochar system similarly produced 63.75% of the theoretical maximum methane. The non-optimal methane production yields in both systems were attributed to uneven gas production rates at low organic loading rates due to gas hold-up, an outcome resulting from both the bulk biochar and swelled chitosan-biochar hybrid materials tending to blocking gas up-flow. This outcome will be addressed in future funding periods.

A randomly selected piece of the chitosan-biochar hybrid support material was removed and fixed for imaging by scanning electron microscopy (SEM). Specifically, a single disc was removed from the anaerobic reactor and immediately submerged within a solution of 0.1 M sodium cacodylate buffer containing paraformaldehyde (2 % v/v) and glutaraldehyde (2.5 v/v %) for 1-2 hours at room temperature. The disc was then cut into ~ 1 cm samples, preferably while immersed (underwater) to avoid excessive exposure to the air-water interphase which causes drying and/or lysing of the cells. The smaller ~1cm samples were then transferred to 0.1M sodium cacodylate buffer for 10 minutes, with a change of fresh solution after the first 5 minutes. They were then post-fixed with 1% v/v osmium tetroxide in 0.1 M sodium cacodylate solution for 1 hour, followed by dehydration in a graded ethanol series of 30%, 50%, 70%, 85%, and 95% v/v for 5 minutes, and 2 changes of solution each. For the last dehydration step with 100% ethanol, 3 changes were required for 10 minutes each. Therefore, the samples were dried by a critical point drier with carbon dioxide, mounted, and sputter coated.

\[1\] The average gas production rate was used to calculate/estimate this value.
SEM images revealed that thick layers of dense microbial biofilms formed on biochar surfaces (Figure 3.2h.4, lower right hand corner) while sparsely populated monolayer biofilms covered the chitosan surface (Figure 3.2h.4, upper left hand corner).

Figure 3.2h.4: SEM image of selected sample of hybrid Chitosan-biochar support.

Publications


References

3.3 Low-Cost Material for Solar Fuels Production

Methods were advanced to produce high-efficiency, low-cost photovoltaics (PV) based on the use of Earth-abundant materials. To improve the morphology, microstructure and photo-conversion efficiency of copper-zinc-tin-sulfo-selenide (CZTSSe) thin film solar absorbers, the post deposition annealing process as well as the printing process were further developed. Thin films obtained with this new method were integrated as solar cells, and test results indicated a doubling of efficiencies achieved during the APRISES 11 research phase.

Among all possible thermodynamic pathways to produce energy from sustainable sources, direct solar-to-electron conversion is considered one of the most efficient routes. However, location and time of PV operation requires storage and transport of produced electricity, both of which incur energetic losses. Storing solar power in the form of chemical bonds is an elegant way to address both energy storage and transport issues. So-called “Solar Fuels” can take various forms (e.g. H₂, CH₄, C₂H₄) and be converted on demand into mechanical or electrical power. Amongst all possible technologies, PV-electrolysis is arguably the most straightforward approach to produce Solar Fuels. HNEI is focused on the PV component of PV-electrolysis to develop low cost methods to produce high-efficiency, low-cost PV based on the use of CZTSSe. This is an Earth-abundant material that has already demonstrated efficiencies of nearly 10%. This work leverages HNEI’s experience in low-cost/high-throughput multi-elemental compound synthesis, thin-film solar cell fabrication, and solar fuel synthesis.

Under APRISES 11, HNEI developed a unique process to synthesis CZTSSe solar cells with inexpensive and scalable methods. This process includes three key steps. In step 1, printable CZTS nano-crystalline inks are synthesized via a “hot injection technique” (Figure 3.3.1a), using precise amounts of metal chlorides (CuCl₂, ZnCl₂ and SnCl) dissolved in ethylene glycol (EG). This solution is then transferred into a 3-neck flask, purged with nitrogen and heated at 250°C. After this step, a second EG solution containing sulfur is injected in the hot CZT/EG mixture, leading to the spontaneous formation of mono-dispersed CZTS nanoparticles, approximately 10 nm in diameter (Figure 3.3.1b). In step 2, ink containing CZTS nanocrystals “building blocks” is printed onto conductive substrates (molybdenum coated glass) using spray techniques. Finally, in step 3, CZTS-coated substrates are placed into a furnace with a few milligrams of elemental selenium and heated at 500°C for 30 minutes. During this crystallization step, the selenium reacts with the CZTS nanoparticles to form large CZTSSe crystals. Finally, the CZTSSe thin films are integrated as solar cells using a standard architecture for thin film-based absorbers (Mo/CZTSSe/CdS/ZnO/ITO). So far, HNEI’s best CZTSSe solar cell can generate short-circuit photocurrent density, open circuit voltage and efficiency of 19 mA/cm², 375 mV and 2.3%, respectively (Figure 3.3.1c).
During the APRIVES 12 research period, the HNEI team worked extensively on the post deposition annealing process (crystallization, step 3) to improve the morphology, microstructure and photoconversion efficiency of CZTSSe thin film solar absorbers. First, X-ray diffraction and Raman spectroscopic measurements were performed on CZTS nanoparticles before and after the crystallization step to better understand the mechanism responsible for the formation of thin films. These analyses demonstrate that the crystallographic ordering of CZTS nanoparticles (Wurtzite) differs from that of CZTSSe thin films (Kesterite), as depicted in Figure 3.3.2a and b. Such differences appear to play an important role in the synthesis of CZTSSe thin films, since the crystallographic phase in which CZTS nanoparticles grow (Wurtzite) is known to be unstable. At this stage of the research, we speculate that unstable CZTS nanoparticles partially decompose during the crystallization process and locally coalesce to form a thin film.
Figure 3.3.2. (a) X-ray diffraction and (b) Raman spectroscopy measurements performed on CZTS nanoparticles before (labelled “Nano-ink”) and after (labelled “Thin Film”) crystallization. These results were obtained during the APRISES 12 research phase.

With this mechanism in mind, we revised our printing process (step 2) to ensure that a compact layer of CZTS nanoparticles is achieved during this printing stage, a pre-requisite to obtain uniform, dense and void-free CZTSSe thin film absorbers. First, the CZTS nanoparticle wash procedure was modified to improve the removal of impurities (mainly chlorides) after the hot injection step. With our new method, CZTS nanoparticles are first collected by centrifugation (10,000 rpm for 5 minutes) and then subsequently washed with hexane. Also, the spray process used to deposit CZTS nanoparticles was replaced by a spin coating technique (1,800 rpm for 1 minute), and a hot plate annealing (in air, 250°C) was added to further remove solvents. Figure 3.3.3 presents cross sections of CZTSSe thin films obtained by spray (APRISES 11, Figure 3.3.3a) or spin coating (APRISES 12, Figure 3.3.3b). Clearly, our new process leads to more uniform and smoother CZTSSe films when compared to those obtained with the previous method.
Finally, CZTSSe thin films obtained with our new method were integrated as solar cells, using 100 nm thick CdS buffers and 100nm/500nm ZnO/ITO transparent conductive oxide layers. The electrical properties measured on 7 cells under simulated AM1.5G illumination (1,000W/m²) at 25°C are presented in Table 3.3.1. The highest efficiency achieved was 4.48%, a value double that achieved during the APRISES 11 research phase. On average, the short-circuit photocurrent density, open circuit voltage and efficiency were 24.7 mA/cm², 389 mV and 3.84%, respectively. For comparison, the highest efficiency of state-of-the-art CZTSSe synthesized via vacuum-based process during the APRISES 12 reporting period is 9.15% (I. Repins, Sol. Energy Mater. Sol. Cells, 2012, 101, 154–159).

Table 3.3.1. Electrical properties of printed CZTSSe solar cells.

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Voc  [mV]</th>
<th>Jsc  [mA/cm²]</th>
<th>FF  [%]</th>
<th>Eff  [%]</th>
<th>Rs  [Ω-cm²]</th>
<th>Rsh  [Ω-cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>414</td>
<td>20.7</td>
<td>29.30</td>
<td>2.44</td>
<td>2.5</td>
<td>88.5</td>
</tr>
<tr>
<td>2</td>
<td>423</td>
<td>25.4</td>
<td>29.72</td>
<td>3.05</td>
<td>1.4</td>
<td>116</td>
</tr>
<tr>
<td>3</td>
<td>419</td>
<td>23.2</td>
<td>34.66</td>
<td>3.37</td>
<td>1.93</td>
<td>196</td>
</tr>
<tr>
<td>4</td>
<td>417</td>
<td>27.4</td>
<td>39.37</td>
<td>4.48</td>
<td>1.48</td>
<td>202</td>
</tr>
<tr>
<td>5</td>
<td>372</td>
<td>21.9</td>
<td>44.46</td>
<td>3.62</td>
<td>3.03</td>
<td>68.4</td>
</tr>
<tr>
<td>6</td>
<td>288</td>
<td>29.5</td>
<td>35.49</td>
<td>3.03</td>
<td>2.7</td>
<td>24.1</td>
</tr>
<tr>
<td>7</td>
<td>392</td>
<td>30.8</td>
<td>31.84</td>
<td>3.84</td>
<td>2.16</td>
<td>55.8</td>
</tr>
<tr>
<td>Average</td>
<td>389.3</td>
<td>24.7</td>
<td>35.5</td>
<td>3.3</td>
<td>2.2</td>
<td>115.8</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>48.2</td>
<td>3.4</td>
<td>5.8</td>
<td>0.7</td>
<td>0.7</td>
<td>71.1</td>
</tr>
</tbody>
</table>
3.4 Hydrogen Refueling Support

The APRISES 2012 activities were focused on two locations: the hydrogen production and fueling station located at the Natural Energy Laboratory Hawaii Authority (NELHA) in Kailua-Kona, and the hydrogen fueling dispenser station located at Hawaii Volcanoes National Park (HAVO), both on the Island of Hawaii. APRISES 12 funding supported the commissioning of hydrogen production and compression equipment at the NELHA site, the procurement of a Power Export Unit to enable a fuel cell electric bus to provide 110/240 VAC power for emergency backup power in support of civil defense operations, and the design of a hydrogen dispensing system and procurement of hydrogen dispensing equipment at HAVO. Funding also supported the development of a grid-connected electrolyzer model operated in support of grid frequency management ancillary services.

As illustrated in Figure 3.4.1, the overall hydrogen fueling concept is to produce hydrogen at a central site and deliver it to distributed dispenser stations using a fleet of hydrogen transport trailers (HTT). This concept provides for optimizing capital utilization for hydrogen production while utilizing distributed dispensing sites with minimum complexity and infrastructure to reduce fuel distribution costs. Central hydrogen production “at scale” leverages the utilization of larger
electrolyzers that in addition to producing hydrogen for transportation, can be used to provide grid support ancillary services that can be monetized to provide additional revenue streams to the hydrogen production company. This in turn offsets the production cost of hydrogen.

It has been demonstrated that an electrolyzer has the potential to be used as a variable controllable load that can be reduced or increased in order to maintain the total load balance and frequency stability of the grid. The high-level objectives of this project are to validate the performance, durability, and cost benefits of grid integrated hydrogen systems by:

- Demonstrating the dynamic operation of electrolyzers to mitigate impacts of intermittent renewable energy sources on the grid – do they respond fast enough?
- Investigating the durability of the electrolyzer over a long duration when used in a dynamic operating mode;
- Developing models that characterize the performance of electrolyzers in the grid support operational mode;
- Demonstrating the potential for multiple revenue streams from the monetization of ancillary services while producing hydrogen;
- Supporting the development of regulatory structures for the permitting and installation of hydrogen systems in Hawaii;
- Supporting the operation of hydrogen equipment at NELHA;
- Supporting the procurement of equipment for the HAVO hydrogen dispensing system;
- Supporting fuel cell bus operations by supplying hydrogen to shuttle buses operated by County of Hawaii Mass Transit Agency (MTA) and Hawaii Volcanoes National Park (HAVO);

The NELHA site design is illustrated in Figure 3.4.2. It is comprised of a 40 ft ISO container that houses 1) a Proton Onsite Model C30 proton exchange membrane electrolyzers that produces 65 kg of hydrogen over a 24-hour period at a pressure of 450 psi, 2) a HydroPac compressor that is capable of compressing 120 kg of hydrogen per day, and 3) an electrical distribution room. The hydrogen is compressed into hydrogen transport trailers shown in the bottom left of the diagram. The trailers supply 450 bar hydrogen to the hydrogen dispenser shown in the upper right of the diagram which then dispenses hydrogen to the County of Hawaii bus (Figure 3.4.3).
Figure 3.4.2 NELHA Hydrogen Production and Dispensing Site Design

Figure 3.4.3 County of Hawaii FCEB
APRises 12 funding supported the commissioning and maintenance of the electrolyzer (Figure 3.4.6) and the compressor (Figure 3.4.7) systems by technicians from Proton Onsite and Powertech respectively to ensure that the equipment and their balance of plant systems were properly installed and functional. This included operation of their respective chiller units and the electrolyzer deionized water supply.
The HAVO hydrogen dispensing system site conceptual design illustrated in Figures 3.4.8 and 3.4.9. The design calls for a dispenser that is supplied with hydrogen from a hydrogen transport trailer. The design supports fueling for the two HAVO buses (Figure 3.4.10) and has parking for
two hydrogen transport tube trailers. A firewall with a 2-hour fire rating separates the hydrogen fueling pad from existing gasoline and diesel tanks in accordance with NFPA-2 setback codes and standards requirements. A small 10 ft ISO container is used to house various balance of plant equipment and the electrical distribution system. The dispenser is weather protected with a canopy. There is also a provision to charge the buses’ onboard batteries using an EV charging station.

A contract for an architectural and engineering design suitable for bidding on the installation of the site infrastructure (using other budgets) was prepared and a contractor was selected. However, the Kilauea eruption began on May 3, 2018 and all activities associated with installing the site infrastructure were halted. The eruption and severe earthquakes have caused extensive damage to the park’s infrastructure and it is uncertain when the park will be ready to receive a hydrogen dispensing station. Other options are being evaluated.

Figure 3.4.8 HAVO 350 Bar Dispensing Station Conceptual Design
A novel automated fueling system for the HAVO buses was developed utilizing a “cascade” filling process - a high-pressure system which is used for the refilling of lower pressure compressed gas cylinders. The cascade system allows cylinders to be filled without a compressor. When gas contained in a cylinder at high pressure is allowed to flow into another cylinder that contains gas
at a lower pressure, the pressures will equalize to a value somewhere between the two initial pressures. In a cascade storage system, several large cylinders are used to bring a small cylinder up to a desired pressure, by always using the supply cylinder with the lowest useable pressure first, then the cylinder with the next lowest pressure, and so on. The problem is that it is only possible to extract about 50% of the hydrogen from the trailer if the bus is to be filled to its full 350 bar capacity. The trailer must then be returned to NELHA for refilling with half of the hydrogen remaining onboard. This essentially doubles the cost of delivering hydrogen and was deemed unsatisfactory.

HNEI tasked Powertech to design and build a hydrogen boost compressor system that will be used to extract the majority of the hydrogen from the hydrogen transport trailers. This will significantly reduce the amount of hydrogen that is back-hauled, and in turn, reduce the number and cost of delivery trips by approximately 50%. Figure 3.4.11 is illustrates the new connection post that contains a small boost compressor. The Hydrogen Transport Trailers were also modified to allow their valves to be operated by the automated control system in the correct sequence required to optimize the dispensing process.

Figure 3.4.11 HAVO Boost Compressor System

APRIZES 12 funding was also used to procure and develop the non-recurring engineering to integrate a 10kW Export Power Unit (EPU) into the County of Hawaii bus (Figure 3.4.12). The EPU (Figure 3.4. 13) allows the bus to power critical loads in a civil defense emergency
such as a hurricane. The EPU can convert input 320-450VDC voltages to an output of 110/220VAC, 10kW, 60/50 Hz. This will allow the MTA bus to provide up to 32 hours of backup power at 10 kW. The bus can then fill its hydrogen tanks in 15 minutes and provide another 30 hours of critical load power. The bus thus becomes a mobile power source. This capability is being very well received by the County of Hawaii.

Figure 3.4.12 MTA Bus Undergoing Conversion

Figure 3.4.13 Export Power Unit, 10kW, Installed on MTA Bus
Under this subtask, a Hydrogen Energy System (HES) simulation tool was developed to evaluate and characterize the performance of an electrolyzer system for grid management applications under realistic island grid load profiles. The simulation tool was developed in the Matlab-Simulink environment to analyze the use of an electrolyzer as a potential grid management tool for a small electrical grid. The HES simulation tool consists of a PEM electrolyzer system model, island electrical grid model, and input sources of power, load and grid frequency signals to drive the simulation. Figure 3.4.14 shows the HES simulation tool in the Matlab-Simulink environment.

![Figure 3.4.14 HES Simulation Tool in the Matlab-Simulink environment](image)

Figure 3.4.14 is a schematic of the main components of the NELHA hydrogen fueling station. The system consists of a Proton Onsite C30 electrolyzer unit with two cooling chillers to produce hydrogen at 30 bar at a rate of 65 kg/day. The 30 bar hydrogen is stored in a small buffer tank and is further compressed to 450 bar by the compressor system at a maximum rate of 120 kg/day. The 450 bar compressed hydrogen is stored in 12 tanks inside a hydrogen transport trailer (HTT) that is connected to a fueling post for onsite dispensing.
The hydrogen generator is a Proton Exchange Membrane (PEM) electrolyzer system configured with three PEM stacks each operating at maximum current of 410 Amps to produce 30 Nm³/h. of hydrogen. The unit has a deionized-water (di-water) production and circulating system to supply di-water to the stacks for producing pressurized hydrogen and oxygen and also removing waste heat. The oxygen is safely vented out to the atmosphere while the hydrogen is separated from water and dried to deliver high purity (99.999%) pressurized product gas. The unit has two liquid cooling systems to maintain stack and power supply temperatures of 50°C and 40°C respectively. Supervisory controls enable safe performance and automatic operation of the electrolyzer unit.

The C30 Proton electrolyzer is a fully automated system that regulates the hydrogen production rate to maintain a set buffer tank pressure. This electrolyzer unit also has a mass flow controller to govern its operation externally via a 4-20 mA output port. This enables the electrolyzer to run in dynamic mode and its hydrogen production to be controlled by a grid management algorithm.

The product hydrogen is stored in a buffer tank before it’s compressed to 450 bar by the compressor system. The compressor only operates when the HTT is connected to the fueling post and the tanks are empty. The compressor starts automatically when the buffer tank pressure is greater than 29.5 bar and runs until the buffer tank pressure drops below 16.8 bar. One compressor cycle takes about 20 minutes. The operation of compressor and the monitoring of all critical pressures and temperature of the system are done by the main PLC controller. The PLC controller is also responsible for the smooth and safe operation of all the main and ancillary components of

Figure 3.4.15: Main Components of the NELHA hydrogen fueling station
the fueling station which includes the hydrogen generator, compressor, three chillers, fueling post, HTT storage, and the hydrogen dispenser.

The dynamic operation of the electrolyzer via a 4-20mA control port is implemented in the PLC controller and is available through the Human Machine Interface (HMI). Normally the hydrogen energy system is operated at a constant maximum production rate from the HMI to generate hydrogen on demand to refill the storage capacity of the fueling station. One of the objectives of this project is to operate the electrolyzer in a dynamic mode using a grid management control algorithm in order evaluate the ability of the electrolyzer to stabilize grid frequency fluctuations caused by fluctuating renewable energy power sources such as wind and solar.

A feasibility study was done to understand the level of grid management the current size of the electrolyzer of the HES would be capable of achieving and what optimal electrolyzer size would be required to achieve the maximum level of grid frequency stability. The impact of operating the electrolyzer in dynamic mode on the production of the hydrogen for the fueling station was also analyzed. A dynamic model of the electrolyzer system and an Island of Hawaii grid model have been developed to be used in an HES Simulation Tool for this feasibility study under different operational strategies and renewable power profile.

The electrolyzer model (Figure 3.4.16) models the PEM stack current and temperature for the production of hydrogen gas, the hydrogen pressure within the electrolyzer (system pressure), and the hydrogen pressure in the buffer tank (product pressure). The electrolyzer system model was developed based on a validated PEM fuel cell model and integrates the control and dynamic characteristics of the Proton C30 electrolyzer system during the startup (powering up) process, safety check and venting procedure, and normal operational process. The thermal, current, and pressure controllers and time constants were designed and tuned to simulate the dynamic ramping characteristics of the electrolyzer.
The model determines, for a given supply current, the voltage of each cell which is then multiplied by the total number of the cells to evaluate the over-all DC power consumed by the three electrolyzer hydrogen production stacks. The pressurized wet hydrogen produced at the cathode side increases the system pressure in the pipes and small volumes in the electrolyzer unit and is then fed into a pressure-swing dryer unit. The dry hydrogen is then supplied as product gas to the buffer tank.

The system pressure is used to control the electrolyzer current. A mechanical back pressure regulator (BPR) maintains constant system pressure and also physically separates the system and product pressures. When the buffer gets full and the product pressure increases above the BPR setpoint, the system pressure increases too, and the controller throttles the stack current and, hence, the hydrogen production.

The Proportional-Integral-Derivative (PID) controller\(^2\) and time constants were implemented into the PEM electrolyzer system model. These were tuned to have very similar initial, transient and steady state operational characteristics as the Proton C30 electrolyzer system during the startup and at normal operation. Controller parameters and the time constants were tuned using measured

\(^2\) Proportional-Integral-Derivative controller automatically applies accurate and responsive correction to a control function
data from the electrolyzer ramping up/down cycle tests during commissioning at Powertech in March 2015.

The buffer tank block in Figure 3.4.17 has the buffer tank model to estimate the pressure of the tank from the flowrate of the dry hydrogen supplied from the electrolyzer. The pressure builds up in the tank until the upper limit is reached after which either the compressor is switched on to consume the stored hydrogen, or the hydrogen production is stopped. The hydrogen compressor is modeled by an algorithm which allows the compressor to switch ON and OFF when the buffer tank is full and empty respectively. The compressor switches ON when the buffer pressure is over 29.5 bar and runs until the buffer tank pressure drops below 16.8 bar. These upper and lower buffer tank pressure limits give a hydrogen compressing time of about 20 minutes, as measured in the actual HES system.

The PEM Electrolyzer system model was validated with measured data obtained during performance tests at Powertech. The electrolyzer system model was setup to run in the same way as the actual Proton C30 Electrolyzer unit from the “Power-up and Prestart State” where all the safety checks are done, the “Generate and Venting State” where the stack operation and hydrogen quality are verified, and the “Normal Pressurized Operation State” for generating the hydrogen as product gas. Figure 3.4.18 shows the simulated results compared to the measured data for the H₂ flowrate, system and product pressures, and a single stack current during the different operational states. The simulated results show that the control parameters and the time constants in the model are well-tuned to accurately estimate the operational characteristics of the actual Proton C30 electrolyzer system operation.
Figure 3.4.17: Simulated results for different operating states compared with measured data from the Proton C30 Electrolyzer.
The performance of the HES which is the combined operation of the electrolyzer and the compressor was also simulated, and the results were compared to the measured data from the combined system. The simulated results for nearly three complete hydrogen production and compression cycles from the HES model were compared to measured data as shown in Figure 3.4.18. The electrolyzer operates at maximum current to support the hydrogen production for the compressor cycles.

To analyze the effects of the hydrogen electrolyzer system on the electrical grid, models of the Island of Hawaii electrical grid and an electrolyzer grid interface were developed. The
conventional model of grid frequency dynamics based on the swing equation\(^3\) was modified to estimate the Island of Hawaii grid model shown in Figure 3.4.19. The grid model includes a system inertia algorithm which characterizes the rotational inertia of the generators and frequency dependent loads while the “governor” transfer function represents the turbine generators in the Island of Hawaii power plant. The model parameters of the system inertia (M, D) and governor (Kp, Ki, time constants) algorithm specifically for the Island of Hawaii grid were obtained from the Hawaii Natural Energy Institute (HNEI) study of a grid-scale battery energy storage system (BESS) on the Island of Hawaii. This study developed these algorithms and validated them with a fast-acting 1 MW Lithium-ion BESS on the Hawaii Island grid system.

The Island of Hawaii grid model determines the grid frequency depending on the total load on the grid such as daily residential, industrial or/and electrolyzer demand, compared to the total power generated on the grid from either fossil fuel turbines, battery energy storage systems, and renewable power sources such as solar, wind or geothermal, available on the Island of Hawaii and connected to the grid.

\(^3\) The swing equation is the relationship between the power and frequency for generators. It is used to determine the change in average system frequency and is defined as the “center of inertia of the system”. This algorithm is valid for reasonable frequency deviations due to imbalances between the instantaneous generation and consumption of electric power which has an accelerating or decelerating effect on the synchronous machines. BESS Project HNEI reference can be accessed at the following link: https://www.hnei.hawaii.edu/sites/www.hnei.hawaii.edu/files/Development%20of%20Real-time%20Closed-loop%20Control%20Algorithms%20for%20Grid-scale%20BESS.pdf
An electrolyzer grid controller algorithm was developed to ramp the electrolyzer system between 80% and 100% of its hydrogen production capacity as a function of grid frequency. The electrolyzer normally operates at 90% of its production rate to generate hydrogen for fueling stations while consuming power from the grid. The electrolyzer grid controller ramps up the electrolyzer from 90% to 100% when grid frequency is greater than 60 Hz and ramps down to 80% when the frequency is less than 60 Hz. Figure 3.4.16 shows the electrolyzer grid controller implemented in the PEM Electrolyzer System block in the Matlab-Simulink-Environment. The regulating frequency, $f_c$, of the electrolyzer grid controller determines how sensitive the grid controller is, in regulating the electrolyzer up or down. When $f_c$ is set to a very narrow window around 60 Hz, then the smallest deviations between grid frequency ($f_{\text{grid}}$) and regulating ($f_c$) frequency, i.e. $|f_{\text{grid}}-f_c| \leq \mu$Hz, would cause the electrolyzer to ramp up or down more often, causing high-dynamic operation of the electrolyzer. Hence, for a particular grid system, an optimal window value of the $f_c$ has to be determined to allow smooth and safe grid management operation of the electrolyzer.

The functionality of the electrolyzer grid controller (Figure 3.4.16) algorithm was tested with a grid frequency profile measured on the Island of Hawaii during the BESS system analysis. The deviation of the grid frequency from the nominal grid frequency of 60 Hz was used to regulate the electrolyzer between 80%-100% of its production rate for the grid management application.
During the grid management operations, after the startup period of 200 seconds, the electrolyzer operates at an average of 90% and ramps between 80 to 100% depending on the grid condition. When there is surplus power (grid frequency > 60.00 Hz) available on the grid, e.g. from the renewable energy sources, the controller ramps up the hydrogen production rate towards 100% and when there are increases in power demand (grid frequency < 60.00 Hz) or generation shortage, the controller ramps down the hydrogen production rate towards 80% thereby decreasing the electrolyzer power demand on the grid.

Figure 3.4.20 shows the performance of the Proton C30 electrolyzer system under the measured Island of Hawaii grid frequency variability. Due to inherent time constants and time delays of the standard off-the-shelf commercial electrolyzer control system, the electrolyzer does not respond to faster transients seen in the measured grid frequency plot and therefore electrolyzer ramps are much smoother compared to the very rapid nature of the grid frequency.

![Figure 3.4.20: Performance of the Proton C30 electrolyzer under a measured grid frequency of the Island of Hawaii.](image-url)
The future objectives of the HES Simulation tool will be to:

- Analyze the effects of renewable solar and wind power on the variability of the grid frequency of the Island of Hawaii electrical grid and identify the level of grid management that can be achieved by different sizes of electrolyzers.

- Determine the optimal electrolyzer size to minimize grid frequency variability that is generated by a particular size of renewable power sources such as wind and solar when connected to the Island of Hawaii electrical grid.

- Perform a trade-off study to determine the optimal proportion of the HES that can be reserved for grid management application while generating adequate quantities of hydrogen for commercial applications.

**Presentations**


**TASK 4: OCEAN ENERGY**

Ocean Energy work included development of Ocean Thermal Energy Conversion (OTEC), Wave Energy Testing and Seawater Air Conditioning. Under a subaward to Makai Ocean Engineering, development of OTEC for both US Navy and commercial applications continued, focused on heat
exchanger design, development, and testing, system operational experience, and corrosion testing. For wave energy testing, HNEI subcontracted with Sea Engineering, Inc. to conduct a market study, procure an ROV, and utilize the ROV for various functions at Navy’s Wave Energy Test Site (WETS). Oceanographic monitoring continued to assess Seawater air conditioning (SWAC) impacts.

4.1 Ocean Thermal Energy Conversion (OTEC)

HNEI subcontracted with Makai Ocean Engineering Inc. to conduct research in support of continued development of Ocean Thermal Energy Conversion (OTEC) for both US Navy and commercial applications. This research has been focused on three major areas: 1) heat exchanger design, development, and testing, 2) OTEC system operational experience, 3) and corrosion testing. Makai’s OTEC work is conducted at the Ocean Energy Research Center (OERC), located within the Natural Energy Lab of Hawaii Authority (NELHA) in Kailua Kona, Hawaii.

Under APRISES12 and in support of OTEC heat exchanger development, Makai designed, built, and tested six configurations of Epoxy-Bonded Heat Exchangers (EBHX). Variations in fin pitch and fin width were tested. The heat exchangers were tested at the 100-kW station, which was designed and constructed to support EBHX testing. Results were promising and encouraged design and fabrication of the Foil Fin Heat Exchanger (FFHX). Design revisions to the 100-kW station are underway to support FFHX testing. APRISES13 built on this APRISES12 work, and focused on new OTEC heat exchanger fabrication methods and designs, and corrosion testing.

This report summarizes the APRISES12 work, which was performed between January 2014 and October 2016 specifically pertaining to:

- 100-kW station design and construction,
- EBHX design, fabrication, and testing,
- Turbine design, installation, and operational testing,
- OTEC Control System autonomous controls, and
- Corrosion testing from October 2013 to September 2014

To advance OTEC system operational experience under APRISES 12, Makai installed and commissioned a 105-kW turbine generator – the first grid connected OTEC turbine in the U.S. – at the OERC in June 2015. Several iterations of loadbank and grid-connected turbine testing followed commissioning activities. Testing and operational knowledge was incorporated into a new version of the OTEC Control System program which now includes the ability to start up and operate the OTEC system autonomously.
To support corrosion testing, Makai has continued to test treatments and improve analysis techniques that were initiated under previous APRISES contracts. As of October 30, 2016, the remaining box beam samples have been tested for over 6 years. Corrosion testing also continues with samples in the multi-column imaging racks (MCIR) and representative heat exchanger samples.

**EBHX Design, Development, and Testing**

The EBHX was a prototype for Makai’s FFHX, which Makai believes to be a solution for OTEC heat exchangers. The most important considerations for an OTEC heat exchanger are: low cost per unit area, low volume, seawater corrosion resistant (for 30+ years), and the ability to withstand high working fluid (ammonia) pressures. Makai’s approach to heat exchanger design was to eliminate as much material as possible, simplify the fabrication process, and only use materials compatible with the working environment. The EBHX/FFHX design points that specifically address Makai’s approach are:

1) The seawater passages are constructed with titanium, so the life expectancy of the heat exchanger will not be limited by corrosion.
2) Titanium is the most expensive component in the heat exchanger by weight, the FFHX design (compared to a traditional plate-and-frame heat exchanger) reduces the amount of titanium used by over 95%, representing a significant savings in heat exchanger cost.
3) The titanium sheets are internally supported, eliminating the need for heavy, steel structures to support the pressure, as in the case of plate-frame or shell & tube heat exchangers.
4) The FFHX incorporates densely packed aluminum fins on the ammonia side, which yields a compact and efficient heat exchanger.
5) The design of the heat exchanger allows for low cost, high-volume manufacturing in the future. Makai envisions a fabrication method in which raw materials are fed into one side of a machine while heat transfer plates are ejected from the other. These foil-fin plates are then stacked into a complete heat exchanger with minimal construction effort and minimal cost.
6) The design of the heat exchanger allows for infinite customization of fluid paths and inlet/outlet nozzles. The heat exchanger is stacked layer by layer and fluid paths can be separated during assembly.

The basic component of the EBHX is the Heat Transfer Plate (HTP), which is essentially corrugated aluminum fins with a thin titanium sheet (foil) overlain on both ends. Epoxy is spread over the surface of the foil and the foil is then pressed onto the aluminum fins. In the process, most of the epoxy is expelled from the fin crest, leaving only a thin layer, where most of the heat
transfer is expected to occur. In the FFHX, foil is joined to the fins using laser welding. Multiple HTPs are stacked together to form an EBHX/FFHX.

Titanium foil thickness was chosen to withstand pressure and to provide sufficient contact length between the foil and the fin crests. Thicker foil will distribute heat more evenly across the foil surface from fin crest but is also less pliable, resulting in reduced contact length at the fin crest. Makai believes contact length to be critical to performance and thinner foil is also more economical.

The aluminum fin height is based on a trade-off between heat transfer effectiveness and ammonia head losses. Thermal analysis predicts the middle section of the current fin has the same temperature as the surrounding ammonia and therefore is not transferring heat. A shorter fin would reduce this dead zone but also reduces the ammonia flow area and increases the head losses. Because ammonia is saturated, increased head losses diminish LMTD and lowers heat exchanger performance.

EBHX fabrication equipment was custom designed and built by Makai. The major components are summarized in Table 4.1.1.

Table 4.1.1. EBHX Fabrication Equipment

<table>
<thead>
<tr>
<th>Component</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Roller Table</td>
<td>• Holds foil in tension for surface prep and epoxy application</td>
</tr>
<tr>
<td></td>
<td>• Applies epoxy at specified thickness on foil</td>
</tr>
<tr>
<td></td>
<td>• Passes foil to Plate Template after epoxy is applied</td>
</tr>
<tr>
<td>Plate Template</td>
<td>• Contains razor guides for foil edge trimming</td>
</tr>
<tr>
<td></td>
<td>• Aligns foil for fin plates and edge bar attachment</td>
</tr>
<tr>
<td></td>
<td>• Holds the plate together until epoxy is set</td>
</tr>
<tr>
<td>Clamping Plate and Frame</td>
<td>• Used to stack HTPs together and ensure clamping pressure is</td>
</tr>
<tr>
<td></td>
<td>distributed evenly</td>
</tr>
</tbody>
</table>

A 100-kW station was designed to test the Makai-designed EBHXs with a nominal duty of 100 kW. For the EBHXs, the working fluid is propane because ammonia is incompatible with epoxy.
The 100-kW station is capable of seawater flow rates up to 650 gpm and propane mass flow rates up to 0.35 kg/s.

The 100-kW station has slots for two EBHX’s (an evaporator and a condenser). An APV titanium plate-and-frame heat exchanger is installed as the accompanying heat exchanger for use during EBHX performance testing. The APV plate and frame heat exchanger functions as an evaporator during EBHX condenser testing and as a condenser for EBHX evaporator testing. An established heat exchanger was used to ensure performance of the tested heat exchanger would not be limited by an untested accompanying heat exchanger.

Figure 4.1.1. Epoxy-Bonded Heat Exchanger (EBHX) condenser and evaporator at the 100-kW test station. The APV companion heat exchanger is the vertical blue component in the background.

On the working fluid side, when propane is boiled in the evaporator, saturated propane enters the separator tank. Propane vapor exits the separator vapor outlet and is condensed in the condenser. From the condenser, liquid propane drains into the buffer tank. The feed pump pumps liquid propane out of the buffer tank into the recirc pump intake line. Liquid propane from the separator liquid outlet is also piped into the recirc pump intake line. The recirc pump pumps liquid propane back into the evaporator. A vapor Coriolis flow meter at the separator vapor outlet measures the propane vapor flow. Pressure and temperature sensors are located at the inlet and outlet of the EBHXs but not in the other portions of working fluid piping.

On the seawater side, seawater flow is measured on a section of the discharge piping that is common to EBHXs but not the accompanying APV heat exchanger. Seawater pressure and temperature sensors are located at the inlet and outlet of the EBHXs but not on the accompanying heat exchanger. The accompanying seawater flow is not measured.

Installation and shakedown testing was completed in November 2014.
The 100-kW station met its designed purpose for testing EBHXs but several areas could be improved with modifications. A check valve between the feed and recirc pump would improve recirc pump operational stability. Horizontal pipes should be angled so propane can be more easily drained and additional valves would make the process of changing out heat exchangers more efficient. More sensors could provide insight into the working fluid state throughout the system. These lessons learned will be incorporated in upcoming modifications to the 100-kW station to support testing of Makai’s FFHXs using ammonia as the working fluid.

Six EBHXs – two evaporators and four condensers – were tested at the 100-kW station. Each heat exchanger had six plates but the fin pitch (in fins per inch, FPI) and thickness, foil material and thickness, and epoxy thickness were varied between the heat exchangers. Regardless of configuration, each heat exchanger was 1.5 m in length and the total heat transfer area was 5.04 m². The configurations and properties are summarized in Table 4.1.2.

The condensers were tested at cold seawater flow rates from 200-600 gpm and at duties from 40-100 kW. The evaporators were tested at warm seawater flow rates from 200-500 gpm and at duties from 40-80 kW.

The seawater channel widths between the plates were the same for each heat exchanger but we attempted to preferentially divert seawater flow away from the channels on the end (because there is no heat transfer on one side) by restricting the end channel widths using epoxy. For the condenser, the epoxy detached from the header during the first test. The epoxy restriction remained intact for the evaporator. Seawater pressure drop (SW dP) is plotted versus seawater flow velocity in Figure 4.1.2 to remove the effects of different seawater flow cross sectional areas. For EBHX-4 and -5, a small adjustment was also made to account for the Al foil being thicker than the Ti foil. Except for EBHX-4 and -5, the SW dPs agreed to within 5 kPa.
Table 4.1.2. Summary of EBHX configurations.

<table>
<thead>
<tr>
<th>Type</th>
<th>Specifications</th>
<th>Epoxy Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBHX-1</td>
<td>Condenser 5 plates of 26 FPI and 1 plate of 51 FPI, all with Ti foil</td>
<td>0.381</td>
</tr>
<tr>
<td>EBHX-2</td>
<td>Condenser 5 plates of 39 FPI and 1 plate of 51 FPI, all with Ti foil</td>
<td>0.381</td>
</tr>
<tr>
<td>EBHX-3</td>
<td>Condenser 6 plates of 51 FPI, all with Ti foil</td>
<td>0.381</td>
</tr>
<tr>
<td>EBHX-4</td>
<td>Condenser 4 plates of 17 FPI with Ti foil and 2 plates of 17 FPI with Al foil</td>
<td>0.381</td>
</tr>
<tr>
<td>EBHX-5</td>
<td>Evaporator 6 plates of 17 FPI, all with Al foil</td>
<td>0.762</td>
</tr>
<tr>
<td>EBHX-6</td>
<td>Evaporator 6 plates of 51 FPI, all with Ti foil</td>
<td>0.381</td>
</tr>
</tbody>
</table>

Figure 4.1.2. Seawater pressure drop (SW dP) vs Flow Velocity for all six EBHXs
Some of the discrepancy in SW dP may be due to inaccuracies in the width of the outermost seawater channels. Agreement is poor for EBHX-4 and EBHX-5; both were 17 FPI and contained Al foil. It is possible that the lower fin density allowed for slightly deeper ripples in the foil which increased resistance in the seawater flow channel and resulted in higher pressure drop. However, it is unclear why EBHX-3 differed from EBHX-6; the same plates which were initially used in EBHX-3 were re-used for EBHX-6.

The U-values for the heat exchangers must also be carefully interpreted. There was no significant difference in U-value between the two evaporators tested. For the condensers, EBHX-3 and EBHX-4 had highest and second highest U-values, respectively. Several factors make the results difficult to interpret.

First, for the condensers, EBHX-1 and -2 had 5 plates of the same fin pitch and 1 plate of 51 FPI. It is unlikely that working fluid flow was uniform between all 6 plates and it is unclear how performance may have been affected. For example, it is conceivable that most of the heat transfer occurred in the 5 plates and little propane vapor entered the 51 FPI plate due to increased pressure drops associated with the smaller cross sectional area.

Another confounding factor that is applicable to both the evaporators and condensers and specific to the EBHX design, is the effective heat transfer area. Heat transfer from propane to seawater occurs mostly in the fin crest region, where epoxy is thinnest. Epoxy is thicker on other parts where the fin and foil are joined. A layer of epoxy also covers the exposed foil between the fins, acting as an insulator and reducing any heat transfer directly through the foil. According to computer models, the contact area is greatest for 17 FPI, followed by 39 FPI, 26 FPI, and 51 FPI; there is ~11% less contact area for 51 FPI compared to 17 FPI. Of course, some variation during assembly is expected. Greater effective heat transfer area should equate to better performance.

Finally, we must also consider difference in thermal conductivity between Al and Ti foils. For the evaporator, EBHX-5 had aluminum foil and EBHX-6 had titanium foil. For the condenser, EBHX-3 had two plates with Al foil while the remaining condensers all used Ti foil. Although the aluminum foil is thicker, the thermal conductivity of aluminum is almost ten times that of titanium.
Figure 4.1.3. Comparison of evaporator U-value vs seawater flow at 40 kW and 60 kW. There is no significant difference between the two evaporators.
Figure 4.1.4. Comparison of U vs seawater flow at 60 kW and 80 kW (top and bottom graphs respectively). EBHX-3, with 6 plates of 51 FPI and Ti foil, had the highest U-value. The EBHX-4 had the second highest U-value.
It is difficult to draw conclusions from the EBHX testing results because there were often several variations between the different heat exchangers. Both evaporators had comparable performance in terms of U-value and working fluid dP. Seawater dP for the EBHX-5 was the highest of all heat exchangers tested. EBHX-3 was the best performing condenser. However, it is unclear whether the degree of improved performance was due to the higher fin density or whether non-uniform working fluid distribution suppressed U-values for the EBHX-1 and -2 low. EBHX-4 performed nearly as well as EBHX-3; the reasons are most likely a combination of the larger contact foil-to-fin contact area at the fin crests, the addition of Al foil for two plates, and improved seawater side convection due to deeper corrugations in the foil.

The turbine generator, including all the structural, mechanical, and electrical systems was successfully installed at the OERC in May 2015. The structural modifications to the testing tower included the addition of a fourth floor for the turbine generator skid. The turbine, gearbox, generator, lube oil system, and electrical / instrumentation panels are mounted on the turbine generator skid. A compressed air system for the turbine control inlet valve (TCIV) and a cooling water system for the lube oil system were also installed. The ammonia vapor piping from the separator outlet to the condenser inlet was modified to include a branch for turbine operations.

![Figure 4.1.5. Layout of turbine deck on the fourth floor of the Ocean Energy Research Center (OERC).](image)

The electrical system consists of the generator, switchgear, loadbank, battery bank, the overspeed resistors, and all the instrumentation and control system. Most of the instrumentation and control starts (or ends) at the Generator Control Cabinet (GCC) located in the Makai office. The GCC also houses Woodward ATLAS II governor (TCIV controller), Schweitzer SEL-700G0 (monitor for the grid tie breaker), Marathon DVR 2000E+ (voltage regulator), HMI 5070L (touchscreen interface for ATLAS), and various meters and switches for manual operation.
Turbine commissioning took place in May and June 2015. A month-long break was necessary to complete modifications to the electrical system. During commissioning, turbine control and safety features were verified. ATLAS control constants were also tuned to ensure a smooth startup.

Although the turbine was aligned, high vibrations and noise were observed during initial operations. One source of the vibration was the permanent magnet generator (PMG), which was not securely mounted on the generator shaft.

When vibrations and noise were still observed after the PMG was correctly mounted, further investigation identified an interference issue with the turbine shroud. The turbine design included a shroud that was fitted onto the turbine blade ring to improve efficiency by reducing the tip clearance (and leakage rate). The shroud was designed to rotate with turbine blades. Sometime during commissioning or operational testing, the shroud slipped about halfway (axially) down the turbine blade ring and was rubbing against the housing. The turbine was removed from the OERC and sent back to the manufacturer to correct the problem. A new shroud was fabricated, this time press fit into the stationary housing instead of onto the rotating blade ring. This new design resulted in a larger tip clearance and was predicted to reduce efficiency by 1% according to the manufacturer.

A separate issue with the gearbox oil was identified during the vibration troubleshooting. Gearbox oil was observed to be very dark colored, indicative of overheating. The gearbox was returned to the manufacturer for inspection. No bearing damage was identified and a faulty oil heater was the most likely cause of the burnt oil. The heater elements were replaced and the gearbox was reassembled without modification.

Makai also replaced the low-speed coupling. Initial vibration measurements on the turbine and gearbox were high when coupled with the generator but within specification when uncoupled from the generator. We suspected misalignment introduced through the coupling may have contributed to the high vibrations. The original set-screw mount low-speed coupling was replaced with a taper lock low-speed coupling.

At the same time, the generator was also removed from the OERC and sent out for re-balancing as a preventative measure in case the vibration issues adversely affected the generator.

Finally, modifications were also made to stiffen the turbine skid by adding a new W8x31 beam between the existing W12x40 beams to reduce flexing of the skid (Figure 4.1.6). Alignment and vibration monitoring was performed again when all components were re-installed. No further issues were identified.
Figure 4.1.6. Turbine skid stiffening modifications.
Turbine performance can be characterized by looking at pressure drop and flow across the turbine and isentropic efficiency. Turbine pressure drop is calculated from the inlet and outlet pressure sensors. The highest pressure drop recorded during testing (using two evaporators and three condensers) was ~ 301.5 kPa and that corresponded to an electrical power output of almost 88.3 kW. Based on estimates from collected data, 325 kPa is required to produce 100 kW. Turbine flow cannot be directly measured and is calculated using the liquid ammonia flow sensors and tank and separator-receiver line levels. Based on collected data, approximately 3.5 kg/s of ammonia vapor flow is required to produce 100 kW. The dP vs Power curve predicts the power to within 10% of the manufacturer’s targeted data points provided in the design document (CDR). The turbine flow vs power curve is up to 20% off, but inaccuracies associated with calculating turbine flow likely contribute to the error.

![Power vs dP](image1.png)

![Power vs Flow](image2.png)

Figure 4.1.7. Turbine power vs dP and ammonia flow. Turbine flow is calculated using a combination of flow sensors and integrated level sensors, so more variability is expected. Based on the projected curve fit, to produce 100 kW, dP needs to be ~ 325 kPa and ammonia vapor flow needs to be ~3.5 kg/s. Manufacturer provided points are marked by ‘X’s.

Calculating turbine efficiency is more complex. During heat exchanger testing, ammonia vapor from the expansion valve outlet to the condenser inlet is slightly superheated; thermodynamic properties can be calculated using pressure and temperature. During turbine operations, depending on the seawater flow rates, temperatures, and turbine power output, ammonia at the turbine exit and condenser inlet may be saturated with unknown quality. Without quality, the enthalpy at the turbine outlet is unknown, and therefore, the isentropic efficiency and turbine work is unknown.
The work required to spin the turbine and gearbox (decoupled from the generator) at 1800 rpm should be constant. For certain combinations of seawater flow rates, when the generator is decoupled and but the turbine and gearbox are spinning at 1800 rpm, ammonia vapor can exit the turbine in a superheated state. By testing several seawater flow combinations and using only data when turbine outlet conditions are superheated, the work required to spin the turbine and gearbox can be found. The resulting averaged gearbox work is 5.75 kW (Figure 4.1.8). Gearbox work can be added to power produced (after taking into account generator efficiency) to find the total work done by ammonia. The total work can then be used to solve for turbine outlet conditions and isentropic efficiency.

Turbine outlet enthalpy in saturated conditions can be calculated using:

\[
h_{\text{turbine outlet}} = h_{\text{turbine inlet}} - \frac{\text{Total Work}}{m_{\text{ammonia}}}\]

where Total Work = Gearbox Work + \(\frac{\text{Generator Electrical Output}}{\text{Generator Efficiency}}\). Because TCIV was 100% open during operational testing, turbine inlet enthalpy was calculated using the temperature and pressure sensors at the turbine inlet vice the separator outlet. Quality was calculated using the turbine outlet pressure and the turbine outlet enthalpy. The turbine design document predicted “2.4% wet at the nozzle discharge”, or a quality of 97.6%. In our data, for the observed turbine inlet and outlet conditions, if isentropic efficiency were 100%, the quality would be no less than 98%. The calculated quality was always greater than 98.4% and decreased with increasing power.
Figure 4.1.8. The work required to spin the turbine and gearbox averages to be 5.75 kW. Ammonia vapor flow is likely non-uniform when turbine control inlet valve (TCIV) is less at 48% open. Enthalpy at the separator vapor outlet (h2b) was used instead of enthalpy at the turbine inlet (h3).
Figure 4.1.9. Turbine outlet quality and isentropic efficiency were calculated using gearbox work $= 5.75$ kW. The manufacturer target for turbine isentropic efficiency is 68% and predicted 97.6% quality at the turbine outlet. Generator efficiency was calculated by interpolating based on power and power factor from manufacturer provided curves.

Isentropic efficiency is calculated using:

$$ \text{Isentropic Efficiency} = \frac{h_{\text{turbine inlet}} - h_{\text{turbine outlet}}}{h_{\text{turbine inlet}} - h_{\text{turbine outlet, isentropic}}} $$

Isentropic efficiency is dependent on the power output and approaches 70%. The design specifications targeted 68% at full-load. Again, because turbine outlet enthalpy is calculated using turbine ammonia flow, the instability in flow is most likely the cause of the data scatter at high power.

Overall, turbine performance is in agreement with the manufacturer provided data. There is significant room for improvement in turbine efficiency. However, as efficiency changes with power output, it may be more important to design for maximum power output, taking into consideration the seasonal variations in seawater temperature rather than maximizing efficiency for a single operating condition.

Part of turbine testing was performed on the loadbank. The loadbank is a series of resistors that can be configured to provide from 0 to 105-kW resistive load in 1 kW increments. The turbine generator output is connected to the loadbank via the loadbank breaker on the GCC. One safety feature is that the loadbank breaker cannot be shut if the grid tie breaker is shut. When the loadbank
breaker is shut, there is a small load because the loadbank blower is powered from the generator output. Digital output signals, controlled from the OTEC Control System, are used to add resistive load. When a load is applied, the generator slows and ATLAS opens the TCIV to speed the generator back up to 1800 rpm. Likewise, when a load is removed, the generator speeds up and ATLAS responds by closing the TCIV to maintain speed at 1800 rpm. Load shedding at 1 kW/second resulted in the generator tripping on overspeed; load changes on the loadbank should be limited to 1 kW/5 seconds. Loadbank testing is not reflective of load changes during grid testing. During grid testing, generator speed is locked in to the grid frequency so load changes can happen as quickly as ATLAS can move the TCIV.

**OTEC System Testing**

Different heat exchanger combinations were used in OTEC system testing. Each heat exchanger had best practice operating conditions, for example, maintaining the APV evaporator at least 50% full of liquid ammonia improved performance, whereas this was not necessary for the CHART evaporator.

The OTEC system was less stable at high power using two (APV and CHART) evaporators and all three condensers. Steady state operations were difficult because it was difficult to control ammonia flow. Proportioning ammonia flow on the evaporator side required trial and error to find the right balance. Bottling in the condensers complicated our ability to maintain stable ammonia flow. At various times, although the buffer tank was nearly empty, liquid ammonia could be seen in the ETHX sight glass (higher elevation than the buffer tank inlet) even when there was little to no difference between condenser and buffer tank pressure. In addition, trying to keep SRLS level between 15-85% made it difficult to keep consistent liquid ammonia flow into the evaporators. The pressure difference between the receiver tank and the evaporator was at times too high for the recirc pump. Instabilities in ammonia liquid flow carry over because turbine ammonia flow is calculated from flow sensors and changes in tank and separator receiver line levels. The increased scatter in Turbine Power vs Flow at higher flow rates and power are most likely due to inaccuracies in flow calculation.

For a fixed heat exchanger configuration, power production is affected by variations in seawater flow rates and seawater temperatures. For an offshore OTEC plant, seawater flow rates may vary due to platform motion. In order to simulate open ocean wave conditions, warm and cold seawater control valves were moved cyclically to produce a sinusoidal flow rate (Figure 4.1.10). Without ATLAS intervention, power fluctuated +/- 1.7 kW with cold seawater variations of 75 gpm amplitude and 20-second period. With ATLAS trying to maintain a set power, the same seawater fluctuations produced +/- 1.5 kW fluctuations in power. ATLAS gains were not tuned to effectively maintain power under the seawater fluctuation condition that we tested. It is most likely
that the gains have to be adjusted higher to allow for quicker response if required to hold a fixed power.

Under warm seawater fluctuations of 150 gpm in amplitude and 20-seconds in period, gross power only fluctuated +/- 1 kW. At first, it appears that changes in cold seawater have a greater effect on power; however, we must consider that the test was performed using the APV condenser and the average cold seawater flow rate was 1250 gpm, which is at the lower limit of flow for power production. It follows that small fluctuations at the lower extreme has greater impact on the system. This test should be repeated at higher power and higher flows prior to changing the gains in ATLAS.
Figure 4.1.10. Comparison of fluctuations in gross power under 1) no seawater fluctuations, 2) warm seawater fluctuation of 150 gpm with 20-second period, 3) cold seawater fluctuation of 75 gpm with 20-second period, and 4) cold seawater fluctuation of 75 gpm with 20-second period and ATLAS attempting to maintain gross power at 10 kW. ATLAS could not respond quickly enough to maintain a significant improvement in power fluctuation over the case where TCIV remained fixed at 100%. However, the low flow condition for cold seawater may be the lower flow limit for the APV condenser. Future testing conducted at higher flow rates may not reveal as large fluctuations in power and the TCIV may perform better at maintaining a fixed power.
Makai completed major revisions to the OTEC Control System, the user-interface to remotely operate the OTEC system. The revisions include:

- Autonomous controls mode
- Long-term heat exchanger performance monitoring
- Updated to feed pump controls logic
- In situ sensor checks
- Streamlining of data collection

Autonomous controls help streamline operations at the OERC by performing testing and operations according to a test plan, which reduces the need for human intervention. Autonomous controls can be used to start up the OTEC system or to transition the OTEC system to a specific operating condition from any state. Autonomous controls also has the added advantage of being able to efficiently monitor trends and take actions to prevent failures or provide notifications of anomalies. In order to preserve the flexibility of the OTEC system as a testing facility and to provide operational experience in OTEC power production, the OTEC Control System has three modes of operation when in autonomous mode: 1) Power Plant Operations, 2) OTEC System Testing, and 3) Heat Exchanger (HX) Testing. In Power Plant Operations, the OTEC Control System can either operate at the maximum net power or hold a fixed net power. In OTEC System Testing and HX Testing, the OTEC Control System follows a user-specified test plan.

There are three layers of controls in the OTEC Control System. In the first layer of controls, control valves and pumps can be directly manipulated by setting the position of the control valve, the pump frequency, or turning the pump on or off. Pump frequency and pump power changes almost instantaneously. The rate of adjustment for control valves is only restricted by the time it takes for the control valve to move. The second layer of controls utilizes local control systems. Local control systems are a grouping of control valves and/or pumps that work together to control a parameter. For example, the warm seawater flow local control system consists of an 18” and a 4” control valve and both are used to control warm seawater flow. When activated, the local control system adjusts valves and/or pumps so the controlled parameter gets to and remains at the target setpoint. Finally, the third layer of controls is autonomous controls. Autonomous controls can directly manipulate valves and pumps, turn pumps on and off, activate/deactivate local control systems, and manipulate setpoints for local control systems.

One of the lessons learned in developing the OTEC Controls System logic was that in a saturated system, small changes can propagate throughout the system. For example, when ATLAS moves the TCIV, evaporator and condenser pressure is affected, which affects ammonia flow, and ultimately evaporator duty. To better stabilize the system and prevent oscillations, the controls utilize a modified proportional-differential (PD) controller which is based on matching the rate of change of the current value (slope, continuously calculated using data from the previous 10
seconds) to a target slope. The error (the difference between the setpoint and the current value) is used to find the target slope from a pre-established look-up table. In other words, the controls are based on affecting the rate of change of the current value towards the setpoint instead of the absolute error.

A secondary advantage to the modified PD controller is the same set of gains can be used for all the operating conditions. The OTEC system is designed to accommodate a wide range of duties, flows, temperatures, and pressures for testing. In a traditional PD controller, each set of conditions would require a unique set gains; tuning of gains can be an extensive, time intensive task.

The controlled parameter can also affect OTEC system stability. For example, when the feed control system is controlling buffer tank level, feed flow into the receiver tank may not be steady. These pulses of cold ammonia from the buffer tank lowers receiver tank pressure, which changes the dP of the recirc pump, which results in oscillations in ammonia flow into the evaporator. Evaporator duty and power also oscillate. The oscillations in ammonia flow can lead to unsteady flow from the condenser into the buffer tank, thereby continuing the cycle of pulses of cold ammonia into the receiver tank. This situation can be resolved by controlling feed flow instead of buffer tank level, which results in a steady, stable condition.

The key takeaways are that stability and slow changes are more important for an OTEC Control System than trying to quickly get to a setpoint.

Long-term monitoring and in situ sensor checks were also included in the revised OTEC Control System. Pressure sensors are calibrated prior to a testing effort but ammonia pressure sensors in the vapor piping are now also checked against each other during stable, no-flow periods. By performing this check immediately after calibration and then periodically during testing, sensors that deviate significantly from the average or begin to drift are identified. Seawater pressure sensors at the heat exchanger inlet and outlet can also be checked in a similar manner. With the heat exchanger primed but under no flow, the difference between the inlet and outlet pressure sensor, i.e., static head, is recorded. Static head is rechecked any time there is a no flow condition. An accurate static head measurement is important because it is used to calculate heat exchanger seawater side losses, which is a component of heat exchanger performance. Sudden changes in dP vs flow could be indicative of a pressure sensor failure, a flow sensor failure, or an issue with the heat exchanger. If static head matches the historical data, pressure sensor failure may be eliminated. Finally, the pressure and temperature sensor at the evaporator outlet during operations should indicate saturated conditions (within sensor accuracy). Gross deviations may indicate sensor failure or a physical anomaly that requires further investigation. The addition of these operational sensor checks makes the OTEC Control System and data collection more robust.
Autonomous can be more effective at identifying trends and intervening to correct potential problems, thereby improving OTEC system reliability and stability while minimizing human intervention. Autonomous controls can be more efficient in power plant operations where an OTEC power plant can be directed to produce the maximum net power possible or operate as dispatchable power source. Instead of relying on a human operator to manually optimize flow rates and determine the required operating conditions, Makai has developed the logic for the autonomous controls to perform OTEC system optimization to provide maximum net power or operate in dispatchable power mode; this logic can be applied to future dedicated OTEC power plants.

**Corrosion Testing**

Corrosion testing continues work conducted under previous APRISES programs. This section summarizes Makai’s corrosion-related findings under APRISES12, from October 2013 to September 2014 only.

In September 2014 corrosion testing included box samples, flat coupons in 3-point racks, representative heat exchanger samples, flat samples in the Multi-Column Imaging Rack (MCIR), and tubular samples in the biofouling rack.

Four-year box samples were removed and processed in May 2014. Samples performed well in warm seawater, mixed in cold seawater, and poorly in deep seawater. In WSW, two (one of Alloy 1100 and one of Alloy LA83I) of the 24 samples had a pit; no pits were found on the remaining 22 samples. Alloy 3003 was the best performer in warm seawater, with a maximum pit depth of < 0.1 mm on one sample. In CSW, Alloys 1100 and 6063 were severely pitted. Both Alloy 6063 samples had deep extrusion defects that were likely pit initiation sites. Both Alloy 1100 samples exhibited severe crevice corrosion. A few pits were identified on the remaining samples but pitting was not severe. Most pits identified by the profilometer were less than 0.1mm deep and could not be found under microscope examination. Alloy 3003 and LA83I were the best performers but each alloy had some severely pitted samples that were removed previously. For Alloy 3003, the pitted sample also had extrusion defects. In DSW, all samples had severe pitting. Although Alloy 3003 performed the best with pits up to 0.5 mm deep. Warm seawater pre-treatment samples performed better than untreated CSW samples. Although Alloys 1100 and 6063 had large pits, pits on the remaining alloys were small and few.

Flat samples were still being tested in September 2014. No pits were observed on the WSW samples. The WSW samples that were still tested were: 1) Alloy 3003 virgin, heat-treated, machined, tee, and welded samples; 2) FSW samples; 3) untreated Alloy 3003, 5052, and 6063 samples; and 4) Alloy 5052 and 6063 electropolished samples. All flat samples in CSW had pits.
The only flat samples remaining were the Alloy 3003 virgin, heat-treated, and welded samples. All other flat samples in CSW were severely corroded and removed earlier.

Representative heat exchanger samples were also being tested. No pits were observed in WSW samples. CSW samples were susceptible to crevice corrosion at the gasket interface, indicating low flow areas should be minimized in heat exchanger design or treated to prevent crevice corrosion.

Four pit mitigation treatments – warm seawater pre-treatment, sulfamic acid, citric acid, and ozone – were being tested in the MCIR in WSW and CSW. In WSW, samples had been tested for 1.3 years and neither the control nor any of the treated samples had pits. In CSW, the control sample had been tested for almost 2 years. The treatment samples were started at different times; exposure times ranged from 0.65 to 1.1 years. Pits were observed on the control sample after 125 days. The warm seawater pre-treatment sample did not have any pits after 1.1 years. Acid treatments were performed either every 2 months or when OCP rose above -800 mV. In the sulfamic acid 2-month interval sample, corrosion product was observed on the trailing edge of the sample after two months. No pits were identified on the sulfamic acid OCP-based interval sample. Pits were observed after eight months on the citric acid 2-month interval sample while no pits were found on the citric acid OCP-based interval sample. The ozone treated sample in CSW had pits 45 days after testing had started. Warm seawater pre-treatment and sulfamic-acid treatments on OCP-based intervals were the most effective at preventing pits.

A biofouling control experiment was also conducted to determine if there was a better treatment than hypochlorination (bleach). Ozone and iodine treatments were tested but hypochlorination was still the best treatment. The iodine system was complex and had multiple equipment malfunctions that most likely resulted in ineffective treatment. Monthly ozone treatment was ineffective in preventing biofouling, there was little difference between the ozone and control samples.

Conclusions

Makai tested six configurations (four condensers and two evaporators) of Epoxy-Bonded Heat Exchangers (EBHXs) at the 100-kW testing station with propane as the working fluid. Both evaporators had similar performance. The condenser with the highest fin density – 51 FPI – had higher U-values compared to the other condensers. Conclusions were difficult to draw from EBHX testing because several variables were changed between configurations. Overall, Makai believes that the fin-foil contact area (fin density x contact length) and material thermal conductivity are most important in determining the overall heat transfer coefficient.
Seawater dP should have been comparable for all condensers and all evaporators but both 17 FPI EBHXs had higher dPs than the other EBHXs. Surprisingly, the 51 FPI condenser also had a higher dP even though the same plates were used in the 51 FPI evaporator. Differences in foil ripple depth are most likely the contributing factor to differences in seawater pressure losses.

With EBHX testing, Makai demonstrated the viability of a fin-foil type heat exchanger. Laser-welded FFHXs are expected to have improved performance because there is no epoxy layer insulating the working fluid side of the foil. Also, because there is no epoxy, ammonia can be used as the working fluid. Improvements to the 100-kW testing station were completed under APRISES13 in 2018 and were followed by FFHX testing.

As part of OTEC system testing, Makai performed turbine characterization tests. Turbine operations complicate ammonia system measurements in two ways: 1) ammonia vapor flow cannot be directly measured as the vapor Coriolis flow meter is bypassed and 2) ammonia exits the turbine in a saturated state of unknown quality. Ammonia vapor flow is calculated using the other ammonia flow sensors and level sensors in the system. A series of tests were set up to find the gearbox work, which, along with a manufacturer provided generator efficiency curve, was used to calculate turbine quality and turbine isentropic efficiency. At higher power setpoints, the turbine is performing to within 10% of the isentropic efficiency specified in the design document. For turbine pressure drop vs generator output, the turbine is performing within 10% of the points provided in the turbine design document.

After the installation of the turbine generator, Makai gained OTEC operational experience that was used to revise the OTEC Control System, which now includes an autonomous controls mode. Autonomous mode is capable of starting up the OTEC system or transitioning the OTEC system to a specified operating condition from any starting condition. Heat exchanger and OTEC system testing can be performed autonomously according to a test plan. Another significant advantage of the autonomous mode is the ability to efficiently perform operational sensor checks and identify sensor malfunctions. This function was included because the autonomous mode relies on accurate instrument readings to determine operating conditions and send appropriate control outputs. Finally, autonomous mode also monitors trends in the OTEC system and performs actions to mitigate potential failures and/or sends notifications about potential problems. The autonomous mode makes the OTEC Control System more reliable and robust and provides a logic basis transferrable to future OTEC power plants.

Corrosion testing has focused on aluminum alloys because of their cost-effectiveness and flexibility of fabrication methods. Testing exposes samples to warm surface seawater (WSW) or cold seawater from a depth of 674 m (CSW) or 915 m (DSW). With the expected lifetime of a heat exchanger in mind, Makai determined that the uniform corrosion rates of the aluminum alloys tested were acceptable. However, after two years of testing, localized corrosion – pitting, crevice
corrosion, or a combination of both – began to appear. Box coupons have been tested for over four years. To date, samples exposed to WSW have been performing well; only a few samples have small, shallow pits. Alloy 3003 has been performing the best in WSW, with a maximum pit depth of 0.1 mm identified on a 3-year sample. The worst performer in WSW was Alloy 1100 with a maximum pit depth of 0.5 mm. In CSW and DSW, all alloys have been susceptible to pitting and/or crevice corrosion. Alloys 3003 and LA83I were the best performing alloys in CSW; yet each alloy had severely pitted samples. For Alloy 3003 in CSW, the two-year sample with extrusion defects was the only severely pitted sample. For Alloy LA83I in CSW, three severely pitted 21-month samples were removed. Alloys 1100 and 6063 were the worst performers in CSW; samples from both alloys had pits greater than 1 mm deep. In DSW, Alloy 3003 was the best performer but still had pits up to 0.5 mm deep. Samples from all other alloys had deeper pits and greater pit coverage area.

Untreated aluminum alloys may not be suitable choices for condensers. The representative heat exchanger samples tested in CSW began to show crevice corrosion at the gasket interface within 2 months. Makai’s research indicates pre-treatment using warm seawater exposure has led to some protection against pitting. OCP-based treatment with sulfamic and citric acid has also produced promising results.

Finally, both WSW and CSW samples have experienced some degree of biofouling. With improvements in the chlorine delivery system, darkening of test rooms, and shielding of seawater supply pipes, the severe biofouling issues have been resolved. An iodine infusion system was tested but equipment failures prevented reliable assessment. Ozone treatments at the concentrations and intervals tested were inadequate as biofouling control, but more significantly, ozone treatments enhanced pitting in CSW samples. Ozone treatment is not being pursued at this time. Hypochlorination, when performed daily, has been effective in controlling biofouling.

4.2 Wave Energy Testing

In support of the Navy’s evolving needs at the Wave Energy Test Site (WETS) off Marine Corps Base Hawaii, HNEI subcontracted with Sea Engineering, Inc. to conduct a market study, procure an ROV, utilize the ROV for various functions at WETS, and provide a final report on the selection process and initial assessment of ROV utility in support of wave energy testing. This was done in consultation with HNEI and NAVFAC.

The original APRIVES12 SOW in this area had focused on two areas of support to WETS; enhanced wave resource characterization through the deployment of two Waverider wave buoys to feed wave forecast and hindcast modeling tools, and testing of prototype/scaled devices at UH’s
Makai Research Pier. As WETS research support priorities evolved over time, funds were redirected from these tasks. Specifically, Waverider buoys were ultimately procured with US Department of Energy funds, and with separate other ONR funds not under APRISES 12. DOE and NAVFAC funds have adequately supported our research to develop a wave forecast tool with high-resolution wind forecasting, as well as a multi-decadal wave climatology to support operations and wave energy converter (WEC) deployment planning and device design.

Further, the idea of testing WEC prototypes at Makai Research Pier has not materialized. While it was envisioned that such a facility would be useful to WEC developers as a step in the direction of larger-scale testing at the open-ocean WETS facility, developers to date have not utilized this facility. Rather, most developers are employing a build-test-build approach that utilizes wave tank facilities and/or local waters near their location of development. This generally proves more cost effective for them than doing scaled testing in Hawaii. While it remains possible that future WEC developers may desire such a test location as Makai, particularly for a Hawaii-based company/development, it was determined that these funds were better utilized in other ways.

However, an emerging need in support of WETS was that of a more robust ROV than the small inspection class ROV that is available through HNEI’s marine services contractor, Sea Engineering. This inspection class ROV is limited in its ability to conduct inspection in currents, has fairly low-resolution video capability, and cannot support tools, such as cutting tools and calipers, that are useful when conducting inspections and minor maintenance on WEC moorings and/or WECs themselves. For this reason, Sea Engineering, in consultation with HNEI and NAVFAC selected, procured, and assessed an ROV, the Sub-Atlantic Forum Super Mohawk (Figure 4.2.1).

![Figure 4.2.1 Forum Energy Technologies Sub-Atlantic Super Mohawk remotely operated vehicle (ROV) selected for use at WETS.](image-url)
The ROV has been delivered to Hawaii, integrated with the WETS site-dedicated support vessel, and put through initial trials and operations. The full final report prepared by Sea Engineering, including appendices for requirements development, market analysis, procedural analysis, ROV purchase documentation, installation aboard the site-dedicated vessel, and operational assessments, is listed below in Reports Resulting from these Efforts, and is available on the HNEI website.

This ROV adds a critically important capability to HNEI’s support to the Navy WETS. With numerous WEC deployments coming to WETS in the 2018-2022 timeframe, the Super Mohawk will be put to use on a regular basis to conduct inspections of mooring hardware and WEC systems (under other funding). Additionally, the deep berth mooring systems at WETS have experienced unexpected wear and failures in the four years since initial deployment in September 2014. As a result, mooring repairs are planned in the coming months under other funding, along with an increased awareness of the critical nature of regular ROV-based inspections of these systems. The new ROV will allow careful inspection of various mooring components known, through numerical analysis, to be potential “hot spots”, or fatigue points, such as joining links, padeyes, shackles/pins, etc. Calipers and high-resolution video will allow assessment of corrosion relative to numerical assumptions, which is particularly important for elements of the systems that will remain in place after the repairs are conducted. In summary, the robust inspection capability afforded to WETS through the purchase of this larger, more powerful ROV, as well as its ability to conduct many light work functions, detailed in the report listed below, will inevitably enhance achievement of Navy test objectives in support of advancing wave energy for potential application to Navy shore infrastructure and offshore energy needs.

More detail is available in the following report on the HNEI website.

Wave Energy Testing ROV Final Report, prepared by Sea Engineering Inc. for Hawaii Natural Energy Institute, University of Hawaii, June 2018.

4.3 Seawater Air Conditioning (SWAC)

To understand the environmental impacts of novel marine renewable energy developments, a comprehensive and long-term oceanographic monitoring program continued under APRISES12 at the proposed seawater air conditioning (SWAC) site. A from District-scale SWAC has been proposed for downtown Honolulu, Hawaii. Under previous APRISES funding, an oceanographic monitoring program was initiated and continued to be maintained under APRISES 12 to assess the environmental impact of this new system on the ocean ecosystem near Honolulu. The proposed SWAC system, to be built by Honolulu Seawater Air Conditioning Inc., will use cold, deep
seawater to air condition buildings via a land-based heat exchanger. The system will upwell water from 500 m, heat the water, and release it back into the coastal ocean via a 20-port diffuser system spanning 100-140 m depth along the benthos (Figure 4.3.1a)

This monitoring program allows the investigation of novel questions regarding the impact of the SWAC system and the artificial deep water upwelling it will create, and a thorough understanding of the pre-existing oceanographic conditions at the future site of the diffuser plume provides essential baseline information for the assessment of changes in the oceanographic environment. APRICES 12 supported oceanographic monitoring at the proposed SWAC site from 03/01/2013-09/30/2015 using 1) long term moored oceanographic instrumentation at the proposed diffuser site, and 2) conductivity-temperature-depth (CTD) profiles and water sampling from both the proposed intake and proposed diffuser sites (Figure 4.3.1b).

Figure 4.3.1a) Diagram showing the proposed seawater air conditioning (SWAC) system. b) Map showing proposed locations of the diffuser and intake for SWAC, and locations for water profiling and long-term moored instruments.

During the period funded by APRICES 12, seven deployments of the long-term oceanographic mooring were completed, and 13 CTD profiling and water sampling cruises were completed. The oceanographic mooring was deployed near-continuously at the proposed SWAC site, and instruments recorded time-series measurements of currents, temperature, salinity, pressure, dissolved oxygen, backscatter, turbidity, chlorophyll, nitrate, and estimated backscatter. The water column profiler took measurements throughout the water column for salinity, temperature, pressure, chlorophyll, turbidity, oxygen, and photosynthetically active radiation (PAR). Bottle samples were taken for oxygen, dissolved inorganic carbon, methane, nitrous oxide, chlorophyll, nutrients, and flow cytometry.
Data collection has allowed for a characterization of the physical and biological properties of the receiving waters of the SWAC system. SWAC-driven artificial upwelling will expel a diffused plume of warmed deep seawater into the 100-140 m zone of the Oahu, Hawaii slope. The plume will have higher nutrient levels and lower oxygen levels than ambient conditions (Figure 4.3.2a and 2b). It will be denser than ambient water, so the plume is unlikely to rise to the surface. High nutrient concentrations in the plume could lead to increases in primary productivity at depth or changes in the community size structure of phytoplankton. The 100-140 m range is slightly below the chlorophyll maximum (Figure 4.3.2a), but PAR data showed that irradiance levels at the effluent depth are sufficient to support net photosynthesis. The depth of the plume is at the base of the pycnocline, which could lead to rapid horizontal advection of the plume along an isopycnal surface and expansion of the spatial scale of impacts (Figure 4.3.2a).

Figure 4.3.2. a) Conductivity-temperature-depth (CTD) cast profiles and bottle data from the 100 and 150 m profiling sites (near the proposed diffuser). b) CTD cast profiles and bottle data from the 500 m profiling site (near the proposed intake). The black lines indicate the mean profiles and the colored lines indicate +/- 2 standard deviations.

Data collected from the long-term mooring show that mean flow at the site of the diffuser is near zero but oscillates tidally. Near-bottom currents oscillate in the across-shore direction, which could advect the plume upslope during certain tidal conditions (Figure 4.3.3). Currents in the mid and upper water column oscillate tidally in the more typical along-shore direction (Figure 4.3.3). Analysis of estimated backscatter data revealed that the mesopelagic boundary community will be
subjected to impacts from SWAC at both their daytime and nighttime depth habitats. The mesopelagic boundary community is an assemblage of micronekton primarily composed of myctophid fishes, squid, and shrimp. The community is associated with the slope of the island and undergoes a diel migration along the slope of the island. In their daytime habitat (near 500 m) entainment of organisms in the SWAC intake pipe is a risk (Figure 4.3.4a); in the nighttime habitat, the community’s depth range overlaps with the effluent plume (Figure 4.3.4b), and the introduced physical gradients may cause attraction to or avoidance of the affected region. Temperature, density, nitrate, chlorophyll, and oxygen all vary tidally and have high natural variability at the proposed diffuser site, due to the effects of internal tides (Figure 4.3.5).

Figure 4.3.3. (a) Bottom layer and mid-water current ellipses plotted over bathymetry show bathymetric steering effects. (b) Current ellipses in 4 m bins throughout the water column. The dominant direction at the bottom of the water column is in the across-shore direction, while in the mid and upper water column, the along-shore direction is dominant.
Figure 4.3.4. Contour plots of normalized estimated backscatter ($S_v$) (scale: 0–1) for a sample 10-day period. (A) Deployment at bottom depth 120 m, where estimated backscatter was generally higher at night. (B) Deployment at bottom depth 517 m, where estimated backscatter was generally higher during the day. (C) Close-up of the bottom layer for two days highlights the diel patterns (upper panel is from the diffuser monitoring area; lower panel is from the deep intake site).
Figure 4.3.5. Temperature-salinity plots showing the variability in density, nitrate, salinity, and fluorescence observed at the bottom mooring location. Trends are visible in these data, particularly that nitrate is higher in cooler, fresher water and oxygen and fluorescence are higher in warmer, higher-salinity water.

Overall, these baseline data provide an understanding of pre-impact conditions at the future SWAC site. More detail can be found in the publications listed below. Data from the CTD cast cruises is available at an open-access database (http://hahana.soest.hawaii.edu/cmoreswac/cmoreswac.html). The deployments of the long-term oceanographic mooring, water column profiling, and bottle sampling were also partially supported by APRISSES 13 funding (with more information available in publications and the final report on the HNEI website). Water column profiling and bottle sampling efforts were partially supported by other funding (NSF, Gordon and Betty Moore Foundation).

Publications and Presentations

Peer Reviewed Publications

**Contributed Presentations and Posters**

Comfort, C.M., Ostrander, C.E., McManus, M.A., Karl, D.M., Luther, D., Vega, L (2013). Observing ocean changes at the nation’s first SWAC system. OTEC Symposium, Honolulu, HI

Comfort, C.M., Ostrander, C.E., McManus, M.A., Karl, D.M., Luther, D (2014). Monitoring ocean changes in response to seawater air conditioning in Honolulu, HI. Ocean Sciences, Honolulu, HI


**TASK 5: GEOTHERMAL RESOURCE ASSESSMENT**

Funding for this task 5 was reallocated to other areas of the program as approved by ONR, as a result of the unforeseen loss of key geothermal faculty.

**TASK 6: MICROGRIDS/GRID INTEGRATION**

**6.1 Solar Monitoring**

PV performance testing and analysis conducted under APRISES11 and 13 were expanded under APRISES12 with the further development of an empirical model to characterize the impact of irradiation, ambient temperature, wind speed, soiling, shading, and aging. While previous efforts focused on the DC performance of individual PV modules, APRISES12 provides an analysis of
the AC performance of PV systems using various PV technologies, system configurations, and power conditioning units (PCUs). This report also describes work done to finalize another analysis tool developed to characterize the impact of shading at cell level, and provides results on the shading tolerance of PV systems and modules.

Results of this work indicate that the most important factor in PV energy production is module technology, with up to a 10% difference between the tested technologies and manufacturers. Shading was found to be the next most important parameter, followed by aging and system configuration, then soiling, and lastly the environmental conditions as tested.

The existing HNEI PV test beds were used, primarily the test bed at Maui Economic Development Board (MEDB), that was commissioned in February 2016 in Kihei, Maui (under previous funding). This test platform consists of 15 grid-connected PV systems using 10 types of PV modules and 3 system architectures using either microinverters, string inverters, or optimizers. The tested PV technologies include 4 standard p-type crystalline (1 mono and 3 polycrystalline), 3 high efficiency n-type monocrystalline (1 with a heterojunction intrinsic thin layer, 1 with rear contacts, and 1 bifacial), and 3 thin-films (2 Copper Indium Gallium Selenide (CIGS), and 1 Cadmium Telluride (CdTe)). All modules are mounted on a carport with 20° tilt and 197°N azimuth. The PCUs in test at MEDB include a 2 kW high frequency string inverters, a 3 kW string inverter especially designed to operate with optimizers, microinverters from 2 different manufacturers, and add-on optimizers i.e. designed to operate with regular string inverters.

Numerous sensors were installed on the MEDB test platform to monitor environmental parameters and PV performance including a reference (secondary standard) thermopile pyranometer, a weather station, and an AC power meter. The equipment was recalibrated once a year, with the latest calibration completed in early June 2018. Testing, hardware, and DC analysis are described under previous reports (including final technical reports for APRISES11 and APRISES13, as well as USDOE Hawaii Distributed Energy Resource Technologies for Energy Security (DE-FC26-06NT42847, DE-EE0003507).

Daily performance is commonly evaluated using the performance ratio (PR), defined by the International Electrotechnical Commission (IEC) 61724 [1]. PR is the operating performance of a PV system corresponding to the daily average efficiency relative to the datasheet specifications defined at standard test conditions (STC). In the following, the AC performance is analyzed using PRAC (Equation 1).

**Equation 1**

\[
PR_{AC} = \frac{\int_{t_0}^{t_f} P_{AC} \, dt}{P_{MP, STC}} \times \frac{G_{STC}}{\int_{t_0}^{t_f} G \, dt},
\]
where \( P_{AC} \) is the AC power of the PV system [W]; \( G_{STC} \) is the STC irradiance [=1 kWm\(^{-2}\)]; \( \Delta t \) is the period of analysis [hour]; \( P_{MP,STC} \) is the power [W] of the maximum power point at STC.

An empirical model, introduced in APRISES13, was developed to estimate the impact of the parameters including irradiation (IRR), ambient temperature (AT), and soiling. Soiling impact was correlated to the number of cumulative days without rainfall that is called in the following, duration of dry period (DDP). The present model (Equation 2) was improved and takes into account additional parameters: wind speed (WS), and aging or degradation.

Equation 2

\[
PR_{AC} = PR_{AC,O} + k_{IRR} \times IRR + k_{AT} \times AT + k_{WS} \times WS + k_{DDP} \times DDP + k_{AGE} \times AGE
\]

where \( PR_{AC,O} \) is the constant term in the fit; \( k_{IRR}, k_{AT}, k_{WS}, k_{DDP}, \) and \( k_{AGE} \) are the weight or impact of each parameter on the performance.

Due to new structures built on the neighboring property that shade a portion of the PV system, periods of operation with shading were removed from the dataset before determining the model coefficients with least-square linear regression. (Shading impacts are further addressed later in this report, under the Cell-Level Shadow Detection Tool.) The dataset was also adjusted to include only the days with irradiation above 2 kWhm\(^{-2}\) due to significant changes in performance in overcast conditions. In such environmental conditions, the PV module performance increases slightly [2], [3], and the inverter efficiency drastically decreases due to operation at a low power ratio. Overcast days with IRR below 2 kWhm\(^{-2}\) account for 5% of the total number of analyzed days (791 days) but only 1% of the total solar energy.

Figure 6.1.1 shows the daily values of the main parameters of \( PR_{AC} \) including IRR, AT, WS, and DDP during the full period of recording from April 4\(^{th}\), 2016 to September 5\(^{th}\), 2018. (Data is missing in March-May 2018 due to issues with data recording and internet connection loss.) The daily irradiation averaged 5.5±1.2 kWhm\(^{-2}\). Daytime temperature averaged 27.8±2.2\(^{\circ}\)C with highs in September and lows in January-February. Wind speed averaged is 2.5±0.9 ms\(^{-1}\). Dry periods were usually less than 30 days in length, with exceptions up to a 77-day dry period from September to December 2016.
Figure 6.1.1: Daily average values of the main PV parameters from April 2016 to early September 2018 at MEDB: irradiation (IRR), ambient temperature (AT), wind speed (WS) and duration of dry period (DDP).

The daily performance of 11 PV systems during the 29 months of operation is shown in Figure 6.1.2. Four of the 15 PV systems in test at MEDB consist of 2 modules each, grid-connected with microinverters. No AC measurement was collected on these systems. For all PV systems, PR_{AC} is estimated between 0.8 and 0.95 in April 2016, and generally decreases overtime with values between 0.74 and 0.86 in early September 2018. Systems were off during summer 2017. Despite a relatively constant variation during the 29 months of operation, PR_{AC} exhibits important drops during winter with lowest values around solstices. This is the effect of shading that, as mentioned earlier, started affecting the PV platform in January 2017. The drop of performance in December 2016 is related to an overcast period.
Figure 6.1.2: AC PV performance ratio (PR$_{AC}$) of 11 PV systems tested at MEDB during 29 months. The legend shows the acronym for each PV system, starting with a letter indicating the PV technology (C for the CIGS thin-film, D for the CdTe thin-film, H for the high efficiency crystalline, S for standard crystalline), followed by a digit to differentiate the manufacturers, and last a letter indicating the system configuration (S for string inverter, O for string inverter with optimizers, M for microinverter).

Figure 6.1.3 shows PR$_{AC}$ as a function of IRR plotting only the days without significant shading (so January to March 2017, and September 2017 to March 2018 were removed). As mentioned above, the performance of the systems decreases for IRR below 2 kWhm$^{-2}$ except for the microinverter system S3M. Thin film C1S system exhibits lower performance than the other systems for IRR below 4 kWhm$^{-2}$. Lower performance of C1S is related to lower performance of the PV modules at low IRR compared to other modules [4]. It is also due to the low inverter loading ratio with only 1.4 kW PV for a 2 kW inverter.
Figure 6.1.3: $PR_{AC}$ of 11 PV systems as a function of IRR (dataset from April 2016 to early September 2018 excluding periods of shading).

Figure 6.1.4 compares the measured and estimated $PR_{AC}$ for a PV system (H1S). The data and model are correlated except during the winter when the system performance drops due to shading. The mean relative error (MRE) between data and model results is between 1.0% and 1.6% for most systems, and 2.2% for C1S. In comparison, the few previous models for daily energy [5], [6] obtained MRE below 5%. As indicated in the textbox of Figure 6.1.4, the average daily energy production during the 29 months is measured at 4.3 kWh m\(^{-2}\) while the model estimated 4.6 kWh m\(^{-2}\). The difference between measured and estimated energy production is allocated to the impact of shading. For this system, energy loss due to shading is estimated at 5% of the actual PV production.
Figure 6.1.4: Measured and modelled \( \text{PR}_{\text{AC}} \) of the PV system H1S during 29 months of operation.

Figure 6.1.5 presents the average performance of the PV systems including the measured and simulated values, the latter providing an estimated \( \text{PR}_{\text{AC}} \) without the impact of shading. \( \text{PR}_{\text{AC}} \) is measured between 78% and 85%. Without shading, the system performance would be between 79% and 89%. Different system configurations were tested on the crystalline systems. For both data and model results, the microinverter systems are most efficient at the site followed by the string inverters and then, the string inverters with optimizers.
Figure 6.1.5: Average PR$_{AC}$ of the 11 PV systems at MEDB from April 2016 to early September 2018.

Figure 6.1.6 shows the estimated PR$_{AC}$ as a function of irradiation for the 11 PV systems at the beginning of the analyzed period (April 4$^{th}$, 2016) operating at mean values of the environmental conditions (AT, WS) and without soiling.

Table 6.1.1 describes the model coefficients providing the impact of the parameters. The following was observed:

- IRR has low impact on the performance of most systems except for C1S exhibiting an increase of PR$_{AC}$ with increasing IRR, and for S3M with much higher performance in overcast conditions than on sunny days (as already seen in Figure 6.1.3). C2S and D1S exhibit the highest PR$_{AC}$ at all IRR level. The next best system is H1S with constant PR$_{AC}$ as a function of IRR except below 3 kWhm$^{-2}$ when S3M has a higher PR$_{AC}$.
- AT impact is mostly negative, meaning higher performance in cooler conditions. Positive impact on D1S could be related to the spectral energy increasing in summer similarly to AT. High coefficient for C1S is arguable and is allocated for now to the distribution of the dataset for this system leading to a less accurate model as seen on the MRE.
- WS has a cooling effect on the PV systems leading improved performance in windy conditions. The difference in coefficients between systems is attributed to the location of the system on the carport i.e. distance from the wind sensor and from a nearby building.
- Soiling impact varies between 0.03% and 0.11% per day. Difference between PV systems could also be related to the system location. Systems more sensitive to WS are also more sensitive to soiling. These systems are located on the east side of the carport near a dusty field. The nearby building that obstructs the Trade wind would reduce the impact of soiling and wind speed on the high efficiency PV systems located on the west side of the platform.
- Aging is estimated between 1.4% and 3.4% per year which is above of the typically warranted degradation of ~1% per year. Microinverter systems exhibit lower degradation than string and optimizer ones.

Figure 6.1.6: \( PR_{AC} \) as a function of IRR for 11 PV systems at the beginning of the analyzed period (April 4\(^{th}\), 2016) operating at mean values of the environmental conditions (AT, WS), and without soiling. Empirical model presented in equation (2) fitted to the first 29 months of operation excluding the periods of shading.
Table 6.1.1: Model coefficients for 11 PV systems estimated during the first 29 months of operation excluding the periods of shading.

<table>
<thead>
<tr>
<th>PV</th>
<th>$PR_{AC,0}$ [-]</th>
<th>$k_{IRR}$ [%/kWhm$^2$]</th>
<th>$k_{AT}$ [%/°C]</th>
<th>$k_{WS}$ [%/ms$^{-1}$]</th>
<th>$k_{DDP}$ [%/day]</th>
<th>$k_{AGE}$ [%/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1S</td>
<td>0.92</td>
<td>1.0%</td>
<td>-0.6%</td>
<td>0.7%</td>
<td>-0.04%</td>
<td>-2.0%</td>
</tr>
<tr>
<td>C2S</td>
<td>0.89</td>
<td>0.2%</td>
<td>0.1%</td>
<td>0.9%</td>
<td>-0.08%</td>
<td>-3.4%</td>
</tr>
<tr>
<td>D1S</td>
<td>0.86</td>
<td>-0.5%</td>
<td>0.2%</td>
<td>1.1%</td>
<td>-0.11%</td>
<td>-2.9%</td>
</tr>
<tr>
<td>H1M</td>
<td>0.96</td>
<td>-0.1%</td>
<td>-0.3%</td>
<td>0.5%</td>
<td>-0.05%</td>
<td>-2.7%</td>
</tr>
<tr>
<td>H1S</td>
<td>0.91</td>
<td>0.0%</td>
<td>-0.2%</td>
<td>0.5%</td>
<td>-0.05%</td>
<td>-3.0%</td>
</tr>
<tr>
<td>H2M</td>
<td>0.98</td>
<td>-0.5%</td>
<td>-0.3%</td>
<td>0.5%</td>
<td>-0.04%</td>
<td>-2.1%</td>
</tr>
<tr>
<td>H2O</td>
<td>0.92</td>
<td>-0.4%</td>
<td>-0.2%</td>
<td>0.6%</td>
<td>-0.04%</td>
<td>-2.4%</td>
</tr>
<tr>
<td>H2S</td>
<td>0.92</td>
<td>-0.3%</td>
<td>-0.2%</td>
<td>0.4%</td>
<td>-0.03%</td>
<td>-2.6%</td>
</tr>
<tr>
<td>S3M</td>
<td>0.89</td>
<td>-1.6%</td>
<td>0.1%</td>
<td>0.7%</td>
<td>-0.08%</td>
<td>-1.4%</td>
</tr>
<tr>
<td>S3O</td>
<td>0.90</td>
<td>-0.8%</td>
<td>-0.1%</td>
<td>0.8%</td>
<td>-0.07%</td>
<td>-2.6%</td>
</tr>
<tr>
<td>S3S</td>
<td>0.93</td>
<td>-0.8%</td>
<td>-0.2%</td>
<td>0.9%</td>
<td>-0.06%</td>
<td>-2.4%</td>
</tr>
</tbody>
</table>

The impact of the parameters was estimated on the total energy produced during the analyzed 29-month period (Table 6.1.2). The most important factor in PV energy production is the selection of the module, with up to a 10% difference between the tested technologies and manufacturers. Shading is the next most important parameter at the location, reducing energy production by up to 5%. Aging decreased energy production by 2-4%. System configuration and choice in PCU also lead to a performance difference of 2-4%. Soiling impact is estimated up to 1.9%. The environmental conditions have the least impact on energy production leading to performance variation below 0.8%, 0.4%, and 0.3% due to IRR, AT, and WS respectively.

Table 6.1.2: Impact of the main parameters as a percent of the total PV energy production during the 29 months of operation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Impact on the energy production</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV technology/manufacturer</td>
<td>10%</td>
</tr>
<tr>
<td>Shading</td>
<td>0-5%</td>
</tr>
<tr>
<td>Aging</td>
<td>2-4%</td>
</tr>
<tr>
<td>System configuration / PCU</td>
<td>2-4%</td>
</tr>
<tr>
<td>Soiling</td>
<td>0.6-1.9%</td>
</tr>
<tr>
<td>Irradiation</td>
<td>&lt;0.8%</td>
</tr>
<tr>
<td>Ambient temperature</td>
<td>&lt;0.4%</td>
</tr>
<tr>
<td>Wind speed</td>
<td>&lt;0.3%</td>
</tr>
</tbody>
</table>
Conclusions

- An empirical model was developed to predict the daily PV energy production (by modelling PR\textsubscript{AC}) with an error below 2.2%. The model accounts for the effect of irradiation, AT, WS, soiling, and aging. Shading is estimated by comparing the data and model results.

- Using the model fit to the data collected during 29 months of operation, the following is concluded:
  - The main parameters are, in decreasing order of importance, the PV technology/manufacturer, shading, aging, system configuration/PCU, and soiling. The environmental conditions IRR, AT, and WS lead to minimal variability of the PV energy production.
  - The system configuration and the type of PCU have an impact on the average PV performance as well as on the degradation. Results suggest that microinverters provide the best system configuration. One type of microinverter improved the performance in overcast conditions, recommending it for overcast locations.

- Long term assessment at MEDB is essential to evaluate if the high estimated degradation (1.4% - 3.4% per year) is related to the early stage of the PV system operation.

Shadow Analysis

As mentioned earlier, shading is an important performance parameter of the PV systems at MEDB. To understand the impact of shading on the performance of the PV modules and systems, the shadow shape needs to be characterized at module and cell level. Different solutions to characterize shadow shape were identified and described in the APRISES13 final report. Image-based shadow detection was chosen for APRISES12 work because of spatial resolution, cost, and development time. Three wireless cameras were installed February 2018 on the structures that shade the PV platform. Shadow detection algorithms were finalized under this subtask using Matlab software. The algorithms and collected photographs were used to evaluate the number of cells shaded per module and the percentage area of shadow on each cell. The goal was to evaluate the relationship between the shadow coverage and the performance of the PV modules and systems. Preliminary results are presented following a short description of the necessary steps for shading analysis.

The method employed included image processing, shadow detection and characterization, and is outlined as follows.

**Image processing:** The pictures from the 3 cameras taken at a 1-minute sample rate were corrected for lens distortion and perspective, and then stitched together in order to provide an overhead view of the PV carport as seen in Figure 6.1.7.
Two images were created to identify each module and cell on the overhead view. The first image (Module ID Mask) identifies the general area of the modules, including the frame. The second image (Cell ID Mask) locates the cells within each module. Cell identification was ineffective for all 3 types of thin film modules due to their plain dark appearance as visible in Figure 6.1.7d).

![Images showing overhead views of solar panels](image)

Figure 6.1.7: Converting the 3 raw camera images (a, b, c) to an d) overhead image.

**Shadow Detection:** A shadow mask (Figure 6.1.8) was created by first thresholding on a black-and-white image created from the Red-Green-Blue (RGB) overhead image. After thresholding, erosion and dilation was applied to fill in the gaps and remove noise from the image.
Shadow Characterization: The final step was to create a table containing the estimated ratio of the area covered by shaded cells. The columns represent the module ID, cell ID, and ratio of area covered in that cell (0-1). To accelerate calculation of the cell shadow ratio, selected cells were analyzed. The shadow mask was first intersected with the module ID mask to find modules with shadows on them. Any module that has more than 0.05% of its area covered with shadow is then analyzed at the cell level.

Important information will be provided with the Cell-Level Shadow Analysis tool as soon as more data are available. Since the cameras were installed at the end of February 2018, only a few days suffered from shading affecting the platform from September to March (as seen in Figure 6.1.2). The following presents preliminary results obtained using the Shadow Detection Tool. Starting with an analysis at system level, the second part compares the shading tolerance between individual PV modules.

Figure 6.1.9 and Figure 6.1.10 show the correlation between the Shadow Ratio and PR_{AC} comparing 2 systems with different system configurations (H1M and H1S) on February 27\textsuperscript{th}, 2018. Figure 6.1.9 displays PR_{AC}, the Shadow Ratio (% of shaded area per system), and the Shadow Module Ratio (% of shaded modules per system). Maximum shading occurs around 4:20PM as seen on the Shadow Ratio similar for both PV systems. Despite a relatively low Shadow Ratio (< 0.1), only one or 2 modules per system are shaded as indicated by the Shadow Module ratio (with 8 modules total per system). This is detrimental for H1S performance, which exhibits an important drop in PR_{AC} as soon as the Shadow Ratio becomes significant, which occurs around 3:40PM. PR_{AC} of H1M however barely shows any impact of shading. Figure 6.1.10 shows PR_{AC} as a function of the Shadow Ratio. The correlation between PR_{AC} and Shadow Ratio is exponential for the string configuration and linear for the microinverter system.
Figure 6.1.9: PR_{AC}, Shadow Ratio, and Shadow Module Ratio for 2 PV systems (H1M and H1S) on February 27th, 2018.

Figure 6.1.10: PR_{AC} as a function of Shadow Ratio on February 27th, 2018 between 3PM and 6PM.

The correlation between the Shadow Ratio and the PV performance for each individual module will allow characterizing and comparing the shading tolerance of the PV modules. Results obtained on February 27th, 2018 suggest a higher shading tolerance under low Shadow Ratio for the module H1 compared to the H2 and S3 (Figure 6.1.11).
Figure 6.1.11: $PR_{DC}$ of the modules H1, H2, and S3 as a function of Shadow Ratio on February 27th, 2018 between 3PM and 6PM.

Conclusions

A Cell-Level Shadow Detection Tool was developed to characterize the modules and cells affected by shading using an inexpensive monitoring system (web cameras) and a Matlab analysis tool. Further analysis will provide a better understanding of the impact of shading on the PV performance by determining the shading tolerance of the PV modules and systems. Under other funding, development and analysis will be continued to further characterize the PV performance and the impact of all parameters including shading. Plans include completing and submitting 4 journal papers drafted under APRISES12 to peer reviewed Energy and Measurement journals.

References


### 6.2 Secure Micro-grids

**6.2a Molokai Load Bank**

An analysis was conducted to estimate the impact of connecting a Load Bank to the Molokai Island microgrid, in order to overcome the grid constraint and increase the amount of Distributed PV generation (DG PV) that can be connected and utilized by the grid. An agreement was executed with the utility, Maui Electric Co., to collaborate on the integration of the Load Bank, including algorithm and control development, and data sharing.

Molokai Island has approximately 2,144 kW of DG PV on the Molokai grid, and there is 133 kW of DG PV approved for interconnection, as well as a 100 kW hydro project that is also approved for interconnection. In addition, there is another 665 kW of DG PV in an interconnection queue pending an increase in the hosting capacity of the grid. In total, there is 3,042 kW of DG installed, approved or nearly approved or in the queue on the Molokai system which has a minimum daytime load of approximately 3,700 kW. In March 2015, Maui Electric Co. started informing customers that the Molokai grid was nearing system-level constraints to further interconnection of DG, and since that time most interconnection requests have been delayed pending near-term solutions to address the grid constraint.

Figure 6.2a.1 illustrates the primary near-term system-level constraint of energy oversupply during periods of low demand and high PV output. If the net load (load – DG PV) falls below the minimum generation level of 1,300 kW, the system will not meet its downward regulating reserve requirement to deal with sudden load losses due to system faults. The dark brown line in Figure 6.2a.1 shows that the net load in 2015 was close to the minimum generation for the system and as such, the system was not able to accept more PV capacity unless the PV system has the ability to reduce its output if the net load falls below 1,300 kW, i.e. unless the PV system is “curtailable”.

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Under future funding, a Load Bank will be used to analyze its performance and effectiveness as an energy safety valve to provide a near-term solution for interconnection and a longer-term grid management asset for a small (microgrid scale) grid. In this application, the Load Bank adds load to the Molokai system, using secure communications within the power plant, when needed as a near-term solution to balance the grid during infrequent periods of excess energy supplied to the grid. While this excess energy would be literally burned off as heat, it would enable the interconnection of all 665 kW of DG PV in the queue which would result in a significant increase overall in renewable energy on the grid, and a relatively small amount of excess energy burned off per year.

Figure 6.2a.2 shows an analysis using hourly system load data from 2009 for Molokai. In 2009 there was only a negligible amount of DG PV on the system, and since then the system load has not experienced much growth. The calculated 2,942 kW of DG PV (2,144 kW installed, 133 kW of DG PV approved for installation and 665 kW in the queue) and 100kW of hydro production was subtracted from the 2009 load data to generate the net load profile vs. the minimum generation limit in Figure 6.2a.2. This analysis shows that with the additional DG PV generation, an additional 1,106 MWh of energy can be utilized from the 665kW of DG PV while only passing approximately 4 MWh of excess energy through the Load Bank.
Figure 6.2a.2: Molokai Generation Profile.

Figure 6.2a.3 shows a bar chart that provides a graphical representation of the additional energy that would be utilized by the grid and the excess energy produced if the 665 kW of DG PV in the queue were added to the grid given the 2009 load profile.
Figure 6.2a.3: Additional renewable energy (RE) from Distributed PV generation (DG PV) in the Queue – 2009 load data.

The ASCO 4800 750KVA resistive Load Bank and step up transformer, shown in Figure 6.2a.4, were installed and commissioned by the utility at the Palaau Power Station on Molokai. The Load Bank, that is owned by the utility, is currently manually controlled by the System Operator through the SCADA network at the power station.
Using APRISES 14, HNEI will work in collaboration with the utility to design and test automated algorithms and controls to automate the Load Bank’s primary use case of managing excess DG PV energy on the grid. HNEI will also instigate additional system benefits that the Load Bank can support beyond the management of excess DG PV energy by developing additional uses cases and test plans. Once the uses cases are finalized with the utility, HNEI will develop a control and monitoring system for the Load Bank that will automate the use case functions with the goal of improving the efficiency of the system as compared to its current manual operation.

### 6.2b Coconut Island DC Microgrid

The objective of this project is to demonstrate the performance and resilience of a DC microgrid designed to serve the loads within two buildings on Coconut Island, off the Island of Oahu, and to provide the island with clean electrified transportation options primarily powered by the sun.

Following the planning, data gathering, energy modeling, component sizing and procurement of the swappable battery system and electric E-car and E-boat under APRISES11 and 13, the procurement and implementation phase of the project was continued under APRISES 12. Under APRISES 12, HNEI completed the conversion of the E-boat to an all-electric vehicle that works with the swappable battery system, and installed the battery charging station for the swappable battery system in the Boat House on Coconut Island.
When complete, the Coconut Island DC Microgrid Project will integrate a DC distribution system into two buildings on the island, the Marine Mammal Research Project (MMRP) building and the Boat House (See Figure 6.2b.1). These two buildings are currently served by one of the utility owned transformers on the island. This project is made possible by funding from previous APRISES awards (APRISES11 and 13), the current APRISES12, and future APRISES14 funding.

Coconut Island (Moku O Loe) is a 28-acre (113,000 m²) island in Kaneohe Bay off the island of Oahu that is home to the Hawaii Institute of Marine Biology (HIMB) of the University of Hawaii. It is an ideal site for a technology-based test bed since it is representative of a tropical marine environment in an isolated location with critical power needs, and one of the goals established for the island is to become a model for sustainable living systems. The island is exposed to persistent trade winds and salt spray resulting in a highly corrosive environment for material and technology testing in micro-climates representative of those that would potentially be encountered by coastal installations.

![Figure 6.2b.1: a) Coconut Island, b) DC/AC microgrid project site.](image)

The objective of this project is to demonstrate the performance and resilience of a DC microgrid designed to serve the loads within two buildings on Coconut Island and provide the island with clean electrified transportation options primarily powered by the sun. The project has the following goals:
- Demonstrate innovative new clean energy technologies
- Economically minimize the energy purchased from the utility
- Provide a research platform to study DC microgrid resources and loads, e.g. energy storage and supporting technology and DC power appliances, in a tropical coastal environment
- Increase the energy sustainability of the island
- Provide solar electric powered transportation for HIMB

The proposed DC microgrid design described in the APRISLES 13 final report utilized a 380V DC bus as the backbone of the DC microgrid. Following the filing of that report, HNEI issued two requests for proposals, one to install the PV and battery energy storage system (BESS) and another to integrate those resources with the fully functioning microgrid.

Unfortunately, the single bid received for the PV and BESS systems was unreasonably high and there were no bids received for the microgrid implementation and integration work. The issue is that 380V DC systems are not common in Hawaii and the uncertainty risk is causing high prices or no bids on requests for proposals. As a result, the HNEI project team decided to revise the scope of the project to utilize a more common 48V bus that would allow the use of 48V equipment and control systems that are more widely available and implemented locally. The system is not as expandable as with the 380V bus, but while expandability is desirable it is not critical to meet the goals of the project.

Some of the key components of the system for the revised project scope include components shown in Figure 6.2b.2 and described below:

1) PV modules installed on MMRP roof as the primary source of energy for the microgrid. The PV size is approximately 20 kW DC which is the maximum capacity allowed by the roof space of the MMRP.

2) A Stationary BESS (between at 24 kWh and 32 kWh of usable energy with minimum 12 kW power) used to store excess PV energy and export that energy to minimize the use of grid power by the DC microgrid during normal operation, and to keep the DC microgrid system operational during utility grid outages.

3) A unidirectional 30 kW rectifier that provides power to the 48 Vdc bus from the grid (3 phase, 120V/208V GrdY) when there is insufficient energy available within the microgrid, and to prevent back feeding power to the grid.

4) Power Monitor Unit (PMU) that can be used to control the microgrid components as needed and produce operational information including local dashboards displaying DC microgrid information and performance.
5) Inverter(s) with a capacity appropriate to supply the AC loads (Computers and Wi-Fi network) within the MMRP buildings to be powered by the DC microgrid.

6) DC lighting and controls in the MMRP buildings that meet applicable office lighting standards.

7) DC powered air conditioning to take the place of all but one of the existing AC powered air conditioning units. (The existing AC powered units will remain in place for possible future use.) The remaining existing air conditioner in the standalone office will be used as a point of comparison with the DC air conditioners.

8) Swappable battery system, designed and manufactured by PUES Corporation in Okinawa Japan (“PUES”), will charge the swappable batteries used in the electric vehicles (E-boat and E-car) and portable power “suitcase battery” system. This station is capable of charging twelve (12) batteries through the DC Bus with a capacity of 1.4 KW and 1.4 KWh each.

9) A 48 Vdc bus that transmits power between energy resources (PV, BESS, Rectifier) and loads (Lighting, Air conditioning, Inverters for AC loads, and Swappable Battery System) within the microgrid.

Figure 6.2b.2: DC microgrid description.
HNEI purchased two vehicles, along with the components of an associated charging station, swappable batteries and two portable suitcase battery enclosures, under APRISES 13. The vehicles included a pontoon boat (the E-boat) and an electric powered John Deere Gator (the E-car) modified to utilize the swappable batteries. As noted above, the battery charging station installed in the Boat House during APRISES12 is currently powered from the grid until the PV system and stationary battery are installed.

The Okinawa Institute of Science and Technology (OIST) and PUES, who are partners on this project and part of the Hawaii-Okinawa Clean Energy Partnership between the U.S. Department of Energy and the Ministry of Economy Trade and Industry of Japan, developed the swappable battery system. PUES and OIST used funds from the Government of Japan to develop and test the first version of the swappable battery system and vehicle. Photographs of this initial design are shown in Figure 6.2b.3. Under APRISES 13, PUES and OIST consulted with HNEI to improve this initial design and develop the next version of the system to be tested at OIST, and on Coconut Island by HNEI.

![Figure 6.2b.3: Version 1 of the PUES Swappable Battery System at Okinawa Institute of Science and Technology (OIST).](image)

The swappable battery charging station that was installed consists of two parts, 1) the battery charging control system and 2) twelve battery receptacles. A schematic of the swappable battery charging station is shown in Figure 6.2b.4 where the control system is shown in blue and the receptacles are shown in green. The completed installation of the charging station in the Boat House is shown in Figure 6.2b.5.
Figure 6.2b.4: Schematic of Battery Charging Station.
As noted above, the E-boat gas powered system was replaced with an all-electric battery powered system. These modifications included replacing the gas engine of the boat with a Torqeedo electric motor, adding two sets of four swappable batteries along with their receptacles and adding a control system to manage the charging of the batteries from four PV panels installed on the boat canopy. Under APRICES 12, the electric power system was installed, tested, and made operational. The E-boat with the Torqeedo motor and charging control system are shown in Figure 6.2b.6. Under APRICES 14, the E-boat is undergoing final preparations and will soon be ready for delivery to the project site for testing.
With the installation of the charging station, the E-car is now operational and being used by HIMB on Coconut Island. The E-car used an electric John Deere Gator that was modified to utilize a swappable battery system to power the car and along with a state of charge (SOC) monitor for the swappable batteries. Figure 6.2b.7 shows added battery receptacles and SOC monitor.

Figure 6.2b.7: Modified John Deere Gator E-car, with battery receptacles (left) and SOC monitor (right).
Implementation of the detailed design and DC microgrid, along with demonstration, testing and evaluation of the DC microgrid and electric vehicles will be completed using APRISES 14 funding. Additionally, HNEI is revising and simplifying the scope of work for this ongoing APRISES project, and will issue a new request for proposals for the installation of the 48V DC microgrid. Under future funding awards, HNEI will test and evaluate the efficiency and resiliency of the DC microgrid and characterize its benefits and limitations.

6.2c Grid Scale Energy Storage

Analyses were conducted on a grid-connected Battery Energy Storage System (BESS) on the Hawaiian Island of Molokai, to better understand the BESS response to faults and other significant events on the grid. Additionally, a control algorithm was developed to better understand the interactions between the BESS response and the conventional generation, and to enable analysis of the impact of the BESS.

The procurement, installation and commissioning of a 2MW, 397kW-Hr BESS on Molokai was completed under previous HEET and APRISES awards. Analysis work on the Molokai BESS was continued under APRISES 12. This included analyses of faults and other significant events on the grid. The BESS consistently responded appropriately to most grid contingencies but responded unpredictably for short periods (1-2 cycles) during faults (short circuits) on the grid. An example of this is shown in Figure 6.2c.1.
Figure 6.2c.1 (A) BESS response to a fault: full view of synchrophasor data. Blue line indicates grid frequency and is aligned with the left axis. Green line indicates simultaneous BESS response and is aligned with the axis on the right. (B) This expansion includes an approximate ideal BESS response as a black dashed line.

Figure 6.2c.1 (A) shows the grid frequency and the BESS response (limited to 500kW) for 80 seconds of time. Figure 6.2c.1 (B) is an expansion near 9.8 seconds after the start of the data capture window where the frequency is under 60Hz due to a fault. The black dash in the bottom plot of Figure 6.2c.1 (B) approximates the ideal BESS response to an under-frequency event. The green trace shows that the BESS was (1) muted during the fault and (2) swung rapidly up and down away from the ideal response. It is possible that the meter feeding the BESS inverter is calculating frequency incorrectly because the grid voltages are unstable during faults.
Outside of APRISES 12, discussions are currently underway to address these problems (e.g., by incorporating a rate limiter within the inverter logic). Discussions are also underway about increasing the BESS authority from the current level of 500kW to 750kW. It was previously determined (under APRISES 13) that increasing the authority also increases the amplitude of the rapid power swings. However, since the swings are short-lived and generally in the right direction (exporting during under voltage periods), they are not expected to worsen the contingencies. That is, the instantaneous BESS power swings can cause instantaneous frequency changes for 1-2 cycles. However, that is not enough time to trip even the east Molokai circuit, which requires 10 cycles of a large frequency spike.

During APRISES 12, HNEI developed a PSCAD version of the existing Molokai BESS control algorithm. The motivation for this effort was to take advantage of a currently available Molokai dynamic grid model, also in PSCAD (developed by HECO) to better understand the interactions between the BESS response and the conventional generation on the grid. The combination of the algorithm and the grid model will enable analysis of the impact of the BESS. For example, it cannot currently be concluded that the BESS has arrested significant grid contingencies. Grid models (such as load flow) that were previously developed under multiple APRISES awards were done in simulation environments that run on course time scales. The PSCAD model is capable of micro-second time steps. Because the BESS is a fast-acting device, this is the type of model that is needed to understand how it interacts with the Molokai grid.

Future work will require the combination of the control algorithm and the grid model. Aside from the motivation indicated above, the combination will be required by the utility company to incorporate future grid enhancements such as:

- Addition of a 750kW load bank.
- Potential addition of a large battery for a PV farm.
- Potential addition of synchronous condenser.

Without the model, the utility company would have required the BESS to deactivate the current fast-response control algorithm in favor of a more conventional droop-type frequency response that would require a large dead-band to maintain system stability.

### 6.2d Power Grid Monitoring and Controls

The overall objective of this multi-year APRISES project was to develop a low-cost real-time power monitor with wireless communications for distribution system operations, controls, and analysis. During APRISES12, the power monitor system was enhanced by adding the capability
for advanced real-time data analysis and controls. Our approach leverages advances in wireless communications, smart meter integrated circuits, and open source software to create a fully integrated device for this application. The device is intended to support HNEI’s research and field demonstrations on the distribution grid as well as to provide a solution that could be commercialized to help solve grid operational issues with high penetrations of distributed energy resources (DER) such as photovoltaics (PV). This work on the system led to a second provisional patent being filed.

Further background on the project is given in the APRISES 11 and 13 reports. Under APRISES 11 funding, we built initial prototypes, established a power monitor test lab with basic tools for 120V AC (alternating current) testing, and offered a junior-level undergraduate engineering project course. Under APRISES 13, we began prototyping a weatherized version of the device and offered a senior-level engineering project course focused on software development.

The objective for the project under APRISES 12 funding was to continue developing and refining the hardware and software of the power monitor system, focusing on adding the capability for advanced real-time data analysis and controls. Previous versions of the device streamed data of root mean square (RMS) current, RMS voltage, active and reactive power, and frequency to a server for archival and post-processing. To provide additional flexibility and support for grid resiliency, it is desirable to implement an edge computing framework where each device can perform onboard analytics and controls in a semi-autonomous manner. Thus operation can continue when communications or the server is compromised, and each device can take actions to restore normal operations. Towards this end, we replaced the microcontroller in the device with a field programmable gate array (FPGA) that has significantly more computing power and flexibility. The FPGA implements logic modules and a soft-core processor that can be completely reconfigured—both at a software and hardware level—to provide the ultimate platform for research and development in real-time grid analytics and controls.

Built-in communications was previously limited to 2.4 GHz WiFi and 900 MHz mesh networking. Under APRISES 12 funding, we identified and integrated a Long Term Evolution (LTE) system-on-package (SOP) that can offer high-speed commercial data communications over AT&T when deployed to pole-top locations. This platform will enable many features in the future including near real-time reporting of raw voltage and current waveforms.

We significantly enhanced the web interface for the device, offering numerous real-time and historical plots. The website is available at [argems.soest.hawaii.edu](http://argems.soest.hawaii.edu), with a password provided by HNEI upon request. Several screenshots of the website are shown in Figure 6.2d.1. We continued our long-term testing and maintenance of an initial device installed at the Frog 1 net zero energy building on the UH Manoa campus. This led to numerous reliability enhancements.
Figure 6.2d.1: Selected screenshots from power monitor website.
HNEI leveraged the power monitoring platform for additional proposals and funding. We submitted an ARPA-E OPEN 2018 proposal that would utilize the device for applied research in grid parameter identification and real-time and predictive distributed modeling. We have responded to reviewer comments and are expecting a decision in October 2018. The device has also been included in an ONR Department of Defense University Research-to-Adoption (DURA) project led by Arizona State University (ASU). One device is now operational at ASU, and nine others will be delivered over the course of the project. The devices will be connected to real-time controllers to perform conservation voltage reduction (CVR) and provide enhanced microgrid resiliency.

HNEI filed a second provisional patent on the system June 29, 2018 entitled "Enabling Ubiquitous Distribution Grid Modeling for Enhanced Visibility and Controls" (#62/692,613). A utility patent application is expected in November 2018. HNEI conducted meetings with potential research and commercial partners.

**Patents**


### 6.2e Conservation Voltage Reduction

Initially funded under APRISES 11, this Conservation Voltage Reduction project led to the invention of a new patent-pending technology, and we worked closely with Hitachi and IKS to develop an initial prototype. The prototype performed well during testing, however, the cost and physical size of the device limited our ability to perform a feeder level field demonstration.

The objective of this project under APRISES 12 was to take this technology to a commercially feasible prototype. The design approach taken by IKS required large capacitors which are expensive. Under APRISES 11, we tested the dynamic voltage compensation algorithm using commercially available inverters. In order for PV inverters to operate, they require DC power which is typically solar modules. A small DC power supply can emulate a solar module so that the inverter is able to operate and is not dependent on time of day. Thus, under APRISES12 HNEI searched the market for a small DC power supply that is capable of “waking up” the inverter. We acquired the Delta ES 0300-0.45 150W programmable DC power supply.
The inverter and DC power supply have been installed at the University of Hawaii Marine Center based on the electrical diagram as shown in Figure 6.2e.1.

![Electrical Wiring Schematic](image)

Figure 6.2e.1: Electrical Wiring Schematic.

Initial tests proved that this relatively small DC power supply is able to power the inverter and thus the technology based on this combination of equipment can be used to produce a cost effective prototype. Under APRICES14 funding, we are continuing to explore industry partners with the right expertise to develop a commercially viable prototype.

### 6.2f Hardware-in-the-loop (HIL) Testing

HNEI acquired and began to set up hardware-in-the-loop (HIL) equipment to test distributed energy resources (DER) and associated devices. The equipment, shown in Figure 6.2f.1, consists of an OPAL-RT real-time simulator with high-speed analog interfaces to control a three-phase bi-directional power amplifier. This setup allows HNEI to mimic real-world grid operation and fault scenarios in a controlled research setting, bringing a new level of flexibility to our testing and increasing our confidence in new technology before it is deployed to the grid.
This platform can be used in many configurations such as those shown in Figure 6.2f.2. HNEI will use Configuration 2, (Real-time Simulation with Real and Forecasted PV) to demonstrate applications of HNEI’s PV forecasting system under DOE funding through the UI-ASSIST project led by Washington State University (WSU). The Distribution Energy Management System will be developed and hosted at WSU, while the virtual grid and PV monitoring and forecasting is at HNEI. HNEI will use Configurations 3 (Controller HIL), 4 (Power HIL), and/or 5 (Power HIL with System-Controlled DER) to test and validate HNEI’s CVR algorithms and devices. Configuration 4 will be used with a test profile (instead of a virtual grid) of various voltages, real and reactive power, and frequencies to validate HNEI’s power monitor.

Under other funding, HNEI is converting detailed models of the Maui Meadows distribution circuit to run on the simulator, which will enable testing under accurate, realistic scenarios. (More information on the Maui Meadows project can be found in APRISES11 and 13 final reports.)

HNEI expects that the real-time simulation and HIL equipment will lead to valuable and productive new projects and collaborations. Under DOE UI-ASSIST funding, HNEI will explore the possibility of connecting the HIL equipment into Idaho National Laboratory’s Real-time...
SuperLab⁴. HNEI has proposed to use the equipment on an ARPA-E Open 2018 proposal that is currently under review by DOE.

Figure 6.2f.2: Various use cases and configurations for the real-time simulation and hardware-in-the-loop (HIL) equipment.

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6.2g Solar Forecasting

Building on previous APRIZES-funded work, under this subtask HNEI continued to develop new solar forecasting methods and systems, employ those systems in an operational framework, and calibrate and validate the predictions generated using ground observations.

The high penetration of distributed, behind-the-meter, photovoltaic (PV) systems in Hawaii can create operational and power quality issues due to seemingly random, short-timescale variations in power output. Problems are exacerbated for the relatively small, isolated, island electric grids, where resources for grid stabilization are limited. Under previous funding, HNEI began development of an advanced solar forecasting system intended to generate operational solar irradiance and PV power predictions over a wide range of time-scales for the state of Hawaii. This system combines three separate components, allowing for the system to generate forecasts from minutes to days ahead:

1) Day-ahead forecasts (DA): A Numerical weather prediction (NWP) component is used to generate hours to days ahead forecasts, providing information useful for planning unit commitment.

2) Hour-ahead forecasts (HA): A satellite image based component is used to generate minutes to hours ahead forecasts, providing information used for unit dispatch and operational reserve management.

3) Minute-ahead (MA) forecasts: A sky image based component is used to generate solar irradiance nowcasts and seconds to minutes ahead forecasts, providing information useful for grid stabilization and fast ramp events.

In the following, we discuss the continued work to develop and test solar forecasting system under APRIZES 12, including: (i) maintaining, evaluating, and improving an operational forecasting system using the DA and HA components, (ii) performing an extensive evaluation of the HA component following an extensive redesign; (iii) continuing to develop, build, and test a new ground-based forecasting instrument, the Affordable High Resolution Irradiance Prediction System (AHRIPS); and (iv) developing a solar irradiance dataset for Oahu, Hawaii.

Under this funding, we completed a redesign of the HA forecasting component that was initiated in late 2017, under APRIZES 13 funding. The main goals of the redesign were: to increase the computational efficiency of the system, to develop new methods so that power forecasts could be quickly generated for large numbers of distributed PV systems anywhere in the state, with varying orientations, and to add functionality to the cloud tracking and advection procedures to deal with multi-layer cloud motion. Under APRIZES 13 funding, we demonstrated the reduced forecasting latency, added functionality, and increased accuracy, using a short time-series of forecasts, of the redesigned HA forecasting component. Under APRIZES 12 funding, we have added these changes to the operational system and initiated a comprehensive evaluation of the HA forecasting
component using over 6 years of archived satellite imagery. Initial results from 1 year of data are presented below.

In the following, HA forecasts are compared against PV power output and irradiance data from two HNEI PV test beds, located at: the UH Manoa campus, on the island of Oahu, built as part of the Green Holmes Hall Initiative (GHHI), and in the city of Kihei, on the island of Maui, built at the Maui Economic Development Board (MEDB). To evaluate the accuracy and precision of the forecasts, plane-of-array irradiance and power production estimates are quantitatively compared against ground-based observations and measurements using four statistical performance metrics:

1) Root Mean Square (RMS) difference - gives a measure of the imperfection of the fit of the estimator to the data in the units of the estimate.

2) Mean Absolute Bias (MAD) - gives the statistical dispersion or mean difference in units of the estimate.

3) Correlation Coefficient (CC) - gives the strength and the direction of the linear relationship.

4) Mean Absolute Percent Error (MAPE) - measures the prediction accuracy, given as a percentage.

We first show HA forecasts for a group of example days from late March 2018 (Figure 6.2g.1). In this set, a clear day (3/28/2018), a cloudy day (3/23/2018), and variable day (3/19/2018) are shown. Irradiance and power forecasts for the MEDB and GHHI sites are shown in Figure 6.2g.1, along with statistical metrics from 1 hour and 2 hour ahead forecasts. The clear sky day shows the level of best agreement for the forecasts, with RMS values of 55.7 and 39.0 W/m2 for the 1-hour and 2-hour ahead forecasts. The cloudy day presented also shows low forecasting error, with RMS values of 61.9 and 92.6 W/m2. As expected, the forecasting errors are higher for the variable day (RMS of 194 and 193 W/m2), however, the forecasts did capture the changes through the day. The forecasting metrics for power output show similar levels of agreement to the irradiance forecasts. This is expected as irradiance is the main source of variability in PV power.
Figure 6.2g.1: Example irradiance (left column) and power (right column) forecasts from three days in late March 2018 at the Green Holmes Hall Initiative (GHHI) and Maui Economic Development Board (MEDB) test sites. Forecasts are indicated by solid dots, with the 1-hour ahead forecasts highlighted in red. Clearsky irradiance (grey thin line - left), pyranometer observations (black thick line - left), power output data (black thick line - right) and daily agreement statistics (1 hour ahead - left side; 2 hour ahead - right side) are also given.
Figure 6.2g.2 shows the statistical results from 1 year of HA forecasts (May 2017 to June 2018). The statistics are computed from data binned with respect to time and forecasting time. The RMS and MAD forecasting metrics increase with forecasting time and vary with diurnal clear sky irradiance. However, the CC and MAPE metrics show little diurnal variability, changing primarily with forecasting time. MAPE and CC for nowcasts and short term forecasts (< 1 hour ahead) show strong agreement (CC > 0.8), with low errors (MAPE < 20%). At 2 hours ahead correlations are above 0.5 and MAPE values are less than 40%. These initial results are promising and demonstrate that the redesign of the HA forecasting component is working correctly. Under APRIES 14 funding, the work will be expanded to a 6-year comparison using pyranometer and PV power data from all four of the main Hawaiian islands.
Figure 6.2g.2: Statistical comparison results from 1 year of Hour-ahead forecasts (HA) forecasts compared against pyranometers at the GHII and MEDB test sites.
Under this funding, we have also continued hardware development for a new ground-based sky imager and solar forecasting instrument, the Affordable High Resolution Irradiance Prediction System (AHRIPS). The design of the third generation of the instrument was completed and construction of five instruments intended for deployment on the island of Molokai was initiated.

Under this funding and in collaboration with researchers from the Department of Atmospheric Sciences at UH Manoa, a long term irradiance database was developed for Oahu, Hawaii. The irradiance database was created using imagery from the GOES-West satellite. This database was then calibrated and validated against irradiance observations from pyranometers located at a variety of locations around the island. A manuscript describing this work was published in the journal Renewable Energy in May 2018, listed below.

**Publications**


### 6.3 Grid Technology Performance Assessments

An array of promising green grid technologies and control systems were analyzed, tested, and evaluated for their performance when grid-connected to a small island utility.

**6.3a Distributed Energy Resources (MC) Maui CC**

The purpose of this project was to demonstrate the performance and integration of certain promising green grid technologies and control systems through implementation and evaluation on the Maui College campus electrical grid. These technologies included integrated PV and on-site storage, renewable energy charging of electric vehicles (EVs), and display of certain results via energy and CO₂ dashboards. The work accomplished in this effort developed from the grid integration tasks initiated under APRISES 11 funding. The goal of demonstrating integrated PV and on site storage was furthered through a number of developments.

An additional 500 kW of rooftop PV and a 500 kW/500 kWh battery were installed. A Power Purchase Agreement (PPA) for the PV and storage, along with an Energy Performance Contract (EPC) for efficiency measures were entered into for longer term support, (beyond the end of this APRISES funding).
A PPA for an additional 1.6 MW of PV and 3MW/12+MWh of battery storage along with an EPC for substantial energy efficiency improvements were executed. Combined with existing systems, the Maui College campus is projected to offset 100% of its electrical usage with renewables within a year.

An important objective of the demonstration project was to effectively integrate the Maui College campus grid with the Maui Electric Co. (MECO) utility grid. Towards that end, an agreement was made to participate in the MECO Fast Demand Response program. This enables MECO to reduce their peak demand by calling on a response from Maui College at certain periods during the month. Maui College responds by reducing its demand on the utility through the discharge of its battery storage system. This is accomplished automatically through coordination of utility-side controls and the campus energy management system.

The goal of developing renewable energy charging of EVs has transformed over the research period. Since DC-DC Level 3 fast charging poses a challenge with renewable energy use, because of the higher voltages, more power, and substantial cost, alternatives were sought.

The solution adopted in this project aimed to take advantage of longer duration stays on the part of staff and students needing to charge their EVs while on campus. This allows the use of lower voltage, lower cost, Level 2 charging. The effort in this phase of the research was to increase the adoption of EVs and to ensure that a greater amount of the electricity would be offset by campus-generated renewable energy resources.

Important lessons were learned through this strategy. When first installed, EV charging was provided free to users. Through most of the day, charging stations were fully utilized. The most pressing challenge was to notify users that their car was fully charged and that they needed to vacate to make room for others. A number of methods were employed to successfully alleviate this problem including campus email to notify charging station users, and campus security to monitor charging station availability.

At a later time campus administration decided to stop subsidizing EV charging. A fee based on usage was determined to be the fairest method for recovering costs. After these fees were implemented, use of the charging stations dropped dramatically as users opted for alternative methods for charging their vehicles. Until existing charging stations are more fully utilized, no plans exist to provide additional EV chargers on campus.

As the utility is highly motivated to increase the adoption of EVs, and also to increase the overall diminishing daytime load on the grid, working closely with HECO/MECO and Hawaii Energy leadership to support managed workplace charging on campus, possibly through some form of cost sharing, is an important strategy. Conversations toward this end have begun.
Meetings with Maui County Department of Transportation were held to explore the use of Maui College campus renewable energy facilities for the charging of public EV shuttles and buses. Both the County and Utility leadership were enthusiastic. In addition, if funds were available, this would be an excellent opportunity to pilot a high power DC-DC fast charger utilizing renewable energy resources.

The goal of demonstrating the use of energy and CO2 dashboards had mixed results.

Although use of the energy and CO₂ dashboard kiosks at Maui College campus has diminished, submetering of individual buildings providing their underlying data has proven useful. Data from eGauge Energy Metering Systems is collected by the campus-wide Metasys Building Automation System and used for crucial energy management tasks such as reduction in campus peak demand and the MECO utility demand response program.

Additionally, British Thermal Unit (BTU) meters are being installed which will provide better assessment of individual building air-conditioning loads. As a result of the campus central chiller plant architecture this information is unavailable to the eGauge building load center metering. Analysis and use of the BTU meter data will be valuable in optimizing overall campus energy management strategies. Further integration of campus assets into a functioning microgrid are planned through the existing EPC and PPA contracts with developer Johnson Controls Inc. without support from APRISES grant funds.

With substantial clean energy generation and storage, as well as a campus-wide energy management system, Maui College is well positioned to participate in both present and future utility grid integration programs. The installation and commissioning of the scheduled large PV array and storage system, will be completed under funding from HEI subsidiary, Pacific Currents.

Currently, energy management strategies are focused on (a) reducing campus peak demand, and (b) participating in the utility FastDR program, designed to reduce the utility peak. Regrettably, these peak demands are not synchronized. Campus peaks can occur mid-day with high-occupancy, when utility loads are small. Reducing campus demand at these times works against utility needs. When utility demand is peaking, typically, between 6 and 8 pm at night, campus load is small. The utility FastDR program is limited to campus minimum load with no export from campus storage systems. As campus generation and storage assets increase, more innovative utility programs involving storage system export should be developed in a potential collaboration between the University, Utility, and Public Utilities Commission.

An area that is ripe to innovate in grid-integration management is the electrification of transportation. Both managed workplace charging, and a pilot, solar-generated, EV-charging
public transportation project can be implemented on the Maui College campus. These strategies could be crucial in addressing the small and decreasing daytime loads experienced by the utility.

An important additional goal, especially in light of recent catastrophic hurricanes, is the plan to increase the resiliency of the Maui College electric grid. Given the potential for 100% offset of day and nighttime loads with campus generation and storage, provision should be made to develop, under other funding, a full microgrid with capacity to either island or interact with the connected utility grid. Plans for additional design and equipment necessary to implement this are underway. The value of a functioning campus microgrid with workshops, labs, food and medical equipment, and other facilities should be realized. In addition, the possibility of being able to export electricity to neighbors would provide additional value to both the utility and community in times of some catastrophic events.

6.3b Demand Side Management (KCC)

The Kauai Community College (KCC) is addressing the challenges of integrating intermittent renewable energy resources into its campus microgrid to help offset rising electricity costs and contribute to grid stabilization. The objective of this subtask was to assess, procure, deploy and analyze the performance and impact of Demand Side Management (DSM) Load Controller technologies and protocols on this microgrid. The KCC intermittent renewable energy technologies, PV and wind turbines, are rated at approximately 800 kW in total, equivalent to approximately 100% of KCC’s peak load. The procurement and deployment of the PV and wind turbine technology was conducted under other funding.

The first phase of this project involved research and benchmarking Load Controller technologies and protocols. Results indicated that distributed lighting controls in each of the classrooms, offices and common areas would address KCC’s needs significantly less expensively than single central building control units. Furthermore, distributed controllers require less extensive training and less operational staff time, reducing the burden on maintenance supervision.

The conceptual design of the system was developed in the second phase of the project, as well as the scope of work, and procurement of the electrical contracting services. To begin the conceptual design, student interns created AutoCAD building plans and system layouts for 25 of the 27 buildings. Douglas Engineering was contracted to finish and review the conceptual design.

The design includes standalone occupancy sensors with ultrasound and infra-red detectors, as well as segmented control relay panels where large areas were previously connected on a single relay
such as the KCC Library. This allows zoning of the area, so that a single occupant has overhead lighting, with the majority of the library remaining lightly illuminated or not at all.

KCC worked closely with RCUH Financial Services as well as UH Facilities and Environmental Health during the bidding process, resulting in a contract with Kauai-based Ron’s Electric to procure and install the equipment.

The third and final phase of the project involved execution of the contracted scope of work, rollout and implementation. This phase included planning, coordination, communication with users, administration of building and office access, as well as finalization of lighting zone layouts and configuration of the respective motion sensors.

Installation of the equipment progressed on schedule and was completed May 23, 2014, with the scope of work fulfilled with no change orders. An independent engineer from Douglas Engineering administered the review, approval and stamping of the final, as built drawings. A follow-up review of the operating status of the equipment by the college’s maintenance staff was conducted on August 26, 2014 and found no complaints or operational issues. Given no change orders were needed, additional motion sensor equipment procurement and installation was made possible.

Learning results included benchmarking international DSM solutions, applying what was learned, and hiring three student interns in the conceptual design, and an additional student intern in the implementation phase.

Motion sensors were installed throughout two of the campus buildings, the One Stop Center and the Learning Resource Center, targeted by the independent electrical engineer as having the most energy cost savings to gain.

The installed sensors deliver a combination of three technologies:

1) Traditional infra-red motion sensing
2) Progressive ultrasound motion sensing, as well as
3) Light receptors, which automatically fade the lights as external outside light shines in.

Findings from this project indicate that distributed lighting controls were significantly less expensive than single central building control units. Standalone occupancy sensors as well as control relay panels allow zoning of the illuminated area, expected to result in a significant decrease in electricity usage and cost.
TASK 7: ENERGY EFFICIENCY

Four projects relating to energy efficiency in buildings were undertaken in collaboration with various consultants, contractors and collaborators: 1) computational fluid dynamic (CFD) methods to assess air movement between internal and external building spaces in naturally ventilated spaces, with consultant Sustainable Design and Consulting; 2) continued monitoring of the Project FROG zero net energy building research platforms with contractor MKThink; 3) the second phase of installing and monitoring the performance of small, vertical axis wind turbines at Crissy Field, in collaboration with the Golden Gate National Parks Conservancy; 4) support of demand response (DR) integration for grid reliability in collaboration with the Hawaiian Electric Company, (HECO).

7.1 CFD Modeling for Naturally Ventilated Spaces

This work was completed in February of 2016 and all of the reports resulting from this study have been posted on the HNEI website. The following is a brief summary of the project.

The project endeavored and successfully delivered on the following objectives:

- Developed a CFD analysis methodology and integrate building ventilation models of the exterior and interior of the buildings. Exterior and interior CFD modeling have a common theoretical basis and similar analysis procedures, but specific applications are different.
- Verified external and internal CFD prediction models of airflow and pressure distribution around and on building envelope and interior spaces.
- Used CFD methods to predict occupant comfort level in naturally ventilated spaces, with and without comfort enhancing technologies.
- Tested prototype installations of naturally ventilated spaces with and without comfort enhancing technologies and assessed the perceived occupant comfort so that actual test data can be correlated with the CFD predictions.

External CFD Investigations: The work involved modeling and validation of wind patterns around the exterior of buildings. Natural ventilation inside buildings is maintained by wind pressures on the building, and external wind conditions are the driving forces for internal air movement. The impact of temperature difference between outdoors and indoors was also investigated. For the research work, only wind induced ventilation (“cross ventilation”) was considered. For effective cross ventilation, a pressure difference between external openings in the building envelope is
required as a driving force to convey air through interior spaces. The most effective of these external openings are on the windward and leeward sides of the building.

The investigations of wind patterns around buildings included assessments of how wind patterns are affected by the building structure under different wind approach conditions. CFD simulations were carried out to predict the wind patterns.

Internal CFD Investigations: Part 2 investigated air movement through interior spaces. The main objective was to identify how internal air movement was affected by external wind conditions and internal pathways. Internal pathways affect the amount of air flow rates through interior spaces. Given the same wind induced external driving forces, internal air flow pathways with the lowest pressure losses cause the highest air flow rates.

Occupant Comfort in Naturally Ventilated Spaces: The basic premise of the investigations into occupant comfort was the performance of so-called “comfort islands”, a term used by the project team. These comfort islands are spaces inside non-conditioned spaces where equipment is installed to provide localized comfort improvements. The value proposition of comfort islands is that by avoiding conditioning the entire space and only providing comfort enhancement measure on a limited localized scale, significant energy can be saved.

External CFD Investigations: The results confirmed that building designers can obtain important insights in the wind patterns and pressure distributions around buildings through the use of advanced CFD simulations, and specifically:

- A naturally ventilated building needs sufficient pressure differentials between external openings to provide the required driving forces for air movements through the buildings.
- Based on results of external CFD simulation the designer can conclude whether the placement and shape of the building can provide good natural ventilation effectiveness.
- Placement and shape of the building includes building orientation relative to primary wind approach direction, wind interactions with adjacent structures and placement and size of external openings.
- While the wind tunnel used to be the preferred method of identifying good wind designs of buildings, CFD simulations are becoming more and more important. The project develops design framework for CFD simulations to predict wind patterns around the buildings.

Internal CFD Investigations: The results showed that CFD simulations can successfully predict air movements in naturally ventilated buildings, and specifically.
The precise prediction of air flow through buildings is necessary to assess the amount of air changes per time period. Such an assessment determines whether or not the naturally ventilated spaces provide code-conformant ventilation rates.

The work culminated in a proposed procedure to predict long-term natural ventilation performance of the building based on CFD simulations combined with long-term wind records.

The outcome is a prediction of the probability that a certain air change in the building can be accomplished by natural ventilation alone, or if additional mechanical assist ventilation would be required.

This application of CFD simulation can be an important design tool for energy saving buildings which rely primarily on natural ventilation.

Occupant Comfort in Naturally Ventilated Spaces: The results confirmed that occupant comfort can be attained in naturally ventilated spaces at any time if comfort enhancement measures, or “comfort islands”, are added to the spaces.

- Typically, naturally ventilated spaces provide insufficient occupant comfort during times of insufficient wind and hot outdoor climate. The research work identified that ceiling fans and combinations of ceiling fans with actively cooled surfaces can provide significant comfort enhancement in naturally ventilated spaces.
- The comfort enhancement through comfort islands can render natural ventilation as a viable alternative to mechanical space cooling and ventilation.
- The investigation also concluded that comfort simulations can successfully predict the level of comfort improvements.

Recommendations for future research and development of comfort islands: Follow-up research into the effectiveness of comfort islands may benefit from the following:

- Using a larger test space. Follow-up tests should use radiant barriers to shield test participants from high radiant temperatures of the surrounding walls and ceiling to improve the effectiveness of radiant surfaces installed around the test subject.
- A dedicated thermal comfort software product should be used in lieu of the generic CFD program that was used during all three parts of the Research Project.
- Validation of the comfort simulations could greatly benefit from the use of instrumented manikins.

Reports produced through these efforts are listed below and available on HNEI’s website.
Reports

References
Zapka, M., Tran, T., Peppard, E., Maskrey, A., Meder, S., Modeling and Validating Thermal Comfort in Naturally Ventilated Spaces, Phases 1, 2 and 3, Volumes 1-14, December 2013-December 2017. (Funded under previous APPRISES grants.)

7.2 Project FROG Monitoring

The Project FROG energy and environmental monitoring work is an extension of the data collection process begun under previous APRISLES grants for the original three Project FROG platforms in Ewa Beach and Kauai, as well as the new platforms installed at the University of Hawaii, all constructed under previous APRISLES funding. The period covered under this APRISLES12 award extends from 2012 through June 2018.

The three first generation FROG platforms were monitored by contractor MKThink for a period of 3 years, and reported in HEET10 and APRISLES11. This monitoring work was suspended from late 2015 through mid-2017, at which time MKThink was contracted to recommission the data acquisition system and begin collecting data that HNEI could use to gauge persistence in performance, as well as establish a more current baseline for which to compare future behavior-related interventions such as education and awareness initiatives and a real-time dashboard to provide feedback to the users. The monitoring typology has been described in detail in past reports, and can be referenced on the HNEI website.

Data was collected from July 2017 through August of 2018, with specific detailed analysis conducted from August through December of 2017, and for February through August 2018. MKThink’s scope for this project included: configuration and implementation; system functionality testing; analysis & visualization support: monthly maintenance of data, including verification, transformation, error removal and data storage.

During the configuration and implementation stage, MKThink tested and refurbished the on-site controllers and sensors, after which data was successfully transmitted to the data server. During functionality testing, MKThink applied a two-step data quality test to determine if sensors were delivering data within acceptable ranges. Step 1 included examining a week’s worth of data (May
20-27, 2017) to see if the results were within an anticipated range. Each type of sensor and corresponding dataset had different minimum and maximum parameters identifying an acceptable range. Please refer to Table 7.2.1 for the sensor error ranges. The first data quality test binned the failed datasets into the following groups: outliers; consistent high single value; pattern exists, but data are too high; data incorrect.

For each sensor at a given timestamp, the following qualitative results were also produced in addition to the quantitative value:

- **good** - if the value is not flagged by any of the following:
- **missing** - no value was received
- **bad** - there was an error converting the raw value
- **too_high** - the value is above the expected maximum value
- **too_low** - the value is below the expected minimum value
Table 7.2.1 Ranges of sensor error for data validation.

<table>
<thead>
<tr>
<th>sensor_name</th>
<th>range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLE_4_SE</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>PLE_5_Center</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>PLE_6_NW</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>FSF_4_SE</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>FSF_5_Center</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>FSF_6_NW</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>AIR_3_E</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>AIR_4_W</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>WAL_3_E</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>WAL_4_W</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>Supply_Air_Humidity</td>
<td>0 ≤ x ≤ 100</td>
<td>RH</td>
</tr>
<tr>
<td>Supply_Air_Temperature_C</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>Room_Air_Temperature_C</td>
<td>0 ≤ x ≤ 50</td>
<td>C</td>
</tr>
<tr>
<td>Room_Air_Humidity</td>
<td>0 ≤ x ≤ 100</td>
<td>RH</td>
</tr>
<tr>
<td>Room_Air_CO2</td>
<td>250 ≤ x ≤ 2000</td>
<td>ppm</td>
</tr>
<tr>
<td>Room_Illuminance_WestWall</td>
<td>0 ≤ x ≤ 350</td>
<td>fc</td>
</tr>
<tr>
<td>Room_Illuminance_Ceiling</td>
<td>0 ≤ x ≤ 350</td>
<td>fc</td>
</tr>
<tr>
<td>Room_Air_Speed</td>
<td>0 ≤ x ≤ 20</td>
<td>mps</td>
</tr>
<tr>
<td>Panel_Feed_pos_kWh</td>
<td>0 ≤ x ≤ 4294967.296</td>
<td>kWh</td>
</tr>
<tr>
<td>Panel_Feed_pos_kW</td>
<td>0 ≤ x ≤ 50</td>
<td>kW</td>
</tr>
<tr>
<td>Panel_Feed_neg_kWh</td>
<td>0 ≤ x ≤ 4294967.296</td>
<td>kWh</td>
</tr>
<tr>
<td>Panel_Feed_neg_kW</td>
<td>0 ≤ x ≤ 50</td>
<td>kW</td>
</tr>
<tr>
<td>Condensing_Unit_kWh</td>
<td>0 ≤ x ≤ 4294967.296</td>
<td>kWh</td>
</tr>
<tr>
<td>Condensing_Unit_kW</td>
<td>0 ≤ x ≤ 20</td>
<td>kW</td>
</tr>
<tr>
<td>Lighting_Main_Space_kWh</td>
<td>0 ≤ x ≤ 4294967.296</td>
<td>kWh</td>
</tr>
<tr>
<td>Lighting_Main_Space_kW</td>
<td>0 ≤ x ≤ 5</td>
<td>kW</td>
</tr>
<tr>
<td>Lighting_Wall_and_Exterior_kWh</td>
<td>0 ≤ x ≤ 4294967.296</td>
<td>kWh</td>
</tr>
<tr>
<td>Lighting_Wall_and_Exterior_kW</td>
<td>0 ≤ x ≤ 5</td>
<td>kW</td>
</tr>
<tr>
<td>Ceiling_Fans_kWh</td>
<td>0 ≤ x ≤ 4294967.296</td>
<td>kWh</td>
</tr>
<tr>
<td>Ceiling_Fans_kW</td>
<td>0 ≤ x ≤ 5</td>
<td>kW</td>
</tr>
<tr>
<td>Fan_Coil_Unit_kWh</td>
<td>0 ≤ x ≤ 4294967.296</td>
<td>kWh</td>
</tr>
<tr>
<td>Fan_Coil_Unit_kW</td>
<td>0 ≤ x ≤ 5</td>
<td>kW</td>
</tr>
</tbody>
</table>

The second step utilized graphic aids, which were then employed to visually inspect dataset patterns and to report on whether or not test range criteria was met. Figure 7.2.1 shows sample data for two of the sensors, Room Illuminance (west wall) and Supply Air Temperature, both in range as is indicated in upper right. Figure 7.2.2 shows a visualization that indicates data is out of range for the Room Illuminance Sensor (ceiling).
Figure 7.2.1 Data validation graphs showing data in range for two sensors.

Figure 7.2.2 Data validation graph detecting out of range data.
Of the 19 datasets that failed the data quality test, 17 did not pass Step 1: Range Check by having values outside the acceptable range. The remaining 2 did not pass Step 2: Visual Inspection. The Table 7.2.2 below lists the reason why each sensor failed the data quality test. In addition, the table below maps each sensor to an error example (e.g. “V-4” is a Visual Inspection - Error Example #4) discussed on the following pages.

Table 7.2.2 Status of sample data points.

<table>
<thead>
<tr>
<th>Sensor Name</th>
<th>Reason Failed</th>
<th>Error Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Kawaiikini West Classroom</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Room Air Speed</td>
<td>Step 2: Visual</td>
<td>V-1</td>
</tr>
<tr>
<td>2 Southeast Floor Surface Temperature</td>
<td>Step 1: Range</td>
<td>R-1</td>
</tr>
<tr>
<td>3 Southeast Plenum Air Temperature</td>
<td>Step 1: Range</td>
<td>R-1</td>
</tr>
<tr>
<td>4 Room Air Temperature</td>
<td>Step 2: Visual</td>
<td>V-2</td>
</tr>
<tr>
<td><em>Kawaiikini East Classroom</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 Supply air humidity</td>
<td>Step 1: Range</td>
<td>R-4</td>
</tr>
<tr>
<td>6 Southeast Floor Surface Temperature</td>
<td>Step 1: Range</td>
<td>R-1</td>
</tr>
<tr>
<td>7 Southeast Plenum Air Temperature</td>
<td>Step 1: Range</td>
<td>R-1</td>
</tr>
<tr>
<td><em>Kawaiikini Weather Station</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 Dew Point</td>
<td>Step 1: Range</td>
<td>R-4</td>
</tr>
<tr>
<td>9 Relative Humidity</td>
<td>Step 1: Range</td>
<td>R-4</td>
</tr>
<tr>
<td><em>Ilma Intermediate Classroom</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 East Wall Surface Temperature</td>
<td>Step 1: Range</td>
<td>R-2</td>
</tr>
<tr>
<td>11 East Wall Air Temperature</td>
<td>Step 1: Range</td>
<td>R-2</td>
</tr>
<tr>
<td>12 West Wall Surface Temperature</td>
<td>Step 1: Range</td>
<td>R-2</td>
</tr>
<tr>
<td>13 West Wall Air Temperature</td>
<td>Step 1: Range</td>
<td>R-2</td>
</tr>
<tr>
<td>14 Northwest Floor Surface Temperature</td>
<td>Step 1: Range</td>
<td>R-2</td>
</tr>
<tr>
<td>15 Northwest Plenum Air Temperature</td>
<td>Step 1: Range</td>
<td>R-2</td>
</tr>
<tr>
<td>16 Center Floor Surface Temperature</td>
<td>Step 1: Range</td>
<td>R-2</td>
</tr>
<tr>
<td>17 Center Plenum Air Temperature</td>
<td>Step 1: Range</td>
<td>R-2</td>
</tr>
<tr>
<td>18 Room Illuminance West Wall(^1)</td>
<td>Step 1: Range</td>
<td>R-3</td>
</tr>
<tr>
<td>19 Room Illuminance Ceiling(^2)</td>
<td>Step 1: Range</td>
<td>R-3</td>
</tr>
</tbody>
</table>

\(^1\) sensor name is incorrect; should be "east wall illuminance"
\(^2\) sensor is "east wing ceiling illuminance"
During data collection, MKThink provided monthly reports on sensor and data quality status. In addition, Task 3 required that data visualization support and training be provided for the use of their tools. This work was continuous throughout the project and was reported on a monthly basis. Figure 7.2.3 is an annotated sample of the data visualization tool, 4Daptive, developed by MKThink. Figure 7.2.4 is an excerpt from the 4Daptive training materials.

Figure 7.2.3 Example of data visualization tool provided by MKThink.

The 4Daptive tool provides the ability to evaluate data collected on any time scale and is capable of drilling down from a one-year or more overview down to a minute-by-minute view. The versatile tool allows on screen selection of single or multiple site locations, single or multiple sensor selection and time frame.
The objective was to gather the one year baseline data for additional HNEI research to compare the first generation to the second generation FROG. MKThink was not tasked with data analysis.

Construction of the two second generation of the Project FROG zero net energy, component-built platforms was completed in late 2016 and initial performance was reported in APRISES13. This section summarizes analysis developed partially under APRISES13, and completed under APRISES12. In addition to being used as classrooms for high school and university students, the structures are being used by HNEI as research platforms to: 1) test efficient building technologies such as energy storage, advanced occupancy sensing, advanced fan control and 2) gather data on actual interior conditions and perceived indoor comfort. The energy performance and environmental conditions are currently being monitored by HNEI with support from the UH School of Architecture’s Environmental Research and Design Laboratory (ERDL).

The energy performance of the two FROG classrooms has on average improved on the first-generation zero net energy FROG designs by up to 47%. The two new mixed-mode FROG classrooms built on the UH Manoa (UHM) campus demonstrate advanced lighting and HVAC
control schemes as well as the impacts of user education and awareness. HNEI monitored energy consumption and generation at circuit-level, and recorded internal environmental conditions to determine the relationship between comfort, environmental factors, energy demand and user response to new controls. A dashboard in each classroom delivers real-time visual feedback to users.

The actual energy performance exceeded both the predictive building simulation models as well as the first-generation all-electric zero net energy structures also built for HNEI, realizing energy use intensity (EUIs) of 8.11 to 10.37 kBtu/sf/yr, excluding solar. This is in part attributed to improved lighting and daylighting controls, and especially a unique, On-Demand approach to controlling the HVAC use. The On-Demand control reduced energy consumption 84% beyond a conventional thermostat scheduled for 7 a.m. to 7 p.m. operation. The On-Demand control is particularly effective in classroom environments where schedules and staffing vary daily and hourly over the week.

This comparison of the five buildings demonstrates that efficiency, advanced controls, user training and real-time feedback are key elements in the FROG’s successful performance. This section compares the performance of the two generations of zero net energy structures (Figure 7.2.5), the performance of innovative energy saving control strategies, and the influence of user preference and behavior on energy consumption.

![First-generation FROG (left) with locations in Ewa Beach, Oahu and Lihue, Kauai. Second-generation FROG (right) located on the University of Hawaii at Manoa campus.](image)

Both generations of the Project FROG structures are component-based and assembled on site. The envelope design integrates basic energy efficient concepts: due north and south orientation to minimize solar gain; overhangs further shield the high performance, low-e glazing from solar gain; and the walls and roofs are well insulated.

The second-generation FROG benefit from more sophisticated lighting and HVAC controls than the first generation. They utilize LED lighting with daylight harvesting controls that optimize lighting levels according to the amount of daylighting available within the space while the first
The second generation HVAC design is fine tuned for mixed-mode performance, delivering slightly higher temperature supply air in order to avoid condensation at the supply registers due to higher room humidity levels. On-Demand controls require users to make a conscious decision to turn the AC ON (i.e. a user preference), which allows the unit to run for one hour only. When the conditions require that it be restarted, the override button is once again pressed. In classroom situations where there may be long intervals between classes, and where users may have different room condition preferences, this feature results in significant savings if the button is not pressed again. As research platforms, the UHM FROG classrooms incorporate a real-time dashboard that displays current and past operating conditions, including indoor comfort indicators, as well as the energy used by different end-uses. Intended as an educational tool, the dashboard and supplemental training for instructors aimed to foster more conscious energy efficient behavior by allowing the building occupants to visualize their energy usage and PV generation.

A comparison of the energy features of both generations of FROG are listed in Table 7.2.3. They share common features such as envelope insulation and glazing, however the lighting, HVAC and approach to natural ventilation are different.

Table 7.2.3 Energy features of two generations of FROG buildings.

<table>
<thead>
<tr>
<th>Energy Features 1st Generation FROG (1,280 sf)</th>
<th>Energy Features 2nd Generation FROG (1,440 sf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• R-24 walls; R-30 roof decks.</td>
<td>• R-24 walls; R-30 roof decks.</td>
</tr>
<tr>
<td>• Operable louvers at the base of the solid wall panels for natural ventilation.</td>
<td>• High and low operable windows for natural ventilation.</td>
</tr>
<tr>
<td>• High and low operable windows for natural ventilation.</td>
<td>• Low-e, PPG Solarban 70XL glazing (SHGC=0.27; U=0.24; VLT=64%).</td>
</tr>
<tr>
<td>• Low-e, PPG Solarban 70XL glazing (SHGC=0.27; U=0.24; VLT=64%).</td>
<td>• External shade structure on south glazing.</td>
</tr>
<tr>
<td>• Roof mounted exhaust fan at high point of the roof for fan induced ventilation.</td>
<td>• Direct/Indirect LED lighting with daylight control.</td>
</tr>
<tr>
<td>• Direct/Indirect fluorescent T8 lighting with photosensor daylight control.</td>
<td>• Six speed, variable speed ceiling fans.</td>
</tr>
<tr>
<td>• Nine speed, variable speed ceiling fans.</td>
<td>• High efficiency split system fan coil and condensing unit (EER: 11.8).</td>
</tr>
<tr>
<td>• High efficiency split system fan coil and condensing unit (EER: 11.0).</td>
<td>• North-South orientation.</td>
</tr>
<tr>
<td>• North-South orientation</td>
<td>• PV systems: 8.0 kW per structure.</td>
</tr>
<tr>
<td>• PV systems: 5.24 kW per structure.</td>
<td>• All electric, no natural gas on site</td>
</tr>
</tbody>
</table>
The first generation FROGs were instrumented and monitored for three years, ending in 2016 and recommissioned mid-2017. The second generation FROGs were instrumented and monitored from September 2016. Table 7.2.4 summarizes the sensing points for both generations.

Table 7.2.4. The sensing points for the environmental and energy data

<table>
<thead>
<tr>
<th>Electrical circuits</th>
<th>Indoor</th>
<th>Weather</th>
</tr>
</thead>
<tbody>
<tr>
<td>HVAC condenser</td>
<td>Room air temperature</td>
<td>Ambient temperature</td>
</tr>
<tr>
<td>HVAC fan coil</td>
<td>Wall surface temperature</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>Lighting (internal and external)</td>
<td>Supply and return air temp.</td>
<td>Solar radiation</td>
</tr>
<tr>
<td>Ceiling fans</td>
<td>Relative humidity (room, supply and return duct)</td>
<td>Wind speed</td>
</tr>
<tr>
<td>Solar PV</td>
<td>CO2 concentration</td>
<td>Wind direction</td>
</tr>
<tr>
<td>Exhaust fan (1st Gen. only)</td>
<td>Illumination</td>
<td></td>
</tr>
<tr>
<td>Panel feed</td>
<td>Air speed (1st Gen. only)</td>
<td></td>
</tr>
</tbody>
</table>

When comparing EUI between the first and second generation FROGs, on average the second generation uses approximately 47% less energy per square foot than the first generation (Table 7.2.5). Consumption data for the second generation is from the calendar year 2017, but calculated rather than actual PV data was used since it was installed in late 2017. Consumption data for the first generation are from August 1, 2017 through January 31, 2018 (six months) and doubled for a one-year estimate. Since the PV generation was lower for these months and not representative of a full year, the 2014-2015 school year PV data was used.

Table 7.2.5. Source energy use intensity (EUI) for 2017

<table>
<thead>
<tr>
<th></th>
<th>1st Generation FROG</th>
<th>2nd Generation FROG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kawaikini East</td>
<td>Kawaikini West</td>
</tr>
<tr>
<td>Total annual electricity energy (kWh/yr)</td>
<td>5,549</td>
<td>2,165</td>
</tr>
<tr>
<td>Actual EUI (kBtu/sf/yr)</td>
<td>14.79</td>
<td>5.77</td>
</tr>
</tbody>
</table>

Energy disaggregation of all five FROGs can be seen in Figure 7.2.6. On average, less energy is used for both lighting and HVAC systems in the second generation than the first generation. Ceiling fans make up a larger proportion of the energy consumed in the second generation by
virtue of the smaller lighting and cooling loads. Led by conscientious instructors, Kawaikini West has developed over time into an anomaly where users have embraced energy efficient practices, using very little air conditioning and taking full advantage of natural daylighting.

Figure 7.2.6 Energy disaggregation all five FROG in 2017.

Addressed in the User Education and Behavior section to follow, when the occupants are committed to reducing energy and are flexible in their adaptation to comfort within their environment (Deuble et al. 2012), EUIs may be minimized as exemplified by the EUI of 5.77 kBtu/sf/yr for Kawaikini West.

Overall energy generation and consumption across the five FROGs is illustrated in Figure 7.2.7. Conspicuously, the Ilima FROG has not hit its zero net energy targets over the past year, with consumption exceeding generation by 29%. This is due to a higher than anticipated use of air conditioning in the classroom, which is located in one of the hottest regions of the state.
Figure 7.2.7 Overall energy generation and consumption comparison of five FROGs in 2017.

All of the other FROGs are hitting their zero net energy goals. The PV systems for the UHM FROGs are oversized relative to their current consumption. The operating hours assumed in the design phase are greater than the current operating schedule, but as the buildings’ utilization increases, the loads are expected to grow.

The UHM FROGs are multi-purpose classrooms whose schedules vary daily throughout the week. The mornings are used consistently by a UH-based charter K-12 school, while the afternoons are used by the UH College of Education, with one or two classes conducted through the afternoon and evenings. Classes may be held from 5 to 10 hours per day over a 12-hour period. The schedules are dynamic in that they change every semester, and to date they are currently operating at an average of 71% of capacity, non-inclusive of extracurricular weekend activity.

These mixed mode buildings are designed to actively engage users while utilizing some degree of automated controls. The lighting utilizes daylight harvesting sensors to reduce lighting energy, although users are encouraged to manually turn the lights completely off when the daylight is adequate to meet class-specific needs. HVAC utilizes an On-Demand control that requires user engagement to activate, but automatically shuts off after one hour. Ceiling fan operation is 100% manual, utilizing a variable speed wall switch. The impact of this hybrid approach to engage the user is discussed later in the Results portion of the report.
Data analyzed for this report are from the fall 2017 semester (August 20-December 16, 2017; 119 days), after instrumentation commissioning was complete and regular classroom scheduling was implemented (previous semester trial schedules were irregular). The period includes 81 school days and 38 non-school days (weekends + holidays). The building schedules differ slightly as shown in Table 7.2.6, with FROG 1 having approximately 10% greater classroom occupancy hours than FROG 2.

Table 7.2.6 UHM FROG 2017 fall semester schedule.

<table>
<thead>
<tr>
<th>Schedule</th>
<th>UHM Frog 1</th>
<th>UHM Frog 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:30-12:30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:45-4:15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4:30-7:00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Energy consumption is distributed among five primary end-uses: HVAC, lighting, ceiling fans and other that includes telecommunications, fire alarm, multi-media, and misc. plug loads, see Table 7.2.7 below:

Table 7.2.7 Energy summary by disaggregated loads (August 20 – December 16, 2017).

<table>
<thead>
<tr>
<th></th>
<th>Air conditioning (kWh)</th>
<th>Ceiling fans (kWh)</th>
<th>Indoor lights (kWh)</th>
<th>Other loads* (kWh)</th>
<th>Whole building (kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall 2017 Semester (24h/7days)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UHM FROG 1</td>
<td>866</td>
<td>283</td>
<td>212</td>
<td>577</td>
<td>1,938</td>
</tr>
<tr>
<td>UHM FROG 2</td>
<td>576</td>
<td>229</td>
<td>222</td>
<td>500</td>
<td>1,528</td>
</tr>
<tr>
<td>Fall 2017 Semester for Scheduled Occupied Hours</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UHM FROG 1</td>
<td>632</td>
<td>147</td>
<td>132</td>
<td>219</td>
<td>1,130</td>
</tr>
<tr>
<td>UHM FROG 2</td>
<td>409</td>
<td>149</td>
<td>103</td>
<td>197</td>
<td>858</td>
</tr>
</tbody>
</table>
*Other loads=Plug loads + Telecommunications + Multi-Media + Fire alarm

Due to the user engagement required to optimize the utilization of the UHM FROGs, education and training are essential. Currently, brief training sessions are held for the instructors using the rooms. In addition, an engaging poster with cues on basic building operation were placed in each classroom. Finally, a dashboard is mounted in each room providing real-time feedback on daily and year-to-date energy generation, daily energy consumption by end-use, and comparative results to the other FROGs.

Lighting energy in the UHM FROGs is controlled by two types of wireless sensors and a control module. Two wireless Lutron Pico occupancy sensors per classroom activate the lights when entering the room. A Lutron QSM daylight sensor mounted on the ceiling automatically sets the light levels according to ambient conditions. A Lutron Energy Saver Node Module interfaces with the daylight and occupancy sensors to manage the lighting operation according to user-programmed criteria. In the main room, four rows of Lutron Lantana LED fixtures are controlled by one occupancy sensor and one daylight sensor. In the entry zone, 2 rows of fixtures have identical controls. The rows are pre-programmed to operate at light levels determined by their distance from the windows. On a typical sunny day, approximately 30 seconds after the lights are activated by the occupancy sensor, the fixtures will dim to the minimum Illuminating Engineers Society (IES) standards required for the space, with the perimeter row dimming to about 10%, the center row to about 25% and the interior row to about 40%. The fourth bank located in the rear of the room, is also at about 40%. On overcast days and evenings, the fixtures will ramp up output accordingly.

The impact of this control configuration is illustrated in Figure 7.2.8a. Various sensor configurations are compared for a hypothetical day with a full schedule. No controls would use the lights at full brightness (0.47 kW) from 7 a.m. to 7 p.m. The occupancy sensor (OS) would turn off lights during the breaks between sessions, saving 13%. The daylight harvesting (DH) in addition to OS is estimated to save 35%.

Considering a full semester, if there were no controls and lights used at full brightness from 7 a.m. to 7 p.m., 457 kWh would have been used (Figure 7.2.8b). However, the schedule was only filled 74% and 68% of capacity (see Table 7.2.8 but percentages account for hours users did not occupy the buildings at their scheduled time), resulting in a reduction to 340 kWh and 309 kWh from the OS (26% and 32% savings). The users manually turned the lights off 43% to 48% of the time they occupied the buildings, reducing the energy to 192 kWh and 160 kWh, leaving less need for daylight harvesting which reduced the energy to 139 kWh and 113 kWh.

As will be discussed in the User Education and Behavior section, the most effective intervention is manual, where the user turns the fixtures off completely, using only daylighting to deliver slightly less than IES standards. In these FROGs, natural daylight can provide adequate light most of the daytime hours.
Classrooms in a university setting have dynamic schedules that may vary significantly by day over the course of a week. The UHM FROGs were outfitted with an On-Demand control for the HVAC system to reduce run time when there are no occupants in the building. In addition, the On-Demand control requires user engagement and decision-making (called technological or environmental adjustment in Azizi et al. 2015), increasing the awareness of building operation.

The On-Demand system integrates the functionality of a vacancy sensor and a timer. In order to run the HVAC, the user must consciously decide that cooling is required, then engage an override switch that turns the system on for an hour. After the system turns OFF, the user must decide whether the interior conditions warrant a second hour of cooling.

To illustrate, Figure 7.2.9 presents two energy profiles for one day, one with a conventional thermostat, and one with an On-Demand thermostat. Based on five-minute averages of the occupied periods over the entire semester, the On-Demand control shows an 84% reduction in energy consumption over the daily energy that would have been used absent controls to limit its operating time.

Another design modification was incorporated into the UHM FROGs, specifically to address issues that can face mixed-mode buildings. Mixed-mode buildings utilize both natural ventilation systems and mechanical systems, frequently on the same day. In humid regions, bringing in air through operable windows also introduces moisture to the space. In the FROG design, the design supply air temperature was elevated to 65°F rather than conventional 55°F supply air temperature, in order to avoid condensation at the supply air registers that could result from the elevated humidity.
The setpoint for the On-Demand controller is 77°F. While the indoor air temperature does not always reach the setpoint, the variable speed ceiling fans provide air motion whose comfort perception is equivalent to approximately 3-6 °F reduction of air temperature.

User behavior and response to a building’s condition can impact energy end-use even more than automated controls.

The UHM FROGs were designed to rely heavily on natural daylighting and daylighting controls. When comparing occupancy sensing controls, daylight harvesting sensors and the human factor of choice (to turn off the lights), the user initiated response saved the greatest amount of energy (Figure 7.8b). If the schedule utilization increased from the current 74% and 68% to 100%, the user choice will represent the largest energy savings by far.

Figure 7.2.10 indicates that different user preferences will impact the decision to switch the lights ON or OFF. A noticeable difference in lighting energy use is seen between the two FROGs, indicating that one classroom is more energy conscious; or the classes require more lighting to reach their educational mission (e.g. art may require greater visual acuity); or a pattern due to habituation to turning lights on has developed over time. The illustration shows that user-choice significantly impacts energy use in otherwise identical classrooms.
A mixed mode building is also dependent on user response to the interior conditions. While the intention is to minimize use of mechanical cooling and rely primarily on natural ventilation through open windows as well as ceiling fans, user preference and/or operational awareness (again technological or environmental adjustment, Azizi et al. 2015) can impact their response. One type of user prefers the fresh air and wishes to save energy. Another user may activate the air conditioning without regard to energy; while yet another is indeed responsive when properly informed of the intent and features of a special zero net energy building, and is willing to physically open and close the windows as necessary.

User behavior in these two buildings can be observed in several dimensions. As suggested in Figure 7.2.11, after a training session was offered during the first week of classes, HVAC consumption dropped whereas consumption in FROG 1 increased. The pattern reflects conscientiousness over HVAC energy system use in the FROG 2 classroom that is not reflected in FROG 1. While this was not a target of rigorous evaluation in this study, anecdotal input from the instructors indicates that training and awareness of how the systems operate affect behavior and overall consumption. The impact of reduced HVAC operation is of course, higher temperature. But as it has been observed by previous researchers (Deuble et al. 2012), occupants with a higher level of environmental concern were more forgiving of their building and prepared to overlook less-than-ideal conditions as compared to less environmentally-conscious occupants. The temperature differential for the two mixed-mode buildings over the entire semester averaged 1.34°F: FROG 1 averaged 79.47°F and FROG 2 averaged 80.81°F.
The second dimension to decision-making and behavior relates to decision mid-session. Once a decision has been made to turn on the On-Demand HVAC, a secondary decision will be when the one-hour ON time period is over. The user must answer the question, “Are we comfortable enough to not need a second hour?” With ceiling fans running, the interior conditions must be assessed against the current comfort levels. If conditions are currently acceptable, a conscious decision can be made to not run the HVAC for a second hour.

A third level of decision-making relies on the awareness of how the building operates, and a commitment to the proper operation of a zero net energy building, primarily dependent upon education and training. We have observed that even though there were only 10-15 minutes left of class, the one-hour override switch was pushed, leaving at least 45 minutes of cooling an unoccupied space. With a conscientious approach, a user might elect to forego HVAC for few remaining minutes of a class with the knowledge that much of it will be wasted. Alternatively, they can turn the system ON, but as aware users, manually turn it OFF when leaving the classroom. These situations require insight into how the controls operate as well as philosophical “buy-in” into the design intent of the facility. This insight is gained through comprehensive and effective training of the users.

Another factor to consider when operating a mixed-mode building is that of air quality, specifically CO2 concentration. In the UHM FROGs, a CO2 build-up was noticed when the HVAC was running, and presumably the windows were not open (Figure 7.2.12). The CO2 concentration increased even more after the HVAC turns off, presumably because they still occupy the building but have not opened the windows. Conversely, when running in a naturally ventilation state, the windows were open and CO2 levels remained low. Over the course of the semester and during occupied hours, the FROG 1 consistently ran the HVAC system more than the FROG 2 (Table 7.2.7). Table 7.2.6 shows consistently higher CO2 concentrations in FROG 1 in the morning.

Figure 7.2.11 Weekly average of HVAC power for morning class session for occupied hours.
session while the building used HVAC more (Figure 7.2.11). Figure 7.2.13 shows an increase in CO2 concentration in FROG 1 over the semester, suggesting that the habit of not opening the windows continued even though the need for HVAC was less as the outdoor temperatures decreased over the fall. This reduction in HVAC use can be seen by trend line in Figure 7.2.11.

![Graph showing CO2 and HVAC power consumption over time.](image)

Figure 7.2.12 Example of CO2 concentration increasing as users remained in building after HVAC turned off (assuming the windows were still closed).

Table 7.2.6 Average CO2 concentrations (ppm) for the morning session for the fall 2017 semester

<table>
<thead>
<tr>
<th>Hour</th>
<th>Mon</th>
<th>Tues</th>
<th>Wed</th>
<th>Thur</th>
<th>Fri</th>
<th>Mon</th>
<th>Tues</th>
<th>Wed</th>
<th>Thur</th>
<th>Fri</th>
</tr>
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<tbody>
<tr>
<td>7</td>
<td>454</td>
<td>506</td>
<td>549</td>
<td>468</td>
<td>476</td>
<td>442</td>
<td>446</td>
<td>445</td>
<td>447</td>
<td>457</td>
</tr>
<tr>
<td>8</td>
<td>749</td>
<td>776</td>
<td>752</td>
<td>706</td>
<td>721</td>
<td>587</td>
<td>555</td>
<td>525</td>
<td>575</td>
<td>602</td>
</tr>
<tr>
<td>9</td>
<td>959</td>
<td>934</td>
<td>862</td>
<td>913</td>
<td>895</td>
<td>680</td>
<td>628</td>
<td>543</td>
<td>678</td>
<td>706</td>
</tr>
<tr>
<td>10</td>
<td>1,102</td>
<td>1,066</td>
<td>1,056</td>
<td>1,082</td>
<td>1,020</td>
<td>737</td>
<td>664</td>
<td>566</td>
<td>722</td>
<td>721</td>
</tr>
<tr>
<td>11</td>
<td>1,151</td>
<td>1,072</td>
<td>937</td>
<td>1,106</td>
<td>1,120</td>
<td>738</td>
<td>692</td>
<td>558</td>
<td>784</td>
<td>709</td>
</tr>
<tr>
<td>12</td>
<td>920</td>
<td>840</td>
<td>716</td>
<td>949</td>
<td>884</td>
<td>671</td>
<td>635</td>
<td>500</td>
<td>720</td>
<td>704</td>
</tr>
</tbody>
</table>

![Graph showing hourly CO2 concentrations for the morning session.](image)

Figure 7.2.13 Hourly average CO2 concentrations for the morning session during occupied hours.
The following preliminary data analysis covers the period January 1-August 10, 2018 and considers both university and high school occupancy of the UHM FROGs, including the second semester of the high school calendar (January 8-May 31, 2018) and two UH semesters, Spring 2018 (January 8-May 12, 2018) and Summer sessions 2018 (1st session: May 21-June 29, 2018; 2nd session: July 2, August 10, 2018). For details please refer to Table 7.2.8.

Table 7.2.8 High school and UH classroom utilization calendars

<table>
<thead>
<tr>
<th>High school calendar</th>
<th>UH calendar</th>
<th>UH calendar</th>
<th>UH calendar</th>
</tr>
</thead>
<tbody>
<tr>
<td>2nd semester</td>
<td>Spring 2018</td>
<td>Summer sessions 2018</td>
<td>Summer sessions 2018</td>
</tr>
<tr>
<td>First day of instructions</td>
<td>Jan. 8, 2018</td>
<td>First day of instructions</td>
<td>May 21, 2018</td>
</tr>
<tr>
<td>Last day of instructions</td>
<td>May 31, 2018</td>
<td>Last day of instructions</td>
<td>Jun. 29, 2018</td>
</tr>
<tr>
<td>School days</td>
<td>90</td>
<td>School days</td>
<td>22</td>
</tr>
<tr>
<td>Holidays</td>
<td>14</td>
<td>Holidays</td>
<td>2</td>
</tr>
<tr>
<td>Weekend days</td>
<td>40</td>
<td>Weekend days</td>
<td>10</td>
</tr>
<tr>
<td>Non-school days (holidays+weekend days)</td>
<td>54</td>
<td>Non-school days (holidays+weekend days)</td>
<td>12</td>
</tr>
<tr>
<td>Total number of analyzed days</td>
<td>144</td>
<td>Total number of analyzed days</td>
<td>34</td>
</tr>
<tr>
<td>Holidays: Jan. 15 (Dr. Martin Luther King, Jr.), Feb. 12 Institute Day; Feb. 19 (Presidents’ Day); Mar. 19-23 Spring Break; Mar. 26 (Kuhio Day); Mar. 30 (Good Friday); May 20 (Memorial Day)</td>
<td>Holidays: Jan. 15 (Dr. Martin Luther King, Jr.), Feb. 19 (Presidents’ Day); Mar. 26 (Kuhio Day); Mar. 30 (Good Friday)</td>
<td>Holidays: May 28 (Memorial Day); Jun. 11 (Kamehameha Day)</td>
<td>Holidays: Jul. 4 (Independence Day)</td>
</tr>
</tbody>
</table>

Both interior and exterior conditions were monitored during the considered period. UHM FROG buildings are equipped with 8kW PV systems which were installed at the end of 2017 and commissioned in January 22, 2018. The weather station installed at the same time as the PV is located on the roof of FROG 1, providing temperature, relative humidity, solar radiation, wind speed and wind direction.

The energy consumption of the building was evaluated using data collected at 5 min average data WebCNTRL instrumentation. The two classrooms were used according to different schedules (morning, afternoon, evening sessions) and hours per month (Figure 7.2.14).
Figure 7.2.14: Number of scheduled hours UHM FROG

Figure 7.2.15 shows the weekly energy consumption of both UHM FROG buildings. The first four weeks of the year 2018 (January 1-30, 2018) have not been included in the analysis due to technical problems with the data acquisition system. Thus, the analysis of the energy consumption covers February 1 to August 10, 2018.
Figure 7.2.15: UHM FROG 2018 weekly energy consumption, February – August 2018

FROG 1 has a higher weekly energy use than FROG 2 due to the higher scheduled usage in the first three months (interesting, FROG 2 has a higher scheduled usage in April but not a higher energy consumption). The first drop of energy consumption (week 12) corresponds to the ULS spring break (March 19-23, 2018). After that, the consumptions increased again but then, the weekly energy usage decreased significantly for both buildings starting from week 20 which corresponds to the end of the Spring semester for UHM students and the end of the second semester for ULS students.

On January 22, two 8kW PV systems were turned on. The electricity production during the investigated period of analysis is shown in Figure 7.2.16.
Table 7.2.9 shows the energy used by appliance for the entire period of analysis (Feb. 1-Aug. 10, 2018). For detailed monthly usage values, please refer to Figure 7.2.17.

Table 7.2.9 Energy summary (disaggregated loads) – February 1-August 10, 2018

<table>
<thead>
<tr>
<th>UH FROG</th>
<th>Air conditioning (kWh)</th>
<th>Ceiling fans (kWh)</th>
<th>Indoor lights (kWh)</th>
<th>Other loads* (kWh)</th>
<th>Whole building (kWh)</th>
<th>PV production (kWh)</th>
<th>Whole building net (kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FROG 1</td>
<td>607</td>
<td>153</td>
<td>204</td>
<td>895</td>
<td>1,859</td>
<td>6,330</td>
<td>4,471</td>
</tr>
<tr>
<td>FROG 2</td>
<td>520</td>
<td>184</td>
<td>218</td>
<td>807</td>
<td>1,728</td>
<td>6,383</td>
<td>4,655</td>
</tr>
</tbody>
</table>

*Other loads = Plug loads + Telecommunication + Window actuators + Fire alarm
FROG 1 used more HVAC and indoor lights during the first months of the year (February-April), then the usage started to decrease and in the last analyzed months (June-August), the building was using more ceiling fans. FROG 2 shows a lower usage of HVAC in the first months (February-March), then the consumption increased up to May and then decreased again. Differently from the other building, HVAC was used in July.

During the analyzed period of time (February 1-August 10) the scheduled occupancy of both building was different and equal to: FROG 1 = 991.25 hours; FROG 2 = 911 hours. By dividing the energy and the scheduled occupancy (occupied hours) the following Table 7.2.10 and Figure 7.2.18 are obtained. Thus, even if FROG 2 was theoretical used for a less amount of time, it shows a higher energy consumption due to the use of more ceiling fans and indoor lights.
Table 7.2.10 Energy normalized by occupied hours – February 1-August 10, 2018

<table>
<thead>
<tr>
<th>UH FROG</th>
<th>Air conditioning (kWh/h)</th>
<th>Ceiling fans (kWh/h)</th>
<th>Indoor lights (kWh/h)</th>
<th>Other loads* (kWh/h)</th>
<th>Whole building (kWh/h)</th>
<th>PV production (kWh/h)</th>
<th>Whole building net (kWh/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FROG 1</td>
<td>0.61</td>
<td>0.15</td>
<td>0.21</td>
<td>0.90</td>
<td>1.88</td>
<td>6.39</td>
<td>4.51</td>
</tr>
<tr>
<td>FROG 2</td>
<td>0.57</td>
<td>0.20</td>
<td>0.24</td>
<td>0.89</td>
<td>1.90</td>
<td>7.01</td>
<td>5.11</td>
</tr>
</tbody>
</table>

Figure 7.2.18 UHM FROG energy normalized by occupied hours

Conclusions

Based on the initial observations of the UHM FROGs, the second generation design has the potential to outperform the first generation design. However, user response to interior conditions and use of the operable features of the buildings, HVAC, lighting, ceiling fans, and windows, will be the primary driver in determining overall energy consumption.

While one of the first generation FROGs achieved an EUI of 12.9 kBtu/sf/yr in the 2015 study year, recent 6 month observations reduce it to an equivalent of 5.77 kBtu/sf/yr.
The second generation lighting system controls, i.e., occupancy sensor and daylight harvesting, contribute at least 35% savings, but considering user behavior of choosing to turn lights off total savings of up to 75% resulted.

Limiting the duration of HVAC operation by using an On-Demand thermostat, savings of up to 84% were observed. These reductions are due to the HVAC system operating only when users are present as well user opportunity to consider natural ventilation options. The On-Demand thermostat is a mechanical equivalent to a vacancy sensor as it must be manually activated, and will automatically shut off.

During this project, HNEI identified future interventions that will improve overall performance of zero net energy buildings, including:

- Provide comprehensive education and training to all users, not simply the instructors, but classroom users (students) as well. This can be done with online mini-training; in-person; or through a “train the trainers (instructors)” approach.

- Reprogram the lighting controls to vacancy sensing, requiring the lights to be manually turned ON between the hours of 8 p.m. and 5 p.m., rather than automatically turned on with an occupancy sensor. Natural daylight may be adequate for classroom purposes.

- Install actuators on manually operated windows will overcome one barrier to natural ventilation: the time-consuming task of opening a multi-window banks of windows.

- Install occupancy sensors for fans.

**Reports and Presentations**

MKThink. 2016. "Net Zero Energy Test Platform Performance Comprehensive Analysis".


**References**

MKThink. 2016. "Net Zero Energy Test Platform Performance Comprehensive Analysis".


**7.3 Small, Vertical Axis Wind Turbines at Crissy Field Center**

This is the second phase study of small, vertical axis wind turbines, which were installed at Crissy Field in San Francisco Figure 7.3.1 in collaboration with the Golden Gate National Parks Conservancy. The first phase, with five (different) wind turbines, was funded under HEET09, N00014-10-1-1310 and was completed in December 2015.

![Crissy Field Education Center, San Francisco, CA. UGE turbines 1st and 4th from the left. Omniflow turbines 2nd and 3rd from the left.](image_url)

Figure 7.3.1 Crissy Field Education Center, San Francisco, CA. UGE turbines 1st and 4th from the left. Omniflow turbines 2nd and 3rd from the left.
This phase of the project provided for the installation and performance monitoring of four vertical axis turbines -- two UGE VisionAire3 systems and two Omniflow1.2 systems, see Figure 7.3.2. These were installed at the site of the previous five wind turbines. The UGE turbine is a Darrieus type design similar to three in the first study but by a different manufacturer, while the Omniflow turbines are of a unique design that combines a Venturi effect with integrated PV cells. A data acquisition system collected wind and power data in one second intervals, with enough resolution to determine response lag. In addition to turbine performance, the project sought to determine the impact of land based, urban obstructions such as vehicles, trees, shrubs and ground surface variations on unobstructed wind.

The objective of the second phase of research was to evaluate and test selected wind turbine technologies to determine the relative effectiveness of differing turbine design technologies; the impact of urban wind conditions (environment-induced turbulence) relative to idealized (laminar) wind conditions under which turbines are tested and rated; and integration with the test platform systems toward the achievement of energy neutrality and/or net positive energy within the test site.”

The Crissy Field site provides an ideal location to conduct wind technology research, as the site is subject to urban wind conditions and is immediately adjacent to the unobstructed area of the San Francisco Bay. The wind regime at the Crissy Field site is quite different than when measured from the unobstructed reference wind site, Anita Rock from which design data was originally taken. Trees and buildings surrounding a site create an “urban wind” effect that reflects diminished velocity and power of the wind, while creating turbulence that may also impact the ability to translate wind into power across a turbine blade.

The subawardee, Golden Gate National Parks Conservancy, contracted with Luminalt Energy Corporation for the design, maintenance and installation of the turbines. Luminalt was also the contractor for the installation of phase I. Consultant Loisos + Ubbelohde were also contracted for the design and installation of the data acquisition systems, including power and wind sensing devices. Weatherflow provided wind data for the Anita Rock wind monitoring site offshore of Crissy Field.
The design team for phase II was tasked with making use of the existing infrastructure from phase I to the greatest extent possible. Existing footings, conduit and conductors were reused, and in the case of the Omniflow units, the towers from the Phase I Venco units were retrofitted to accept the new turbines. Existing footings were evaluated for by structural engineers, Plump Engineering, to confirm structural adequacy for the new turbines and to design adapter plates to match the new bolt patterns.

The majority of the components for the project were purchased by the project prime contractor, Luminalt Energy Corporation. Luminalt purchased the two UGE Vision AIR 3 turbines, 7 meter towers, associated electronics and adaptor plates (and required engineering) from Castle Energy LLC. Castle Energy is a registered distributor for UGE products. Figures 7.3.3 through 7.3.6 highlight various phases of the installation process.
Figure 7.3.3 UGE Turbines and Towers delivered to Crissy Field.

Figure 7.3.4 UGE Turbines unpacked and stored for installation at site.
The Parks Conservancy contracted directly with Omniflow to purchase two turbines and associated electronics. The Omniflow is configured as a hub with fan blades that spin on a vertical axis. A flange mounted to the bottom perimeter of the hub features 2 rows of photovoltaic silicon cells, as shown in Figure 7.3.7.
Figure 7.3.7 Omniflow photovoltaic cowling before assembly (l). Omniflow turbine prior to installation of photovoltaic flanges (r).

Figure 7.3.8 Omniflow controller unpacked.

Figure 7.3.9 Fully assembled Omniflow in preparation to raise.
Figure 7.3.10 Completed Omniflow (left) and UGE (right) turbines.
All components and equipment for upgrading the data acquisition system (DAS) system for Phase II were sourced by project sub-consultants Loisos + Ubbelohde, who were responsible for the design and installation of the system as well as for developing and implementing the data monitoring protocols.

For the new DAS design, the team at Loisos + Ubbelohde sought to both enhance the earlier system’s data collection capacity and correct for the correlation issues identified in Phase I. The design team was able to reuse most of the installed infrastructure from the Phase I DAS system, but the requirements for Phase II necessitated additions/modifications to both the physical hardware and the data collection design.

In Phase I, wind speed and turbine power output were sampled at different time intervals. The former measured instantaneous samples and the latter recorded sixty second averages. For Phase II, a new data collection protocol was developed – the sampling rate was standardized to 1 second for wind speed, direction and turbine power output. This enables a more precise analysis of correlations between data sets allowing for instance, analysis of the turbines’ responses to changes in wind direction and speed.

In order to meet the new experimental requirements in Phase II, additional monitoring equipment needed to be designed and installed (Figure 7.3.12). To enable the investigation of on-site wind patterns associated with an “urban” wind regime, anemometers were added to each wind turbine tower.
The following describes the protocol to be used to collect wind and power data for the updated Crissy Field Center wind turbine project. The monitoring system will collect data at a 1-second interval as well as at the 10-minute interval used by the existing system. This memo summarizes the 1-second data collection protocol. We understand that new wind turbines include models by Omniflow and UGE. Sensors being monitored include wind speed and wind direction at each of the four new wind turbine towers as well as instantaneous power production by each wind turbine. The 1-second measurements will not include solar power from the Omniflow turbines.

A dedicated controller collects data at a 1 second interval. The data collection is initiated by a series of commands to the sensors via serial communications. This series of commands includes 5 distinct requests for data (one request is for all wind sensor data, and the other 4 requests are for individual power measurements). These requests are sent out sequentially, allowing time for the device to respond with data before the bus is used for the next request. All commands are sent and data received within the first 700 milliseconds of the 1-second interval.

Table 7.3.1 below lists the sensors that will be monitored at an interval of 1 second. The device ID and sensor ID numbers will be used in the data files to differentiate data points. The following table shows the sensors that are monitored at a 1 second interval. The device ID and sensor ID numbers are used in the data files to differentiate data points. Please note that we installed the monitoring equipment such that “negative” power refers to power entering the panel (i.e. power produced), while “positive” power refers to power leaving the panel (i.e. power consumed).
Data files will contain rows as follows, where values include integer values as well as converted 32-bit floating point values:

```
<timestamp>,<deviceID>,<sensorID>,<value>
```

Timestamp is given as 'YYYY/MM/DD hh:mm:ss'. Data files are saved with measured data at a 1-hour interval; the identifier will be approximately the first timestamp measured, as a Unix timestamp.

To facilitate the revised data protocol, Loisos and Ubbelohde developed a design and specifications for new equipment, as shown in the installation schematics below (Figures 7.3.13 - 7.3.15):
Figure 7.3.13 Monitoring equipment locations at Crissy Field Center.

Figure 7.3.14 Data acquisition system architecture.
Data files are first saved locally on the controller. A cloud-based server was developed to retrieve, convert, and transfer data files. This server is implemented as a Flask server running on Heroku. Since FTP access to the controller and HNEI servers required whitelisting of the server IP address, a service was added to the Heroku server to provide a static IP address via a proxy server. The Heroku server and the proxy server incur a monthly cost, which we will include with our monthly maintenance budget. The controller was programmed to save data hourly and to contact the server after a new data file has been saved. The server then retrieves any data files from the controller, converts the data to engineering units as described above, transfers both the raw and converted data to the UHM HNEI FTP server located at crissy.soest.hawaii.edu, and finally deletes the original files from the controller. The data transfer server has been deployed, and the data transfer process is operational.

A .csv data file was downloaded and checked for potential errors. Wind speed, wind direction, and power were plotted for each wind turbine, using a 2-second average to enhance readability. At the time of this initial check, the UGE wind turbines had not yet been fully commissioned. A second data file was downloaded to examine UGE data. The data check of each of these files showed data range and variation consistent with expectations (see Figure 7.3.16). In particular, we note:

- Wind speed and direction vary, but patterns are consistent across sensors.
- Power monitoring of the Omniflow turbines shows increases that seem to correspond to increasing PV output.
- Wind speed resolution is somewhat coarse – this is unavoidable since the execution interval of data collection is so small. The sensor uses a pulse signal with each full rotation of the anemometer, so there is no way to measure a fraction of a rotation.

- UGE North turbine and wind data for wind speed and power generated show very similar patterns of variation.

- UGE North turbine shows high frequency variation in performance that is different from the UGE South turbine.

Figure 7.3.16 Data check for key metrics power, wind direction and wind speed

In the process of commissioning the UGE power monitoring, L+U discovered an unexpected and unusual issue. The UGE inverters are connected to the electrical panel using 2-pole breakers. During lower levels (<280W) of power output, the direction of current in each wire is opposite, and the total power produced or used is the difference between the readings. This required a change to explicitly monitor net positive power and net negative power. The original method measured total power – or the sum of the absolute values for power on each phase. This showed a near constant 300 W of power produced, even though the totals were much lower. For example, L+U performed a test on site where the UGE North turbine was switched from power production to “free spin” mode, and then back to power production mode (see Figure 7.3.17). This shows the variation in power logged in each wire (L2 and L3), in the calculated Net Power, and in the
calculated Total (absolute) Power. This graph further demonstrates why Net Power needs to be calculated rather than using the Total Power.

Luminalt and Loisos + Ubbelohde researched the issue and discussed these observations with Ginlong, the turbine manufacturer, and with Dent Instruments, the manufacturer of the Powerscout meters. The team identified low power factors as a likely cause of these observations, as described in more detail in this document, posted by Continental Control Systems, another power meter manufacturer: https://ctlsys.com/support/inverter-power-factor/

While this issue presents further monitoring challenges for the dashboard data collection (see below), for purposes of the high frequency monitoring, it confirms that our monitoring of net power will accurately capture total power production or use at any given moment in time.

![Figure 7.3.17 Annotated results from UGE data acquisition testing](image)

The issue described above regarding the need for logging of Net Power is an issue for the existing monitoring system, because the existing Powerscout 18 is not capable of logging Net Power. It logs Total Power, or the sum of power from each phase. As a result, it will over-estimate power production any time Net Power production is less than around 280W.

L+U identified three potential solutions to monitor the power production of these UGE units:

1. The Powerscout 18 unit can be replaced with a Powerscout 24 unit that is capable of sensing the direction of current flow and can track Net Power.
Due to the observed behavior of the current flowing from the inverter, it appears that a calculation could be applied to estimate power produced by the UGE turbines. In the graph above, note that L3 power is always positive, and that L2 power switches to positive when L3 power is above approximately 280W (although this limit is inconsistent). In order to infer the sign of L2 power, we can test to see if L3 power is above or below 280W, and assign a negative number to L2 if L3 is below 280W.

The document provided by Continental Control Systems (see link above) provides a method for calculating total power by monitoring apparent power and power factor for a single phase. This calculation could be performed for data from a single CT using the Powerscout 18, thus allowing us to calculate corrected total power from one CT.

L+U further investigated the second and third solutions by recording detailed data for each UGE turbine using the Powerscout 24 to both simulate data collected by the Powerscout 18 and to measure net power. We were thus able to test each potential calculation method. We found that calculating total power using the 280W threshold was slightly more accurate than calculating the total using data from a single CT, and it was also easier. Based on our test of using the 280W threshold, we found this would produce accurate results for small or large power values, and an occasional error up to ±50% when total power is around 280W. We found that this error was larger for the UGE North turbine, which exhibits a high frequency pattern of variation in its output, than for the UGE South turbine. See figures below for the percent error vs measured power for each turbine. We also plotted the measured and calculated values over time, and we note that when taken as a whole, the calculated values tend to show a similar overall pattern (i.e., when measured power is high, calculated power tends to be high as well).

The Omniflow turbines have several features that required additional analysis and engineering by Loisos and Ubbelohde. First, the units produce power from both a wind driven generator and photovoltaic panels. Second, the units are equipped with a battery that is charged by the wind/PV sources and is used to power the system’s inverter and controller.

Simple measurement of the unit’s output using a currency transformer will yield aggregated, undifferentiated information from all three of these sources. Loisos and Ubbelohde summarize their recommendations for collecting disaggregated data specific to the turbine:

The objective of the power monitoring in the project is to establish a relationship between variations in wind speed and direction and variations in power produced by wind turbines. Data will be collected at a 1-second interval in order to study this relationship at a fine resolution. The electrical design of the Omniflow generator includes a source of solar power and a set of batteries; these components add complexity to the monitoring plan since wind power needs to be
disaggregated from the total. To disaggregate wind data, we recommend using data collected at night to eliminate solar power data, and short-term supplemental monitoring to understand the behavior of the battery.

Based on documentation provided by Omniflow and a phone conversation with Pedro Ruão, the founder and CEO of the company, the Omniflow system will function in different modes depending on the voltage charge in the battery. When the battery is below 24V, all power generated is directed to charge the battery (Figure 7.3.18a). When the battery charge is between 24V and 26.7V, the inverter is switched on, and power is directed to the grid as well as to charging the battery (Figure 7.3.18b). When the battery is at 26.7V, it is fully charged, and all power is directed towards the grid (Figure 7.3.18c). When voltage from power production drops, the battery discharges to feed the controller and inverter (Figure 7.3.18d).

Figure 7.3.18a: Battery Charging Mode. Grid connection shows 0 Amps, which is less than what the turbine is actually producing.
Figure 7.3.18b: Battery Charging and Inverter Mode. Grid connection may show more or less than the power produced by the wind turbine.

Figure 7.3.18c: Inverter Only Mode. Grid connection will show more than the power produced by the wind turbine.
The planned monitoring system includes monitoring of the electricity produced by the system as it is being transferred to the electrical panel. This measurement will be affected by system operating mode, showing less power produced whenever the battery is being charged and potentially more power when the battery is discharged. This measurement will also include any solar energy being produced.

The controller in the Omniflow system has data points available via serial connection that include battery voltage and current, although the accuracy of these measurements is questionable and the data connection to the device has not been tested. Furthermore, the monitoring system was not designed for additional serial devices and may not have the capacity for additional data collection.

In order isolate wind energy produced directly, either the energy being produced by the wind turbine must be measured directly, or the aggregate data will need to be processed to isolate times when the system is feeding exclusively wind energy directly to the grid. Direct measurement of wind energy would either involve relying upon inaccurate current measurements taken by the controller, or identifying monitoring equipment capable of measuring variable AC power. These direct measurement options are problematic due to potential accuracy issues and/or project budget constraints.
Alternatively, the recommended approach included isolating wind turbine energy by studying night hours (to eliminate PV power production) and when the battery is fully charged (Figure 7.3.18e). By studying these times, the team should be able to eliminate any potential contribution of solar power or battery buffering. However, this approach includes risks, such as:

- The time period of buffering is unknown. If a partially filled battery charges quickly and stays charged for long periods of time, then it will be easier to disaggregate the contribution of the battery from the data. However, if battery charges and discharges frequently, then it may be difficult to disaggregate the effect.

- Diurnal wind patterns will not be captured since daytime wind data cannot be disaggregated from solar.

![Diagram](image.png)

**Figure 7.3.18e: Night Inverter Only Mode. Grid connection will show isolated wind power production.**

In order to understand the contribution of the battery, the team should consider short-term high resolution monitoring of battery performance to assess battery behavior and identify any further steps needed to isolate the behavior of the battery. Using the controller as a source of battery voltage data is untested. We know that data is available from the controller, but it is likely going to be difficult to integrate these data points with the specified data collection system. Rather, it may be fairly straightforward to temporarily monitor voltage using data loggers such as those from Onset (e.g. a HOBO U12-013, 0-24V input sensor and a voltage divider for an effective input range of 0-48V).
Detailed analyses are underway under other funding, and should be complete by year end 2018, with findings presented in future reports.

**Reports**


**References**

Loisos + Ubbelohde, “Crissy Monitoring Installation Report”, internal correspondence to Golden Gate National Parks Conservancy, May 24, 2017

Loisos + Ubbelohde, “Crissy Monitoring Software Update and Commissioning Report”, internal correspondence to Golden Gate National Parks Conservancy, June 21, 2017

**7.4 Demand Response Portfolio Plan Assistance to HECO**

HNEI provided financial support, data and project evaluation for several HECO demand response (DR) demonstration projects developed under the first phase of its implementation of its Demand Response Portfolio Plan. The projects were meant to demonstrate how different combinations of customer-sited energy resources could deliver the following grid services: capacity and load shifting, fast frequency response, and regulating reserves. HECO selected vendors through a competitive solicitation process. The selected projects represented an array of end-use technologies installed at different types of customer facilities that could provide information on
technology and operational performance of DR technologies and market acceptance by customers and vendors. The projects were also intended to inform and refine the implementation of HECO’s future DR program portfolio.

Five projects were implemented:

1. Regulating Reserves – Web-based solution configured to support and interface with automatic generation control, remote terminal units and a “virtual power plant”, that aggregated resources to present a single forecasted DR capability to HECO.

2. Fast Frequency Response, Regulating Reserves, Capacity – Enlisted existing residential customers with PV and battery storage and EV chargers to determine the capability of systems to follow regulating signals.

3. Fast Frequency Response, Regulating Reserves, Capacity – Enlisted a commercial customer with battery energy storage systems (BESS) to determine the capability of systems to follow regulating signals.

4. Regulating Reserves – Aggregated two commercial BESS to determine the capability of systems to follow regulating signals.

5. Capacity – Remotely controlled the thermostat of five small business customers to test the customer acceptability to internal space temperature changes, and track the reduction in electricity use.

HECO considered the projects to be successful based on the results of each project where each vendor met expectations to provide reliable, repeated responses to demand response events. In addition, HECO stated it learned several lessons including that FFR requires accurate forecasting to ensure an accurate response, policy and technical issues must be resolved before 2-way EV charging response can be used in practice, and that aggregators must find ways to balance customer needs with utility grid service availability needs.

Conclusions

Excerpt from HECO Final Report to PUC:

“In reflecting on these projects and the subsequent analysis and assessment of them, the Companies have identified several key takeaways worth noting. These observations have or will have a direct bearing on the evolution and maturation of the Grid Services market and the Companies’ ability to deliver Grid Services through third party vendors utilizing
customer resources. Specifically,

**Optimizing the balance between customer needs and grid needs:** While this seems apparent, it is much more difficult to achieve in practice. When a customer purchases resources to serve their needs, e.g., demand reduction or resiliency, that need typically comes first before grid or DR needs. Vendor algorithms that maximize or optimize the amount of the resource available to the grid are very complex, require tuning, and active post-installation monitoring. A majority of the resources utilized for these demonstration projects were employed primarily to serve customer needs rather than DR. For example, some battery energy storage systems were utilized primarily to reduce the peak demand charge of commercial customer sites. The customer and vendor partnership is based primarily on the peak demand charge reduction, and secondarily participation in demand response. This balance needs to be managed by the vendor to ensure both utility requirements and customer requirements are met. As a result, careful assessment by vendors must be performed to determine management of the customer’s resources to fulfill these competing needs. These determinations will ultimately culminate in valuing Grid Service delivery during GSPA contracting and operation.

**Customer acceptance and concerns:** During outreach to customers, many customers were skeptical of the opportunities offered by the Demonstration Vendors, which resulted in numerous calls to the Companies. As a result, co-branding with the Companies was added to the GSPA to help reassure customers of the legitimacy of the DR opportunities presented to them.

**Assessment of Regulating Reserve delivery:** The regulation signal that was used for the Regulating Reserve projects reflected several real-world operating examples based on actual grid performance, i.e., “good” and “bad” renewable generation production. These real-world examples included a highly variable regulation signal that existing, established assessment tools do not fully address, as discussed in section V.A.2.d. For future assessments of Regulating Reserve, the time window will be shortened to better capture the fast and highly variable nature of the Companies’ regulation signal.

**Application of value Grid Service delivery:** The Grid Service Value table was included in the draft GSPA, as a result of discussions with Demonstration Vendors around the relationship between maximizing value, forecasting accuracy, and targeting customers for demonstration project participation. The Grid Service Value table reflects the hours of the day in which the delivery of Grid Services is the most beneficial to the Grid. Using the Grid Services Value table, Grid Service Suppliers can target customers who would be the most effective and productive during the most valuable hours. This in turn helps to ensure the delivery of Grid Services to the Companies is reliable and dependable.

**Assessment of market and technical readiness:** DR control technology that was layered onto installed homogenous populations of resources was enabled significantly faster than
those that required new resource installation or interconnection. Enabling resources already “in the ground” is key to quick enrollment, and having similar or identical installed resources enabled efficient installation processes. New equipment installations must pass through the predefined Hawaiian Electric interconnection process, which may also require inverter manufacturers to qualify their inverters and formally certify to UL 1741 Supplement A, using the Company’s applicable Source Requirements, especially for new inverter models. Some vendors faced delays with regards to interconnection, while others that did not install new equipment moved far more quickly through the demonstration phase. During the contracting process, it will be critical to assess each vendor’s enablement plan in terms of acquisition schedule and installed resources to ensure the targets are achievable.

Specific technologies have a role: While many demand-side resources can be enabled to deliver Grid Services, certain technologies and resources are more adaptable to deliver Grid Services than others. For example, FFR, which is deployed in response to a contingency event on the grid, requires accurate forecasting and accurate delivery to ensure grid reliability. Through the Demonstration Phase, it became apparent that the most reliable way to deliver this Grid Service was to employ a battery energy storage device and reserve a portion of the battery for FFR at all times to ensure availability. All Demonstration Vendors chose this method to deliver FFR. Other demand-side resources can accurately delivery Grid Services, but it is accomplished by forecasting or committing significantly less Grid Service than is available so as not to under or over deliver. During GSPA contracting process, vendors will need to demonstrate (if they haven’t already done so) their ability to comply with FFR delivery requirements.

Capacity Grid Service continues to evolve: During the Demonstration Phase, Capacity Load Shift tests consisted of participant systems following the utility TOU rate, which applied to all 24 hours of the day. Specifically for Project 2 participants, the TOU rate implementation changed participants’ daily load profile by building load or charging energy storage during daytime hours and reducing load or discharging energy storage during the evening hours. While a standard feature of participant’s systems, the load shift demonstrated was a static and constant weekday shift. As implemented, the system was not able to perform Load Shift “on demand” or be dispatched to address grid conditions. However, this additional “on-demand” flexibility would allow dispatch of Capacity Build on a high solar production day or Capacity Reduction to address a capacity shortfall which is a much more utilisable resource. Independent dispatch of Capacity also allows respondents to the Grid Services RFP to include a greater variety of end-use resources since Capacity Build and Reduction are not required to be symmetrical as they would be under Capacity Load Shift. The Companies anticipate that Capacity Grid Service will continue to be refined as the Grid Service is implemented.
**EVs offer Grid Services delivery opportunities:** Utilizing 2-way EV charging as a DR resource was a proof of concept during the Demonstration Phase; while successful, there are still policy and technical issues with this end-use resource that need to be addressed before 2-way EV charging can be used in practice at scale. EV participants were generally interconnected under the Net Energy Metering (“NEM”) interconnection agreement, which explicitly allows for export of customer-generated renewable energy to the grid. There is no process in place to verify that the stored energy in an EV battery was generated by a renewable resource (e.g., not charging from a non-renewable resource: workplace charging, chargers installed at shopping centers, Hawaiian Electric DC fast chargers, etc.). That being said, there is however meaningful potential for 1-way charging to deliver Grid Services, as there are no interconnection requirements for 1-way chargers since there is no potential for customer back-feed to the grid.

**Participant resources do have limitations:** Each participant’s technology and situation impacts the availability and reliability of their resources to deliver Grid Services. While the Internet of Things (IoT) is anticipated to offer the level of coordination, interoperability, reliability, and security required to enable a resource to deliver Grid Services, it remains an evolving sector. Demonstration Vendors relied on customer Wi-Fi or cellular data, or both from the Demonstration Vendor’s head-end system down to the customer end-device. Cellular was implemented as a backup in cases, where the participant’s Wi-Fi was not always available, either due to participant behavior or location. There is considerable expense involved in adding and maintaining this backup communications path at scale. But, establishing reliable communications is very important so that the resource can reliably deliver Grid Services. Further, a customer’s existing infrastructure greatly influences their ability to provide Grid Services. For example, reliance on customer HVAC systems for load reduction requires a properly sized HVAC system, which was not always the case amongst the Companies’ existing customers in practice. Utilizing HVAC for demand response will also definitely compromise customer comfort, so it is up to the aggregator vendor to properly compensate the customer for their participation. As a result, vendors may incur additional expense to ensure reliable delivery of Grid Services, which would likely be reflected in their costs to the Companies.” (HECO, 2018).

Additional details can be found in HECO’s final report to HNEI, “Demand Response Demonstration Phase: Final Report (June 2018)”, posted on the HNEI website as well as the their August 31, 2018 Final Report submitted to the Hawaii Public Utilities Commission in support of Docket 2015-0412, (both referenced below).
References
