FINAL REPORT

UH-Manoa Sustainability Initiative 2011-2013: Research Program on Water, Energy, and Soil Sustainability (WESS)

Faculty

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Admin

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Industry

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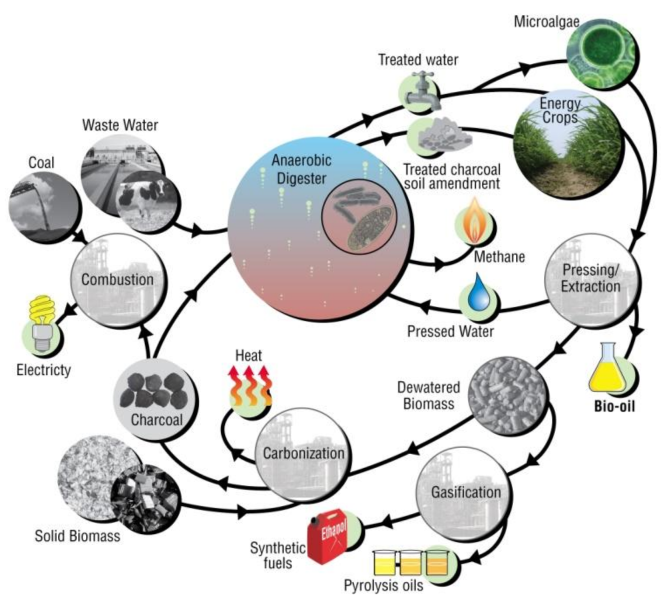


Dedicated to the memory of Goro Uehara

Executive Summary of Key Outcomes

- ***We have well executed three demonstration scale projects of UH*** technology and/or research knowledge deployed at off-campus locations in local industry. The projects (anaerobic-aerobic digestion at a WWTP, anaerobic digestion at a grease trap waste processing facility, and energy crop growth trials in biochar amended soils) are covered under omnibus research agreements between UH and the host sponsor and represent a "working model" of how the University could develop a "distributed" pilot tech park model. The concept is to invest University funds in building demonstration scale unit operations applying UH developed technology within targeted local business that agree to support its application and evaluation in the context of applied research. In this manner a "distributed" pilot tech park could be created that would foster applied research collaborations between the UH and local industry under real-world conditions that commercial production.

- ***Field trials characterizing growth of jatropha and safflower energy crops*** grown in soils amended with anaerobically treated and untreated biochar (made from mixed woods and animal sewage sludge) have been executed. The biochar was treated with effluent from anaerobic digesters. The lands were infused with the biochar. The Department of Health granted a permit for its deployment. The crops have been planted and will be harvested during a period from late this summer until well into 2015. Key results are indicating a significant enhance in soil water retention owing to the addition of biochar. Correlations to oil seed yield will have to wait until sufficient harvesting has been accomplished.

- ***Greenhouse trials executing extensive investigations on the impact of biochar*** (made from mixed woods and human sewage sludge) added to various Oahu soils have been and continue to be executed. The biochar was treated with effluent from anaerobic digesters. The extensive trials have characterize and correlated plant growth to a number of key characteristics including water retention, nutrient retention, soil microbiology, root interaction with the soil, replanting, nutrient addition among others. These results will provide a base against which the field trials can be compared.

- ***A demonstration scale application of anaerobic digestion technology*** developed at UH to treat grease trap waste wastewater has been deployed off-campus at Pacific Biodiesel's grease trap waste processing center. The 3,000 liter anaerobic reactor system has been operating since June 2013 and will provide data that is critical to determining whether, or not, the successful laboratory scale treatment of grease trap waste wastewater can be scaled up to commercial operation. .

- ***An omnibus research agreement*** covering the use of the demonstration scale anaerobic digester at Sand Island by University of Hawaii faculty has been executed. The omnibus agreement as currently crafted allows for faculty across campus to approach the host operator (Pacific Biodiesel) with additional project ideas or technologies to utilize the AD reactor system. This "model" agreement demonstrates how a network of distributed demonstration scale applied research facilities can be established at off campus pilot sites in industry.

- ***A 6000 gallon demonstration scale high rate anaerobic digestion reactor system*** has been installed and tested at the Hawaii Kai Sewage Wastewater treatment facility in Hawaii Kai. The treated effluent from these reactors was used to soak the biochar and produced the "treated" biochar that was used in the greenhouse and field energy crop growth trials. Project results were reviewed by an Industrial Advisory Board and discussions in early 2013 supported the modification of the anaerobic digester reactor system. WESS funds supported the retrofit of this reactor system and experimentation has commenced on the new system which will continue well into 2014.

- ***An alternative "hybrid" concept proposal for the creating of a Pilot Technology Park*** that would host faculty and industry applied research collaborations on off-campus University lands was developed and presented to the Dean of CTHAR. The concept proposal detailed a hybrid model wherein a hypothetical CTHAR research station would be used re-purposed to host a number of small businesses that would connect together to create a water, energy, and soil sustainability cycle. The model incorporated the growth of dairy cows with the treatment of their solid and liquid waste into materials that would support the growth of energy crops. The de-lipified plant matter was to be recycled and animal feed for the cows. Three companies (Naked Cow, RealGreen Power, and Pacific Biodiesel) joined the proposal.

- ***Field demonstration trials characterizing the crop growth and CO_2 sequestration capacity*** of biochar amended soils has been started. These results will provide yet another source of data detailing the potential value of adding biochar to soils.

- ***An undergraduate course*** titled Sustainable Systems Analysis has been developed and incorporated into the technical elective option programs of the Civil and Environmental Engineering undergraduate program.

- ***Detailed studies on the physical and chemical properties of biochar*** produced from human sewage sludge have been executed. The source of sludge was the dried anaerobic solids produced at the Hawaii Kai wastewater treatment plants. This data will be used to help explain the impact of biochar addition to soils obtained from the greenhouse growth trials.

- ***A catalytic afterburner*** has been installed and tested on the demonstration scale flash carbonization unit situated on campus behind the Biomedical Sciences building. If successful, the modified flash carbonization unit will provide an additional source of field trial quantities of biochar produced on campus will become more available.

Acknowledgements

- As Vice Chancellor of Research and Graduate Education at the University of Hawaii at Manoa, **Dr. Gary Ostrander** created developed and funded the University of Hawaii Sustainability grant program. I would like to thank and acknowledge Dr. Ostrander for his support and funding without which there would be no WESS program.

- As Director for UH Manoa sustainability initiatives, **Dr. Pete Mouginis-Mark** served as the program manager for the WESS program. I would like to thank Dr. Mouginis-Mark for his time and effort and in particular his insight to resolve the inevitable issues that arrive. His timely help at key junctures in the program were critical to the execution of a few of the research lines.

- As president of Diacarbon Energy Inc. **Jerry Ericsson** provided the field trials quantities of biochar for the field tests and the required biochar to fill the demonstration anaerobic digesters at Sand Island. In particular Diacarbon went to great lengths to produce the odd sized biochar needed for deployment in the anaerobic digesters and to produce field trial quantities of biochar made from animal sewage sludge (no small feat!). Without question Jerry Ericsson's constant willingness to find a way to deliver the biochar was critical to the output of this program. I am very grateful.

- Both Hawaii American Waters and Pacific Biodiesel have hosted demonstration scale anaerobic digesters and their integration into plant operations. Without this help and support from **Bob King** and **Lee Mansfield** major components to the program would not have been achieved. I am again very grateful.

- RealGreen Power has continued to support operation of their anaerobic digesters at Hawaii Kai wastewater treatment plant and their continued operation through the retrofit process of the reactor. I would like to thank **Dennis Furukawa** for this support.

- Pacific Biodiesel generously offered collaborative use of their crop lands to support additional crop growth trials beyond those originally planned for University lands. I would like to thank **Bob King** for this support and also the "on-hand" support and help of **Matt Johnson** and his crew at the Pioneer site. The addition of these crop growth trials is yet another demonstration of the benefit of university research applied in the commercial sector in collaboration with industry.

- **Dr. Brian Taylor** continued support for the WESS program as interim Vice Chancellor of Research and Graduate Education after Dr. Ostrander stepped down to accept a new position in Florida. I am grateful for his mid-stream support for the program.

- I wanted to acknowledge **Richard Ogoshi** and **Richard Kablan** for their extraordinary "extra" effort in the developing the off-campus jatropha crop growth trials on such a modest budget. The effort is truly extraordinary and the result is more a jatropha farm than an experiment. The effort required to seed those soils with biochar in a scientifically

reproducible manner was tremendous and underappreciated by anyone who has not done it. Richard and Richard also helped to soak the biochar with effluent from anaerobic digesters down at the Hawaii Kai sewage treatment plant which was a lot of work.

- Finally, I wanted to acknowledge the support of **Richard Rocheleau** and **David Oride** for their support in HNEI's management of the fiscal side of this program. The funds were managed by HNEI and given the quite demanding reporting requirements (in particular the budget tracking) imposed by the VCRGE, I am very grateful for David's excellent efforts. It was not an easy task and it is almost impossible to manage a program on six month installments of funds to units across campus without a good fiscal officer.

- *Michael Cooney*

STATEMENT OF WORK

General project description

We propose a research program that both attracts and guides the integrated effort of all UH faculty, Hawaii industry, State government, venture capital, legal/regulatory authorities, and private sector persons with an interest in providing for the water, energy, and soil sustainability (WESS) of Hawaii (Figure 2). Specifically, we seek to create a program of fundamental research and pilot test sites at which WESS technology developed at UH can be rapidly deployed and evaluated within a framework that provides for (*i*) the rapid deployment and evaluation of WESS technology, (*ii*) master agreements that define site access, IP ownership, and technology licensing for future activities not defined in this proposal, (*iii*) comprehensive peer review and evaluation of WESS technology in a *real world systems* context, (*v*) shared costs between the host site/company and the UH, and (vi) infrastructure that can be leveraged by UH faculty for securing extramural funds that target fundamental research, small business development, and student education.

Project goals

Our short term goal is to execute a set of specific tasks, as defined in Table 1, that present the groundwork necessary to build a WESS research industry in Hawaii, as defined in our statement of goals for the post funding period (Figure 2).

Our long-term goal is to develop a research industry in Hawaii on *Water, Energy, and Soil Sustainability* (WESS) that attracts, guides, and supports the integrated effort of all UH faculty, Hawaii industry, State government, venture capital, legal/regulatory authorities, and private sector persons with an interest in providing for the water, energy, and enhanced food production (through soil sustainability) in Hawaii. A conceptual description of how we propose to achieve this vision is presented in Figure 2. Specifically, we will seek to develop pilot test sites in Hawaii, at which UH developed WESS technology can be rapidly deployed and evaluated within a framework that provides for: (*i*) the rapid deployment and evaluation of WESS technology at pilot test sites, (*ii*) master agreements for each pilot test site that define site access, IP ownership, and technology licensing to streamline future activities not defined in this proposal, (*iii*) comprehensive peer review and evaluation of any given technology deployment from a *real world systems* perspective, (*v*) shared costs between the host site/company and the UH, and (vi) the competitive solicitation of extramural funds that target WESS fundamental research, small business development, and student education. If successful, this model can be used to create an extended "Research Park" environment embedded within Hawaii industry that facilitates the borderless interaction between UH faculty, thus helping the UH to take a leading role in the development of a WESS research industry in Hawaii that provides for a sustainable Hawaii.

Project tasks

Table 1 – List of Program Tasks for Funding Period
Pilot Testing
• Establish Jatropha crop growth trials at the UH Maui Agricultural Test Station; • Establish a pilot test site at Pacific Biodiesel's Sand Island's wastewater treatment facility; • Establish a pilot test site at an off-campus waste water facility; and • Identify additional candidate pilot test sites for recruitment into the WESS program.
Fundamental Research
✓ Characterize the performance of novel immobilization materials (e.g. biochar) for their performance in high rate biofilm anaerobic digesters in terms of treatment efficiency and biogas production; ➢ Characterize the fundamental properties of biochar made from solid biomass waste collected from existing and potential pilot test sites (e.g., dried anaerobic sludge, dried "rag" layer from waste trap grease); • Characterize the fundamental properties of soils supporting high bio-oil productivity from Jatropha crops; ➢ Evaluate biochar removed from anaerobically treated wastewater as a base material to make Terra Preta soils; and ✓ Characterize the capacity of amphiphilic extraction solvents to detoxify delipified Jatropha meal, thus providing an additional value stream as an animal or fish feed.
Education
• Develop one capstone course in Engineering that addresses the WESS concept; • Support Global Environmental Science Undergraduates conducting WESS research; and • Submit one REU proposal targeting the WESS concept, for future GES students.
Business Development
• Create business-friendly master agreements that can be used as templates between the UH and any potential host test site that would be recruited into the WESS program; • Develop comprehensive business plans, fundraising portfolios, and economic analyses that enable the UH administration to solicit funds to create a WESS research industry in Hawaii; and • Establish a permanent and neutral administrative group within HNEI that can manage interdisciplinary research projects and proposals between UH faculty, industry, government, the private sector, and all combinations thereof.
Legend: ➢ indicates activities to be jointly funded under this program and cost share; √ indicates ongoing research activities cost-shared for this project; • indicates activities solely funded under this program.

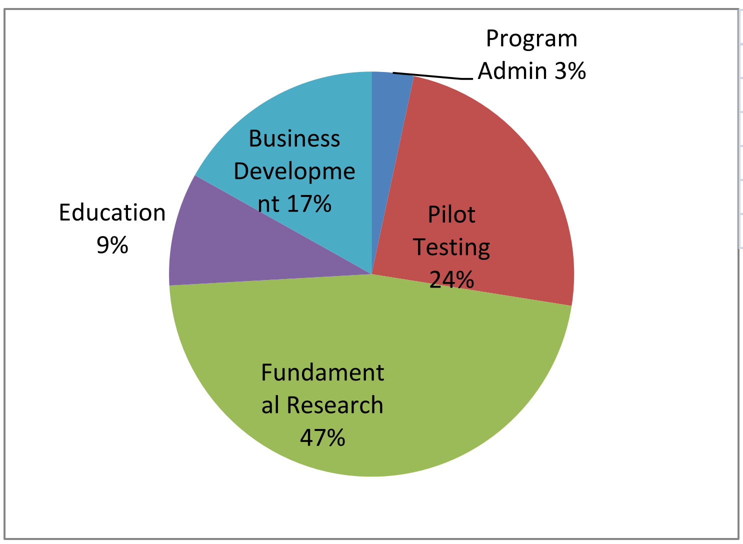
Deliverables

1. Task Reports. Quarterly.

2. Final Report. Provide summary of all accomplishments. Due within 30 days upon termination of the Agreement.

BUDGET
Summary

		Funds UH	Cost Share
Administration			
	Program management	33,529	33,529[1]
	Subtotal	**33,529**	**33,529**
Pilot Testing			
	Waste water treatment facility	0	650,000[1]
	Pacific Biodiesel Sand Island site	65,232	0
	Maui Agriculture Site	176,131	0
	Subtotal	**241,363**	**650,000**
Fundamental Research			
	Anaerobic Digestion	0	155,177[1]
	Carbonization	242,908	124,5131
	Terra Preta soils	157,853	0
	Extraction	65,000	135,000[1]
	Subtotal	**465,760**	**414,690**
Education			
	GES students	44,929	0
	Capstone Course	45,287	0
	Subtotal	**90,216**	**0**
Business Development			
	Master Agreements	50,000	0
	Advertising materials	15,000	0
	Fundraising	11,000	0
	Business plan	84,897	40,000[2]
	Economic Analysis	7,726	0
	Subtotal	**168,623**	**40,000**
	Total	**999,492**	**1,138,219**



	UH Request
Program Admin 3%	33529
Pilot Testing 24%	241363
Fundamental Research 47%	465760
Education 9%	90216
Business Development 17%	168623
Total	**999492**

[1]Cost share provided by DOE and ONR grants to HNEI

[2]Cost share provided by PACE program

SENIOR PERSONNEL

Administration

Project Management. Dr. Cooney is charging 3 months (1.5 per year) of his time to administrate the WESS program. This includes administration of the budget, facilitating the collaboration of all activities, project reporting, and leading the search for extracurricular funding past the 2 year funding period.

Fundamental Research

Carbonization. Prof. Antal is charging one month (0.5 per year) of his time to supervise the carbonization aspect of the proposed WESS program.

Business Development

Master Agreements/Business Plans/Fundraising. Dr. Robinson is charging 3 months (1.5 per year) of his time to administer the business development aspects of this grant. He will personally take charge of the development of business plans, marketing, and fundraising as described elsewhere.

OTHER PERSONNEL

Pilot Testing

Maui Agricultural Test Site. The research associate will be responsible for the installation, monitoring, and data collection and analysis of the field trials. The treatments in the field trials include tree population density, fertilizer rate, irrigation rate, and biochar application. A graduate student will assist the research associate to install, monitor and collect data from the field trials.

Fundamental Research

Carbonization. Funds are request to support Lloyd Paredes (Scientific Instrument Designer) to work 50% time on the carbonization project for two years. Mr. Paredes will be responsible for assembling, maintaining, and safely operating the lab-scale and demonstration-scale Flash Carbonization (FC) reactors in the laboratory of Dr. Antal. Funds are requested to support one M.S. graduate student in Mechanical Engineering on the carbonization project. Funds are requested to support one part time student at 20 hours per week for 24 months will be supported to assist Mr. Paredes and the graduate student with general laboratory work supporting the carbonization of biomass.

High rate anaerobic digestion. Funds are requested to support one M.S. graduate student in Bioengineering or Civil Engineering for 2 years. The student will execute the anaerobic digestion work investigating the co-digestion of aqueous phase waste trap grease with distilled glycerin. This work will support the evaluation of waste stream at Pacific Biodiesels Sand Island facility. This work will generate fundamental data that supports the case for the development of a pilot project that fits under the umbrella of a master agreement.

Terra Preta soils. Funds for one year are requested to support a Research Associate who will be responsible for conducting the laboratory incubation and greenhouse experiments. The Research Associate will coordinate and supervise the graduate and undergraduate student activities. Funds are also requested to support one M.S. graduate student in the Department of Tropical Plant and Soil Sciences to conduct laboratory incubation and greenhouse studies during the first year of the *Terra Preta* project. Funds are also requested to support one part time student at 20 hours per week for 24 months to assist the research associate and graduate student with general laboratory and greenhouse work supporting the *Terra Preta* research.

Education

Capstone course. Two undergraduate students are requested to assist Dr. Antal in the development of course materials. This would include conducting literature searches identifying research papers addressing an appropriate systems approach to the application of WESS technology, creation of problem solutions, development of systems diagrams and other course presentation material, and other tasks as required.

Global Environmental Science. Funds are requested to support five GES seniors for one full year at 50% time during their senior thesis research on WESS projects. This support will permit local students, many of whom must work part time to support their way through school, the necessary financial support to more fully dedicate themselves to the project.

STIPEND POSTDOC

Fundamental Research
Extraction. Funds are requested to support one stipend postdoc to work 50% time for two years on the extraction of bio-oils from Jatropha oil-seeds. The student will also assist in providing the Carbonization project with de-lipified Jatropha meal for carbonization studies.

PERMENENT EQUIPMENT

Fundamental Research
Carbonization. Funds are requested to overhaul the lab scale Flash Carbonization reactor in the laboratory of Dr. Antal. These funds will enable Dr. Antal to replace his current reactor, which has been highly modified from the original design, with one designed specifically to mimic the design of a commercial unit and with one outfitted with proper instrumentation for effective operation. These funds will prove most useful as according to UH/OTTED Dr. Antal's Flash Carbonization patents have attracted more commercial interest than any other patents in the UH portfolio. In view of this achievement, Dr. Antal's laboratory Flash Carbonization unit has been overused (to date) to produce the needed quantities of biochar for testing and has consumed precious man-hours of effort). The overhaul in its design is necessary to produce sufficient biochar for testing in anaerobic digesters and for use as soil amendments. Also it will permit us to make measurements needed for the progress of our research. Its performance will be used to guide future modifications of the UH Demo FC reactor.

MATERIALS AND SUPPLIES

Pilot Testing
Maui Agricultural Test Site. Materials for the field trials are to include environmental monitoring instruments and plant production supplies. A weather station ($2,500) and soil moisture instruments ($13,500) are to monitor the effect of biochar and irrigation on soil moisture in the root zone. Seed ($4,000), fertilizer ($1,000), and irrigation supplies ($3,000) are to be part of the installation of the field trials.

Fundamental Research
Carbonization. Funds are requested to support the carbonization work in Dr. Antal's lab. These funds will support the maintenance of both the lab and demo FC reactors, and the assembly of a catalytic afterburner for the demo FC reactor to handle its emissions.

Terra Preta soils. Funds in the amount of $15,000 are requested to support soil analytical work to be conducted in Dr. Deenik's lab (Dr. Deenik is a collaborator on the project). These funds will be used to buy the following: 1)laboratory supplies including chemical reagents, glassware, and filtering supplies associated with soil extractions; 2) consumables related to the operation and maintenance of a discrete analyzer (Systea Co.) for the analysis of inorganic N in soil extracts and a Shimadzu TOC auto analyzer for the analysis of dissolve organic C and total N in soil water extracts; and 3) pots, irrigation materials, and greenhouse user fees required to conduct the greenhouse experiments.

REPAIR/MAINTENANCE

Fundamental Research

Carbonization. A modest request is made to support the recalibration and overhaul of the BET surface area adsorption instrument in the laboratory of Dr. Antal. Such instruments are not trivial to operate or maintain, and require periodic service to maintain good operation. In order to be available for this project, and to characterize the essential physical properties of the biochar fabricated from waste biomass (i.e. surface area, pore size distribution,…etc.), the requested funds are necessary to support the servicing of this instrument by a mainland technician. Once in service, the graduate and undergraduate students supported by this project will receive training on this instrument.

TRAVEL

Pilot Testing

Maui Agricultural Test Site. The research associate and graduate student will require travel to the field trial on the island of Maui to install instrumentation, monitor plots, and collect data. Site visits are planned twice a month. The team leader will attend a national meeting of the Soil Science Society of America to present the findings from the field trials.

Business Development

Fundraising. Funds are requested to support travel related to the publicizing and fundraising for these pilot projects, leading to commercialization. The goal will be to find additional sources of cost share funds, such as the Hawaii State Hydrogen Fund, and non-profit organizations such as the Ulupono Initiative.

SUBCONTRACTS

Pilot Testing

High rate anaerobic digestion of waste trap grease. Funds are requested (in the event master agreements are achieved) to subcontract RealGreen Power to design and install two high rate anaerobic digesters at pilot scale at Pacific Biodiesel's Sand Island waste trap grease processing facility. The bioreactors would target the treatment of the aqueous phase of waste trap grease, with the concomitant production of biogas that would be combusted on site for heat energy. The reactors would be designed in such a manner so as to support the deployment of additional WESS technology that adds to or amends the process, so long as the host site agrees to the additional trails.

Business Development

Master Contracts. Funds are requested to support the development of a master contracting template for all intellectual property and commercialization associated with these projects. This will necessitate consulting from appropriate experts, in particular intellectual property attorneys.

OTHER DIRECT COSTS

Pilot Testing

Maui Agricultural Test Site. Funds ($7,000) are to be provided to the Kula Agricultural Research Center to cover the costs that support the field trials. These costs include the operation and maintenance of heavy equipment and irrigation water. Soil and plant tissue samples are to be analyzed for chemical composition. Soils will be analyzed for pH, P, K, Ca, Mg, Cu, Fe, Mn, Zn and Total C (256 samples, $8,200). Tissue samples will be analyzed for N, P, K, Ca, Mg, Cu, Fe, Mn, and Zn (256 samples, $6,800). All analyses will be performed by the Agricultural Diagnostic Service Center, University of Hawaii.

Fundamental Research

Carbonization. Funds are requested to provide for servicing our gas sorption analyzer and training graduate students in its use.

Terra Preta soils. Costs associated with the characterization of the structural (^{13}C NMR analysis) and chemical composition (mass spectrometry) of the treated and untreated biochar samples are estimated to be $2,000. Costs associated with analysis of inorganic N (NH_4^+ and NO_3^-) in soil extracts from the biochar incubation experiment are estimated at $6,240 ($10 per sample X 624 samples). Soil and tissue analysis for greenhouse experiment will require $60 per pot for a total of $4,000. An estimated $5,000 will be needed for quantifying the cation exchange capacity of the biochar materials and the mixtures of biochar and soil.

PROGRESS REPORT

Project Title: Research Program on Water, Energy, and Soil Sustainability (WESS)

Reporting Period: July 1st 2011 to June 31st 2013

Name of Principal Investigator: Dr. Michael Cooney (Hawaii Natural Energy Institute)

Contributing staff: Michael J. Antal[1], Goro Uehara, Richard Rocheleau, Jane Schoonmaker, Robert Robinson, Richard Ogoshi, Jonathan Deenik.

PROJECT STATUS SUMMARY (*as of July 15th 2010*):
Schedule Status: We are on Schedule: YES__X___ or NO ____
EXPLANATION: Project has just started

Budget Status: We are on Budget: YES__X__ or NO ____
EXPLANATION: Only budgeted charges have been heretofore encumbered.

Task	Percent Complete	Comments
Task 1: Establish Jatropha crop growth trials at the UH Maui Agricultural Test Station	100%	Field Trials planted and in progress at two sites on the island of Oahu.
Task 2: Establish a pilot test site at Pacific Biodiesel's Sand Island's wastewater treatment facility	100%	Lab experiments completed, Demonstration scale reactor installed and now under demonstration operation.
Task 3: Establish a pilot test site at an off-campus waste water facility	100%	Reactors installed, operational, and inoculated. Retrofit for additional research completed and new trials underway
Task 4: Identify additional candidate pilot test sites for recruitment into the WESS program	100%	Concept proposal for pilot tech park at Waialee Livestock station completed and presented to CTHAR Admin. Omnibus Agreement between Akuo Energy, a French owned company building a PV driven power station/greenhouse facility and the UH signed.
Task 5: Characterize the performance of novel immobilization materials (e.g. biochar) for their performance in high rate biofilm anaerobic digesters in terms of treatment efficiency and biogas production	100%	Experiments utilizing corn cob biochar completed and manuscript published. Follow on experiments at demonstration scale at increased packing density with mixed wood biochar ongoing at PB's Sand Island facility
Task 6: Characterize the fundamental properties of biochar	100%	Corn cob and sewage sludge

made from solid biomass waste collected from existing and potential pilot test sites (e.g., dried anaerobic sludge, dried "rag" layer from waste trap grease)		characterization well covered. Rag layer initial trials deemed negative. Biochar from animal sewage sludge processed and delivered to UH for field trials. Greenhouse trials using sewage sludge completed.
Task 7: Characterize the fundamental properties of soils supporting high bio-oil productivity from Jatropha crops	100%	Significant data obtained from Maui crops and reported. Field trails on Oahu with biochar soils ongoing for past six months.
Task 8: Evaluate biochar coated with anaerobically treated wastewater as a base material to make Terra Preta soils	100%	Greenhouse trials utilizing corn cob and dried anaerobic sludge biochar completed. Manuscript in preparation.
Task 9: Characterize the capacity of amphiphilic extraction solvents to detoxify delipified Jatropha meal, thus providing an additional value stream as an animal or fish feed	100%	Extraction of phorbol esters from jatropha oil-seeds completed. Manuscript In Press. Additional work evaluating solvent ability to pretreat biomass for enzymatic hydrolysis to simple sugars completed and published.
Task 10: Develop one capstone course in Engineering that addresses the WESS concept	100%	CEE course titled Sustainability Systems Analysis set for Fall 2013. Over 30 students registered. Course materials nearly completed.
Task 11: Support Global Environmental Science Undergraduates conducting WESS research	100%	Students supported and several conducting research for senior thesis project.
Task 12: Submit one REU-esque proposal targeting the WESS concept, for future GES students	30%	Concept proposal to Castle Foundation championed by Sea Grant, Sea Grant recruited as admin home, still recruiting PI.
Task 13: Create business-friendly master agreements that can be used as templates between the UH and any potential host test site that would be recruited into the WESS program	100%	Omnibus agreement executed between UH and PB. Additional agreement between Akuo Energy and UH in progress.
Task 14: Develop comprehensive business plans, fundraising portfolios, and economic analyses that enable the UH administration to solicit funds to create a WESS research industry in Hawaii	50%	A master plan for application of WESS at off campus site completed and presented to CTHAR Admin. One PACE cohort group evaluating jatropha crop cultivation, harvesting, and processing

		completed.
Task 15: Establish a permanent and neutral administrative group within HNEI, that can manage interdisciplinary research projects and proposals between UH faculty, industry, government, the private sector, and all combinations thereof	90%	WESS program administered quite well. NSF proposal to PFI-BIC program submitted from HNEI – includes faculty assigning RTRF to four separate units. Still searching for continuation funds.

WORK PROGRESS:

<u>Task 1</u>: *Establish Jatropha crop growth trials at the UH Maui Agricultural Test Station*

The execution of this task requires two fundamental inputs: land and significant quantities of biochar. With respect to land, the WESS team has decided to move the trails to Oahu and has identified two potential sites that will be available in 2012. The first, is the Poamoho Research Station located in north central Ohau. This site could accommodate Jatropha crops planted in the same "poor" soils that are being used in the greenhouse trails. More, this station could afford long term growth trials of this perennial crop which takes just at 3 years to reach full maturity. Also, the soil at this station is poorer than that at the Maui site, and it is the goal of the WESS group to characterize the extent to which treated biochar can be used to improve poor soils to meet the kind of productivities found in good soils (like those found Maui). Composite soil samples from the Poamoho Research Station have been collected from three plots at depths of 0 to 8 and 8 to 16 inches. Soil samples have been analyzed for pH, P, K, Ca, and Mg. Plot I is deficient in P, K, Ca, and Mg and thus suitable for the fertilizer rate study to be conducted. Plots F and J-2 have high levels of P and K, sufficient level of Ca, and deficient in Mg. As such, Plots F and J-2 will be used for the irrigation and population density trials.

Plot	Depth (inches)	pH	P (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)
I	0 - 8	5.5	7.0	182	569	139
	8 - 16	6.1	5.0	124	770	155
F	0 - 8	6.9	857	511	1767	237
	8 - 16	6.9	506	308	1659	177
J-2	0 - 8	6.6	760	516	1647	178
	8 - 16	7.0	839	380	1855	191

Plots I and J-2 have been plowed. Weed seeds are being allowed to germinate. The plots will be plowed a second time to eliminate the weeds.

The second site is managed by Pacific Biodiesel Inc. PBI is now making regular plantings of annuals such as Safflower and other varieties of energy crops. Their next planting is in April and they have offered to host trials in soils incorporating biochar. The majority of crops they are investigating are annuals which operate on 4 month rotations – not a condition suitable to Jatropha. The option exists, assuming a significant amount of biochar can be obtained, to do both.

With respect to biochar for field trials, we have purchased and received just at 4000 lbs. of biochar from the Canadian company Diacarbon (http://www.diacarbon.com). Diacarbon operate a 25 MTPD beta unit that carbonizes wood chips and pulp sludge outside of Vancouver, BC. Diacarbon's principle market is biochar as a co-additive to local coal-fired power plants that operate under significant coal taxes (a tax per unit of fossil fuel derived coal burned) and would find it financially viable to dilute their coal use with non fossil fuel derived coal. Diacarbon's process is based upon a screw-agar technology with after burners used

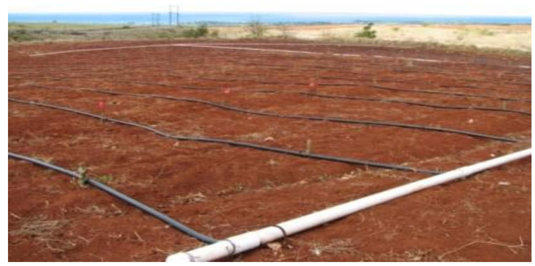


Figure 1. Plot I after initial plowing at the Poamoho Research Station, Waialua, Oahu (top). The same plot after installation of irrigation system, application of biochar, and planting of trees in October, 2012 (bottom).

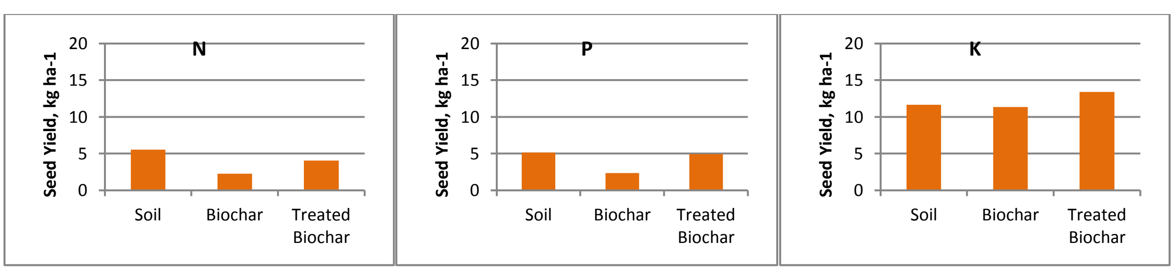
to treat air emissions. Such technology is often acknowledged as a leading candidate for commercially mature large scale carbonization process in terms of overall energy balancing and mechanical operation, at least in the foreseeable future.

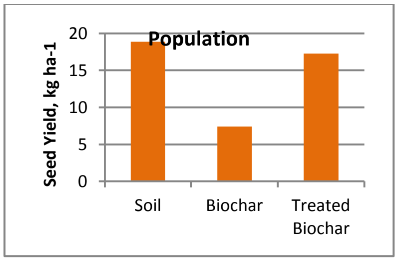
The Diacarbon mixed wood biochar to be used in these field trials has been treated with anaerobically treated primary clarifier effluent. This was accomplished by placing 25 lbs. bags of biochar into a 250 gallons tote container that was filled with effluent from the pilot scale anaerobic digesters put in place at the Hawaii Kai Wastewater treatment facility (see Task 3 below). The bags of biochar were soaked for a minimum of two days while the treated effluent in the tote container was turned over (replaced) three times per day. The treated effluent was characterized for a number of water quality parameters. Those important to the treatment of biochar include total nitrogen (24.0 mg/l), soluble nitrogen (24.0 mg/l), total nitrogen as NH_3 (20.5 mg/l), total soluble nitrogen as NH_3 (29.0 mg/l), total phosphorous (15.8 mg/l), soluble phosphorous (13.6 mg/l), volatile organic acids (0.0 mg/l). *The anaerobically treated biochar is now being tested according to Hawaii Department of Health (HDoH) standards. Once approval is obtained from HDoH, the field trials are to be installed at the Poamoho Research Station and the Pacific Biodiesel site.*

The HDOH approved the application of effluent treated biochar to open fields in September, 2012. Six field trials were initiated the following month, five at the Poamoho Research Station and one at the Pacific Biodiesel Farm site. All trials are in Waialua, Oahu.

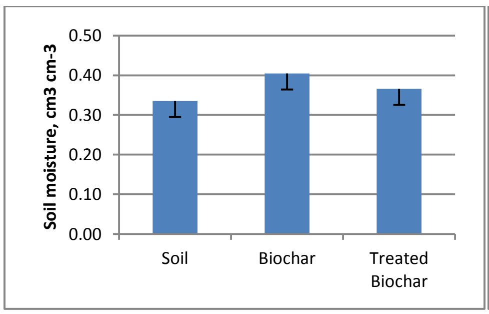
The trials at the Poamoho Research Station are intended to examine Jatropha oil yield as affected by biochar applied to soil in combination with either fertilizer (N, P, K), irrigation, or tree population density. The experimental design is a split-plot with four replicates. The main-plot treatment are four rates of fertilizer/irrigation or five population densities. Fertilizer rates are 0, 50, 100, and 150% of recommended rates for N (224 kg ha^{-1}), P (258 kg ha^{-1}), and K (82 kg ha^{-1}). The four irrigation rates are 0, 33, 67, and 100% of water routinely applied. The five population densites range from 828 to 5,997 trees ha^{-1}.The sub-plot treatment are effluent treated biochar, biochar, and no biochar. Biochar was applied to 22 kg of soil immediately surrounding the tree at a rate of 2.5% by dry weight. The sub-plot consists of two trees. Trees are spaced 1.8 x 3.0 m apart.

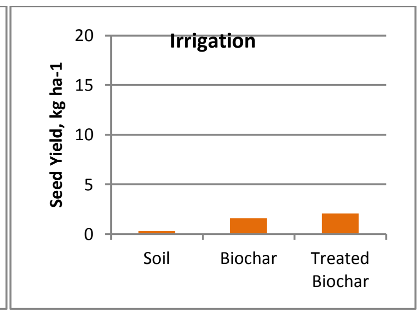
Many Jatropha trees began flowering in May, 2013. Initial yield data was collected the following month and statistical analyses performed. The differences in mean yield due to treatment effects were not statistically significant. However, there is a consistent pattern among the nutrient (N, P, K) and population density experiments, application of treated biochar produced greater yield than biochar. The Jatropha trees are expected to continue fruit production through October. Yield data will continue to be collected and it is expected the statistical analyses will increase in power with the additional data.





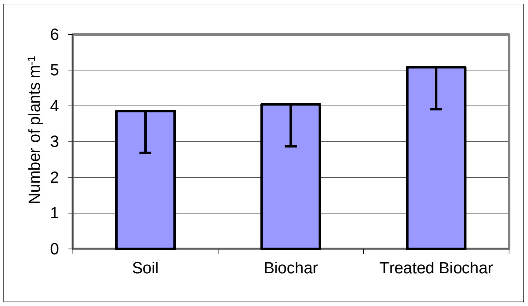
Soil moisture measurements in the irrigation trial showed that the application of treated biochar significantly increased the soil moisture content. The effect on yield is not yet statistically significant, but as the season progresses, data will continue to be collected and this correlation may develop with time.





The experimental design at the Pacific Biodiesel Farm site is a randomized complete block with four replicates. Treatments are treated biochar, biochar, and no biochar. Sunflower was planted as the test crop. Biochar was applied to soil at a rate of 2.4% by weight. A single plot is 0.9 x 9.1 m.

The number of sunflower plants established during the experiment was significantly greater in plots where treated biochar was applied.



In a follow-on experiment, safflower was planted into the same plots in April. Initial soil moisture readings show that adding biochar, increases soil moisture, but not statistically significant. Yield is expected to be measured in mid-July.

To facilitate the operation and scaleup of the HNEI commercial-scale, Flash Carbonization™ Demonstration (FC Demo) Reactor on campus, we designed, purchased the needed materials (e.g. pipe, flanges, fittings, Unistrut parts, air blowers, monolith catalysts, etc.), and completed the fabrication of the new catalytic afterburner (CAB). The CAB was assembled and welded in the SOEST machine shop. It consists of a mixing chamber (carburetor), a combustor that houses the monolithic catalysts, and a stack. The CAB was moved to the HNEI fenced, concrete pad (behind the Biomedical Sciences Building) where it was coupled to the FC Demo Reactor. We initiated tests of the CAB using propane as a fuel in late May, 2012 and began testing the CAB together with the FC Demo Reactor in August, 2012. Since then we have run the FC Demo Reactor using the 1' D canister on a regular basis emphasizing macadamia nutshell feedstock. Despite the fact that we are located very near the EHSO building and the MidPac campus, we have received no complaints concerning smoke. Emissions of CO depend strongly upon the temperatures realized immediately above the catalytic monolith in the CAB. These temperatures are controlled by delivery of secondary air into the CAB, as well as by control of pressurized air delivery to the FC Demo Reactor. Temperatures near 900 C in the CAB result in CO levels near 100 ppm, but it is not wise to expose the steel body of the afterburner to such high temperatures for extended periods of time. Currently, we are adding firebrick insulation to the interior of the afterburner to protect the steel vessel. We anticipate that if the firebrick is preheated, the catalyst monolith will not be needed.

We have now produced 100+ lb of good quality macadamia nutshell charcoal. A large sample of this charcoal was shipped to the Cabot Norit Corporation in Holland for evaluation. Cabot Norit is the world's largest producer of activated carbons. Likewise, we delivered a large sample to Elkem in Norway for evaluation as a reductant in the manufacture of silicon from quartz. Elkem's initial analysis of the charcoal indicated that its composition is good for silicon production, but the charcoal would need to be briquetted for use in the silicon smelter. We are actively seeking other commercial partners with an interest in evaluating macadamia nutshell charcoal. To this end we acquired 1000 lb of macadamia nutshells from the Big Island and will carbonize all this material during the coming months. We also acquired a trunk load of waste bamboo cuttings from a Big Island grower. This bamboo is very dense and carbonized nicely our lab reactor. We will carbonize the remainder in the Demo Reactor and explore its potential markets as well. We believe that these dense biomass materials, which grow well in Hawaii, will produce biocarbons with desirable properties that will command high values in the marketplace.

In addition to the design, fabrication, and testing of the CAB described above, during the past two years various needed equipment to maintain and operate the Demo FC reactor (e.g. a new hoist, a JOBOX field station, a new 12 kW power generator and two new air compressors), and an instrument to analyze the exhaust of the CAB (a micro GC) were purchased. Needed maintenance of the Demo FC reactor (e.g. painting the gantry and tall ladder, lubricating the hoist, etc.) is ongoing. The permit to operate the FC Demo reactor was renewed. The State boiler inspector was satisfied that the pressure vessel and all its components meet the national code requirements.

Future Goals

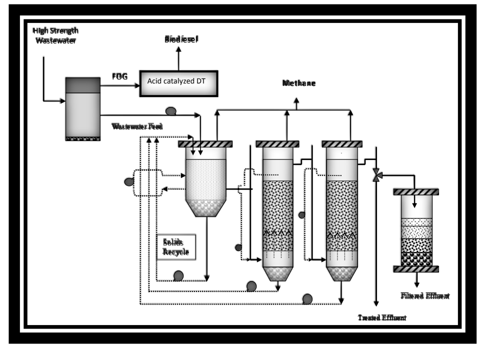
WESS sponsored research has enabled us to detail the disposition of heavy metals during sewage sludge carbonization. By early August we will know the concentration of heavy metals in the CAB exhaust. If these do not exceed EPA limits we will begin carbonizing sewage sludge in the FC Demo Reactor and deliver the biochar to soil scientists for testing. If the heavy metal concentrations are too high, we will explore the acquisition of a scrubber to eliminate heavy metal emissions from the exhaust.

An NSF grant, which was awarded during the WESS project, enables a strong collaboration with the Norwegian University of Science and Technology in Trondheim. The Norwegians have a keen interest in charcoal briquettes as a solid fuel replacement for wood pellets and torrefied wood pellets that are used for home and district heating. Also there is keen interest in the substitution of charcoal for coking coal in the metallurgical industry in Scandinavia. Our future plans also emphasize continuing collaborations with the Scandinavians.

Additional attempts to secure field trial quantities of biochar (processed from anaerobically processed sewage sludge) from off-campus vendors have been accomplished. Specifically, Diacarbon has processed and shipped field trial quantities of biochar made from processed sewage sludge. The materials are beign sent to Dr. Deenik for his work with Susan Crowe on crop growth and CO2 sequestration.

<u>Task 2</u>: *Establish a pilot test site at Pacific Biodiesel's Sand Island's wastewater treatment facility*

A research contract has been signed between PBI and UH to characterize the performance of a High Rate Anaerobic Digestion process utilizing biochar as an immobilization material. This research project has been completed at lab scale and this data presented to Pacific Biodiesel. Results have shown up to a 90% reduction in total and soluble COD, up to an 80% reduction in TSS, total gas production rates of approximately 6 l/l/d, and average methane head space compositions (averaged across all reactors) greater than 65% for hydraulic retention times as low as 1 day for feeds (grease trap waste wastewater) possessing COD values of approximately 20 gCOD l^{-1}.



This data was used to "size and cost out" a pilot scale (~1000 gallon) system to be located at PBI's Sand Island Facility. These discussions have covered as materials of construction, volume, flow rates at all locations, key control points, expected total gas production and the like. *A research contract for $105,000 has been approved and forwarded to PBI to build the Pilot Plant and to execute*. Installation and plant modifications are set to begin on June 11th, with testing beginning after that. The reactors have been fabricated with connecting pipes and control systems still to be added. The WESS has purchased 4 m^3 of biochar from Diacaron at cost to fill these reactors.

To further support this effort an SBIR was submitted by PBI to NSF on June 18th. This was not funded. This will serve as a template for additional funding. The objective of the SBIR is to execute the Pilot Testing after the fabrication of the Pilot Scale reactor. The role of UH in this SBIR would be to fabricate and provide a novel packing material that could improve the results (reported above) by a factor of ten, potentially transforming the field of anaerobic digestion.

An umbrella research agreement that permits additional UH faculty access to the pilot test facility has been signed and executed. This Omnibus agreement addresses the execution of additional research projects under a single corporate-to-corporate agreement between the University of Hawaii and PBI. The Omnibus Agreement does not preclude any UH faculty member from pursuing their own solo research agreements/projects with PBI that are outside the Agreement. This traditional avenue is still available to

UH faculty. What the Omnibus Agreement will do, however, is permit those faculty willing to work under the terms of the Omnibus Agreement to start projects immediately, without the need of securing a separate corporate-to-corporate agreement, assuming PBI approves the statement of work and budget.

<u>Task 3:</u> *Establish a pilot test site at an off-campus waste water facility*

Two 3,000 gallon anaerobic digesters have been installed at the Hawaii Kai Wastewater facility to test the treatment of primary clarifier effluent as a means to produce methane gas and to reduce the organic loading rate on downstream aerobic units. These reactors employ UH patented immobilization material licensed to RealGreen Power by OTTED. The two (2500 gallon working volume, each) high rate column anaerobic digesters were leak tested, inoculated with roughly 500 gallons of anaerobic sludge (acquired from on-site anaerobic solids reactors) and then fed primary clarifier effluent supplemented with waste grease trap wastewater operated at a 10 day hydraulic retention time over a 3 month period. After this period the reactors were transitioned onto pure primary clarifier effluent (the target feedstock) and then transitioned to HRT's of 3 days or lower. Results for a 3, 2, and 1 day hydraulic retention time have been completed. Results show that at a 3 day HRT, the total suspended solids of the primary clarifier feed was reduced by 85%, the total COD was reduced by 23.5% and the total five day BOD (BOD5) was reduced by 49%. The volumetric rate of COD reduction achieved was 0.023 kg m^{-3} d^{-1}. No gas production was observed at a 3 day HRT. *One key take away result is that the reduction TSS, at 14.2mg/l, met the national discharge limits of 30 mg/l while the BOD5 of the effluent, at 49 mg/l, is still slightly above the national discharge limit of 30 mg/l.*

Treated effluent from these reactors has been used to soak mixed wood biochar that has been deployed in field trials (see Task 1). An Open House was hosted in February at the Hawaii Kai Wastewater Treatment Facility where local dignitaries, potential stakeholders, and interested parties were introduced to the project and facilities. Dignitaries that were invited included representatives from Hawaii American Waters, AECOM Hawaii, HNEI, and the UH Manoa's Office of the Vice Chancellor for Research and Education, and representatives of venture capital interests that had invested in RealGreen Power.

REALGREEN POWER
Zero Pollution, Zero Waste

Report 6/13/12
HKWWTP Project

Characteristics of the RGP anaerobic system at the HKWWTP
System HRT 3 days 5/23/12 thru 6/6/12

	PC			R1	R2	Final			average	notes	method
	value	deviation +/-		value	value	value	deviation +/-				
TS mg/L	4,920			5,250	5,050	4,900				1	
TSS mg/L	78.6	14.4	(10.6)	23.4	17.0	14.2	2.8	(2.2)	*	2	
TSS reduction %	85.62%								*		
TCOD mg/L	300	52.8	(39.3)	230	233	230	30.3	(15.8)	*		Hach 8000
SCOD mg/L	198	4.7	(14.3)	200	218	203	13.0	(23.0)	*	3	Hach 8000
TCOD removal	23.48%								*		
TCOD loading rate kg/m3 RXR/day	0.098								*		
TCOD removal rate kg/m3 RXR//day	0.023								*		
TBOD5 mg/L	94.8	23.2	(14.6)			48.0	16.3	(9.7)	*	4	
SBOD5 mg/L		62.0	62.0			44.3	14.7	(8.8)	*	4	
TBOD5 removal	49.33%								*		
TN mg/L	25.3	10.7	(10.3)	31.0	27.0	24.0	2.0	(10.0)	*		Hach 10072
STN mg/L	24.0			23.0	27.0	24.0				5	Hach 10072
NH3-N mg/L	19.3	22.0	(5.3)	32.0	28.0	20.5	10.5	(6.5)	*		Hach 8155
SNH3-N mg/L	26.0			32.0	31.0	29.0				5	Hach 8155
TP mg/L	15.0	5.2	(2.6)	11.7	13.4	15.8	6.0	(5.3)	*		Hach 8190
STP mg/L	9.6			17.9	14.2	13.6				5	Hach 8190
TVOA mg/L	24.5	9.5	(24.5)	20.8	10.2	0.0	0.0	0.0	*		Hach 9196

Notes:
1 6/6/12 10 mL dried samples (24 hrs 105C)
2 average 5 periods; 49 mm 1.5 micron filter
3 1.5 micron filtered
4 analysis performed by HAW
5 6/6/12 data

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5 THIRD STREET – SUITE 808 – SAN FRANCISCO, CA 94103 USA
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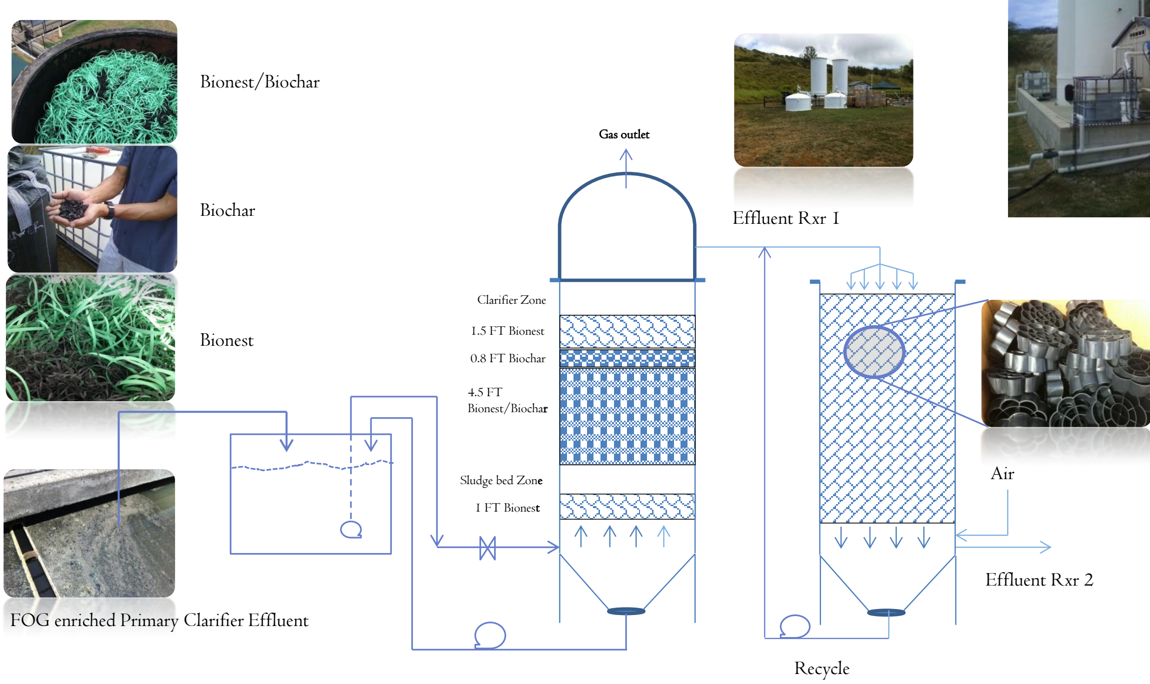
The results discussed above indicate some progress is needed to achieve a system that reduces the BOD5 of the treated effluent to below the national discharge limit of 30 mg/l on a 30 day average. To do this, two approaches are to be pursued in 2013. In the first, additional packing material in the form of biochar will be added to the reactors. Biochar is seen as a much better support for biofilm development as opposed to the filamentous plastic substance (i.e. Bionest) currently employed. The Bionest material, being a hydrophobic plastic, was largely designed to absorb fats from low strength dairy wash down wastewaters. The biochar is an absorptive material that supports biofilms and could improve biofilm efficiency and absorption of biologically oxidative material.

In the second, the adaptation of the system above to incorporate a trickling bed aeration (energy efficient) reactor will be employed. The tricking bed filter will sit downstream of the anaerobic digester and will treat its effluent. The combined hybrid system comprised of an anaerobic digester coupled to a tricking bed reactor is novel and not currently tried in the wastewater treatment industry. Overall this system is poised to combine the best of anaerobic and aerobic digestion systems. This system could lead to a final treated effluent that meets national discharge limits for BOD5 and TSS and low nitrogen levels, making it quite acceptable as an alternative to aerobic treatment of primary clarifier effluent. One of the key outputs will be the overall HRT that can be achieved. The lower the HRT that can be achieved the smaller the overall reactor size that will be needed.

The retrofitting is set to occur during the month of June 11th. All materials have been purchased. A program of experiments have been developed that includes different loading and recirculation rates will be run during the remaining part of 2013. Aerobic effluent is expected to have residual BOD5 and ammonia-N each less than 10 mg/L. The program was presented to and accepted by the Industrial Advisory Board (representing AECOM Hawaii, Hawaii American Waters, and RealGreen Power) on Tuesday June 18th 2013.

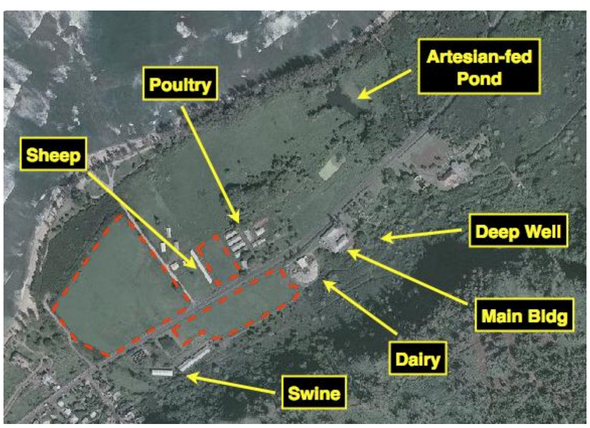


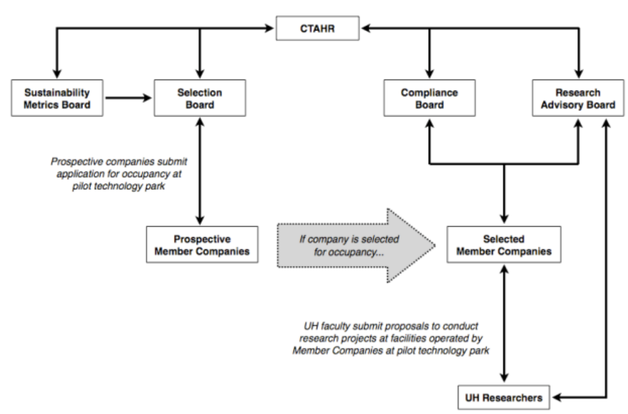
<u>Task 4:</u> *Identify additional candidate pilot test sites for recruitment into the WESS program*

A model test site to implement of sustainability program such as that proposed in WESS was considered. The model test site was the Waialee Livestock Experimental Station. This site previously served as significant agricultural livestock station that was part of CTHAR's extension program. Currently, the Livestock Station has been closed and the land and preexisting infrastructure are uninhabited. Using WESS funds, a concept proposal was prepared to outline how such a sustainability program could look. This was submitted to CTHAR administration for review. The initial concept imagined to execute dairy production of butter with the cow and milk parlor wastewater being treated by high rate anaerobic digestion with the treated water being used to water Jatropha and other energy crops. Three local companies, Naked Cow Dairy, Pacific Biodiesel, and RealGreen Power, were used to develop a model cycle. The official response form the Dean of CTHAR (6/16/2012) is below:

"*We met with some of our faculty whose research and extension programs focus on sustainable food and energy production to brief them on the proposal and to ascertain their interest in participating in the pilot technology park and/or co-locating their work at Waialee. Although a range of viewpoints were expressed, there was general agreement that a focus on sustainability was appropriate for Waialee and should be supported. There was also agreement that the pilot technology park was a good approach, but that CTAHR had a fiduciary responsibility for Waialee and financial, legal, and other matters had to be in place at the start, rather than the end, of the project….. Dr. Maria Gallo will assume the position of CTAHR Dean, and we have briefed her on the WESS Master Plan. Future discussions on the proposal should be held with Dr. Gallo as she will have purview over the college's on- and off-campus facilities…."*

A follow on meeting with Dean Gallo and other CTHAR administrators was held in Fall of 2012. At this meeting the general concept was reintroduced as was the reality that a more appropriate University held piece of land might be Waimanalo Research Station. It was noted that some interest by industry and potential VC funding was still interested in the general concept and CTHAR noted that such a "type" of idea was relevent to its current evaluation of land use. In summary, the report was formally given and received and discussed and a positive contribution to CTHAR's long term planning made.

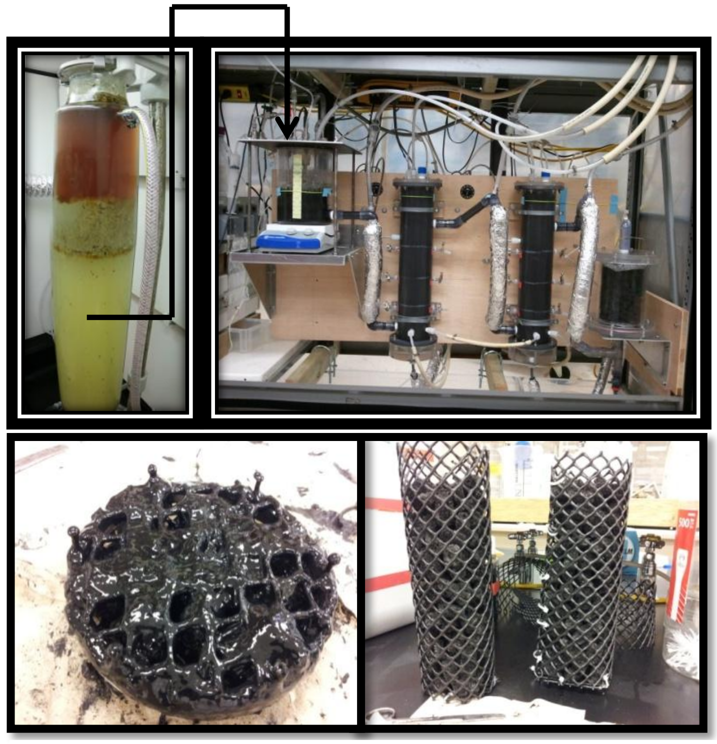




Finally, an Omnibus agreement between UH and Akuo Energy has been signed. This is to cover a future power delivery infrastructure that Akuo intends to build in Hawaii. The facility will link farmers to solar PV delivered to support intensive greenhouse farming. The Omnibus Agreement fits the WESS philosophy and will pave the way for an additional off campus demonstration scale facility that will permit faculty to work with farmers in the real world.

Task 5: *Characterize the performance of novel immobilization materials (e.g. biochar) for their performance in high rate biofilm anaerobic digesters in terms of treatment efficiency and biogas production*

A three phase high rate anaerobic digester system filled with corn cob biochar has been employed to characterize the efficiency of high rate anaerobic digestion feed grease waste trap wastewater. The characteristics of this wastewater are given in the Table below. In general this wastewater is characterized by low pH, high COD values approaching 20 gams COD per liter, and possesses high concentrations of volatile organic acids. Initial studies evaluated performance using moderate amounts of biochar placed in 3 separate discs placed at equidistant heights in the two column reactors. Performance of this system was fully characterized on a synthetic food waste composed of a glucose/peptone/yeast extract media as well as the GTW wastewater. It was also tested on GTW wastewater at an HRT of 3 days. This system (i.e., 3 thin discs of biochar) performed ably, with reductions in soluble COD approaching 60%, methane headspace compositions above 65%, and no visible gas hold up. Upon draining and opening the reactors the biochar discs were found to be coated with healthy biofilms (see image below). With these positive results, the reactors were repacked with full biochar loadings (see image below) and the same feedstock processed at HRT's of 3, 2, and 1 day.



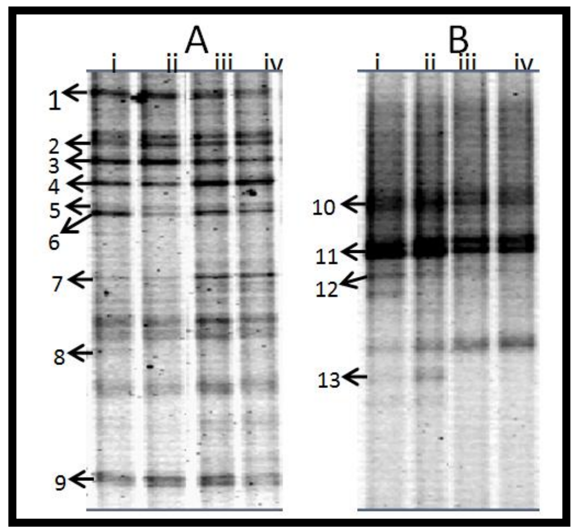
Biochar in thin discs recovered from the anaerobic digesters after 6 months of operation (A) and the packed columns of biochar leading to the data presented in the Table above (B).

Characteristics of GTW wastewater

Parameters	**Values**
pH	4.0 - 4.4
COD (g L^{-1})	16.6 - 19.5 (total) / 13.4 - 15.1 (soluble)
TN (g L^{-1})	0.15 - 0.43 (total) / 0.14 - 0.37 (soluble)
TP (g L^{-1})	0.24 - 0.97 (total) / 0.19 - 0.79 (soluble)
TVOA (g L^{-1})	2.9 - 4.3 (soluble)
TSS (g L^{-1})	1.9
COD/TN	38.6 – 130 (total) / 36.2 - 107.9 (soluble)
COD:N:P	100:0.77:1.23 - 100:2.59:5.84 (total) 100:0.93:1.26 - 100:2.76:5.90 (soluble)

The results for the fully packed column at HRT's of 3, 2, and 1 day is presented below. In general, anaerobic digestion efficiencies that yielded COD reductions up to 95% and methane headspace concentrations between 60 and 80% were achieved along with FOG to biodiesel conversion efficiencies of 90%. Methane production yields (m^3 per kg COD reduced) achieved theoretical maximums with near total depletion of the volatile organic acids. High resolution images of biochar samples revealed extensive coverage with thick biofilm communities and microbial analysis revealed broad spectrum populations of anaerobic bacteria that ferment organic substrates to produce acetate, ethanol, and hydrogen as major end products as well as archaeal populations that produce methane gas. Energy calculations confirmed that the option of co-producing biodiesel and methane gas from GTW is a competitive option relative to its co-digestion with sewage sludge. The results have been submitted to the Journal of Renewable Energy.

Microbial communities in the biofilms recovered from biochar in the bioreactors were determined by DGGE and cloning. Samples were collected by draining the biofilm coated biochar laid out on absorbent paper, and total genomic DNA was extracted using the UltraClean DNA extraction kit (MoBio) according to the manufacturer's instructions. Microbial community structures were visualized using polymerase chain reaction using the bacterial 16S rRNA gene primers PRBA338F and PRUN518R and the archaeal 16S rRNA gene primers rSAf(i) and PARCH519R followed by denaturing gradient gel electrophoresis (PCR-DGGE). Subsequently, cloning and sequencing were conducted to obtain sequence information for the major bacterial and archaeal populations identified by PCR-DGGE.



DGGE gels showing microbial community profiles for the bacteria (panel A) and archaea (panel B) in the anaerobic reactors (R1 and R2) based on 16S rRNA genes. DNA sequence information was obtained for the numbered DGGE bands.

DNA sequence information was obtained to determine the phylogenetic affiliation of some major bacterial and archaeal populations detected by PCR-DGGE. The nine major bacterial populations include six Firmicutes, two Thermotogaceae, and one Spirochaetes. All the *Firmicutes* populations are *Clostridia*, a group of anaerobic bacteria that ferment organic substrates to produce acetate, ethanol, and hydrogen as major end products. The two *Thermotogae* populations are also likely important contributors to the anaerobic digestion process, as most cultured species of *Thermotogae* are obligate fermenters of sugar and other complex organics and produce lactate, acetate, ethanol, and hydrogen as major end products. As one would expect for anaerobic digesters, all of the archaeal populations are methanogens, including two *Methanobacteriales* and two *Methanomicrobia*.

Phylogentic affiliation of major microbial populations identified by DGGE.

Band	**Top match (accession number)**	**Identity[a]**	**Phylum**	**Domain**
1	*Thermotogaceae* strain SulfLac1 (FR850164)	99%	*Thermotogae*	Bacteria
2	*Spirochaetes* clone DhR^2/LM-B02 (HQ012843)	92%	*Spirochaetes*	Bacteria
3	*Thermotogaceae* clone B3112 (HQ133023)	91%	*Thermotogae*	Bacteria
4	*Pelotomaculum* sp. FP (AB159558)	95%	*Firmicutes* (*Clostridia*)	Bacteria
5	*Clostridium* sp. clone K13-19 (HE862234)	91%	*Firmicutes* (*Clostridia*)	Bacteria
6	*Desulfotomaculum thermobenzoicum* (AJ294430)	93%	*Firmicutes* (*Clostridia*)	Bacteria
7	*Clostridium thermocellum* (CP002416)	90%	*Firmicutes* (*Clostidia*)	Bacteria
8	*Symbiobacterium* sp. clone BL1_11 (JX101989)	99%	*Firmicutes* (*Clostridia*)	Bacteria
9	*Symbiobacterium* sp. clone BL1_11 (JX101989)	94%	*Firmicutes* (*Clostridia*)	Bacteria
10	*Methanobacterium formicicum* strain KOR-1 (JX042445)	100%	*Euryarchaeota* (*Methanobacteriales*)	Archaea
11	*Methanobacteriaceae* clone B11-A-115 (JN836424)	100%	*Euryarchaeota* (*Methanobacteriales*)	Archaea
12	*Methanosaeta* sp. clone BUH10-1 (JQ282391)	100%	*Euryarchaeota* (*Methanomicrobia*)	Archaea
13	*Methanoculleus bourgensis* MS2 (HE964772)	97%	*Euryarchaeota* (*Methanomicrobia*)	Archaea

Research has been underway to evaluate the development of packing material that is comprised of biopolymer coatings applied to the activated carbon. The biopolymers being considered have shown some efficacy at reducing biofilm growth and it is considered possible that partially or wholly coating biochar with these polymers may reduce biofilm growth. Packing material of extremely high surface area (as activated carbons are) that support growth of thin film biofilms offer potential to improve performance (relative to that shown above) by 10 to 100 fold. These values would transform the anaerobic digestion industry and provide a mechanism of high rate anaerobic digestion to treat isolated point sources of wastewater are small to medium scale (relative to the volumes of water entering wastewater sewage treatment facilities. *These ideas were the subject of an unsuccessful NSF proposal in Spring of 2012 but will be the subject of a NSF proposal submitted in Spring of 2013.*

Packing density (g L-1), System HRT (d), OLR (kg COD m-3 d-1)									
	25, 3.0; 5.53			25, 2.0, 9.75			25, 1.0, 21.2		
	HYD	**R1**	**R2**	**HYD**	**R1**	**R2**	**HYD**	**R1**	**R2**
pH	5.96	6.95	7.17	6.01	6.89	7.21	5.95	6.97	7.24
TSS (g L^{-1})	2.75	1.4	0.45	4.8	3.8	0.7	2.6	3.6	2
TSS reduction (g L^{-1})	-45	26	76	-71	-36	75	-8	-50	13
COD (g L^{-1})	8.6, 3.6(s)	3.0, 0.6(s)	1.0, 0.4(s)	18.5, 10.8(s)	8.5, 2.4(s)	1.6, 0.7(s)	11.7, 8.4(s)	7.8, 2.7(s)	4.0, 1.1(s)
COD reduction (%)	48, 73(s)	82, 96(s)	94, 97(s)	5, 28(s)	56, 84(s)	92, 95(s)	45, 51(s)	63, 84(s)	81, 94(s)
COD reduction (kg COD m^{-3} d^{-1})	2.67; 3.27(s)	4.53, 4.27(s)	5.2, 4.33(s)	0.5, 2.15(s)	5.5, 6.35(s)	8.95, 7.2(s)	9.5, 8.9(s)	13.4, 14.6(s)	17.2, 16.2(s)
TVOA (mg L^{-1})	1.275 (s)	0.149 (s)	0.044 (s)	2.798(s)	0.498(s)	0.080(s)	2.834(s)	0.980(s)	0.313(s)
TVOA reduced (%)	57	95	99	34	88	98	15	71	91
TGPR (m^3 m^{-3} d^{-1})	1.77	0.852	0.177	2.49	1.38	0.918	5.77	3.12	1.2
CO_2 (%)	42	23	22	36	23	22	44	22	19
CH_4 (%)	55	77	70	61	77	78	55	78	81
CH_4 (m^3 m^{-3} d^{-1})	0.974	0.656	0.124	1.52	1.06	0.72	3.17	2.43	0.97
CH_4 per COD_{red} (m^3 $kgCOD^{-1}$)			0.34			0.39			0.38

Task 6: *Characterize the fundamental properties of biochar made from solid biomass waste collected from existing and potential pilot test sites (e.g., dried anaerobic sludge, dried "rag" layer from waste trap grease)*

Proximate analysis, ultimate analysis, and extractable nutrient analysis have been completed for biochars made from both the Waimanalo corncob (CC) and Hawaii Kai sewage sludge (SS) (Table 1). Several results are of particular note: (a) the SS biochar had a much higher ash content than the CC biochar; (b) the SS biochar was characterized by higher total nitrogen (N) and extractable phosphorus (P), while the CC biochar had a very high potassium (K) content; (c) treatment of the CC biochar increased the extractable N content and decreased the extractable K content, but left extractable P unchanged, but treatment of the SS biochar decreased the extractable N content, increased the extractable P content, but left extractable K relatively unchanged; (d) both chars showed low arsenic (As) content despite high As in the sewage sludge feedstock.

Selected characteristics of the corncob and sewage sludge biochars.

Determination	**CC char (untreated)**	**CC char (treated)**	**SS char (untreated)**	**SS sewage char (treated)**
	%			
Proximate analysis				
Ash	8.42	7.34	64.17	67.22
Ultimate analysis				
Carbon (total)	79.8	84.32	30.24	30.45
Hydrogen (total)	2.27	2.8	1.29	0.54
Oxygen (total)			<0.01	<0.01
Nitrogen (total)	0.84	0.91	3.13	2.62
Sulfur (total)	0.12	0.16	3.81	4.12
Elements in the ash				
CaO	1.79	1.62	9.13	9.41
K_2O	36.9	23.6	2.13	1.91
P_2O_5	10.07	12.65	20.86	22.38
	mg/kg			
Extractable nutrients				
Nitrogen ($NH_4^+ + NO_3^-$)	11	31	216	33
Phosphorus	19	19	402	1304
Potassium	16269	7860	1200	1015

Contrary to our initial expectations, the results showed that anaerobic treatment of the biochars did not always increase extractable inorganic N and P. Of particular note is the very high ash content of the SS biochar, which sets it apart from what is traditionally considered charcoal.

Early in the WESS project, detailed elemental analyses of 6 sewage sludge (SS) charcoals, raw Hawaii Kai (HK) SS, and a representative soil sample were accomplished by Hazen Research, Inc. The raw data was distributed to the WESS researchers. This data became the basis of the U. Ghent MSE thesis of Sam Van Wesenbeeck. A summary of this work and its implications is given below.

The heavy metal concentration limits for land application of sewage sludge in the USA, which is EPA controlled (40 CFR part 503), Europe (controlled by the Directive 86/278/EEC of 12 June 1986) and

Belgium (VLAREA) are given below as taken from Sam Van Wesenbeeck's thesis. These regulatory limits are important benchmarks for our work.

Heavy metal	**Arsenic**	**Cadmium**	**Copper**	**Lead**	**Mercury**	**Moly.**	**Nickel**	**Selenium**	**Zinc**	**Chromium**
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
USA[a]	41	39	1500	300	17	75[e]	420	36	2800	1200
State of Hawaii[b]	20	15	1500	300	10	15	100	25	2000	200
Europe[c]	nr[f]	20-40	1 000-1750	750-1200	16-25	nr	300-400	nr	2500-4000	nr
Belgium[d]	150	6	375	300	5	nr	50	nr	nr	250

[a]40 CFR Part 503 Regulation (EPA)
[b] HAR 62 (Hawaii Administrative Rules)
[c]Council directive 86/278/EEC
[d]Vlarea (Openbare Afvalstoffenmaatschapij voor het Vlaamse Gewest)
[e]Ceiling concentration (the rest is average monthly concentration)
[f]nr=Not regulated

In our WESS research, 2 samples (SS1 and SS2) from Hawaii Kai were sent to the Hazen Laboratory for analysis. They were sampled with a one month time lapse. A high variability in heavy metals exists between SS1 and SS2 (see Tables 5.11 and 5.12). Sewage sludge feed SS1 cannot be directly applied on land in the USA (and in the State of Hawaii) and Belgium due to heavy metal concentrations (arsenic and copper) that are too high; whereas sewage sludge feed SS2 can be applied because its heavy metal concentrations are below the regulatory limits for both the USA, Europe and Belgium.

Table 5.11: Concentrations of heavy metals in the sewage sludge feed and charcoal (SS1) (mg/kg).

		As	Cd	Cu	Pb	Hg	Mo	Ni	Se	Zn	Cr	B	Mn
sewage sludge	feed	188	4.1	443	41	0.27	8.6	32	9.38	1360	67.6	83.9	114
	charcoal	16.7	6	712	60	0.11	13	71	14.0	2360	67.6	148	212

Table 5.12: Concentrations of heavy metals in the sewage sludge feed and charcoal (SS2) (mg/kg).

		As	Cd	Cu	Pb	Hg	Mo	Ni	Se	Zn	Cr	B	Mn
sewage sludge	feed	6.8	3.3	325	13	0.53	11	30	8.58	956	97.4	66.9	66
	charcoal T/M[a]	16.3	8.8	815	37	0.02	40	65	15.5	2360	281	197	174
	charcoal B[b]	15.4	8.4	727	29	0.10	21	78	15.8	2160	209	138	146
corncob	feed	0.18	0.1	4.27	1.5	≤0.01	2.8	1	≤0.05	35.1	9.56	2.6	6.90
	charcoal	0.56	0.5	24	2.1	0.59	16.4	14	0.89	164	24.7	24	21.2

[a]T/M=Top and Middle of FC reactor.
[b]B=Bottom of FC reactor.

After carbonization, the sewage sludge charcoal SS1 can be applied in the USA (but not in the State of Hawaii because of too high of a concentration in molybdenum and zinc) and also conforms to European regulations. It cannot be applied in Belgium because of too high cadmium, copper and nickel concentrations, but other countries of the EU may have less stringent regulations thereby allowing the application of the sewage sludge charcoal.

Surprisingly, sewage sludge charcoal SS2 cannot be applied to land in Belgium or the USA (and in the State of Hawaii) due to prevailing regulations. The sewage sludge charcoal SS2 shows too high concentrations of cadmium, copper, nickel and chromium for both sewage sludge charcoal originating from top and bottom of the reactor as far as Belgian regulations are concerned. The concentration of molybdenum and zinc are too high for EPA and HAR regulations and therefore the sewage sludge charcoal cannot be applied in the USA or in the State of Hawaii. On the other hand, European regulations allow application of this sewage sludge charcoal.

Corncob charcoal is below the regulatory limits for every heavy metal analyzed for the USA, Europe and Belgium.

Using mass balances, the displacement of heavy metals during carbonization can be calculated. Both depletion and uptake ratios have been calculated and are discussed below.

$$Depletion\ ratio\ element\ i\ = 1 - \frac{\sum_j M_{char,j}.C_{char,i,j}}{M_{feed}.C_{feed,i}}$$

Negative values of depletion ratios in table 5.13 (below) show an uptake and values greater than 100 % are possible if the initial concentration is negligible compared to the amount taken up. Depletion ratios do not completely show a correlation with boiling point as shown in Yoshida and Antal (2009). The low boiling point heavy metal mercury shows a high tendency to vaporize for all samples (SS1, SS2, run 5 and run 6) and is partly absorbed by the corncob charcoal or migrates out of the FC reactor into the atmosphere. Arsenic, which is the heavy metal with the second lowest boiling point (in elemental form) of the heavy metals analyzed, does show almost full depletion in SS1 in contrast to the low depletion in SS2. This is due to different experimental conditions during these 2 FC experiments.

Table 5.13: Depletion ratios of heavy metals in sewage sludge and corncob (SS1, SS2 and previous FC experiments done by Yoshida and Antal (2009)[a]) (g/g).

		As	Cd	Cu	Pb	Hg	Mo	Ni	Se	Zn	Cr	B	Mn
SS1	sewage sludge	0.96	0.53	0.25	0.31	0.81	0.29	-0.04	0.30	0.19	-0.18	0.17	0.13
SS2	sewage sludge	0.08	-0.07	0.03	-0.04	0.96	-0.16	0.03	0.26	0.03	-0.04	-0.03	0.00
	corncob	-0.19	-0.90	-1.14	0.47	-21.47	-1.23	-4.33	-5.78	-0.78	0.02	-2.52	-0.17
run 5[a]	sewage sludge	0.80	0.63	0.26	0.02	0.96	na[b]	0.29	0.82	0.17	0.39	na	na
run 6[a]	sewage sludge	0.85	0.62	0.06	-0.09	0.97	na	0.13	0.70	0.06	0.23	na	na

[b]Not analyzed.

Assessment of the migration of heavy metals to different places (i.e. SS charcoal, corncob charcoal and the atmosphere) is made by uptake ratios in table 5.14. Uptake ratios are calculated as:

$$Uptake\ ratio\ element\ i\ = \frac{\sum_j M_{char,j}.C_{char,i,j}}{M_{feed}.C_{feed,i}}$$

High uptake values for sewage sludge charcoal (>90 wt%) can be seen for arsenic, cadmium, copper, lead, molybdenum, nickel, selenium, zinc, chromium, boron and manganese, meaning that these heavy metals have a low tendency to vaporize and that the sewage sludge charcoal is able to retain these heavy metals.

Low uptake values of heavy metals are seen for the corncob charcoal with the exception of mercury and molybdenum, which seem to accumulate in the corncob charcoal. Mercury, molybdenum, and selenium have a tendency to go to the gas phase and care should be taken of the gases leaving the FC reactor.
The heavy metal analysis conducted by Yoshida and Antal (2009) established that mercury, arsenic, selenium, and cadmium have high depletion ratios, which has been corroborated within limits in this research where arsenic and cadmium are found to stay in the sewage sludge charcoal for SS2.

Table 5.14: Uptake ratios of heavy metals in sewage sludge and corncob (SS2) (g/g).

	As	Cd	Cu	Pb	Hg	Mo	Ni	Se	Zn	Cr	B	Mn
SS → SS char	0.92	1.03	0.94	1.01	0.04	1.12	0.93	0.72	0.94	1.00	1.00	0.96
SS → corncob char	0.00	0.02	0.01	-0.03	0.24	0.18	0.08	0.02	0.02	0.00	0.06	0.01
SS → gas[a]	0.08	-0.04	0.05	0.02	0.72	-0.30	-0.02	0.26	0.05	0.00	-0.06	0.03

[a]Elements released in the atmosphere.

The behavior of heavy metals is highly dependent on the experimental conditions used during the FC experiment.

Following these exploratory runs and analyses, six sewage sludge runs were conducted that employed our most effective operating conditions. The results of these six runs are summarized in the Table below.

FC experiment (yymmdd) and (N°)	position in reactor	VM (wt%,dry)	Ash (wt%,dry)	fC (wt%,dry)	fC/fC+VM	fC/VM	fC+VM/Ash
121026 and 1	top	56.8	28.1	15.1	0.21	0.27	2.6
	middle	41.5	38.5	20.0	0.33	0.48	1.60
	bottom	6.10	58.9	34.9	0.90	15	0.40
121114 and 2	top	1.60	89.9	8.40	0.84	5.3	0.11
	middle	2.80	80.1	17.1	0.83	6.3	0.25
	bottom	2.20	67.8	29.9	0.93	14	0.47
121120 and 3	top	2.30	75.4	22.2	0.91	9.7	0.32
	middle	2.60	71.4	26.0	0.90	10	0.40
	bottom	2.80	66.7	30.5	0.92	11	0.50
121213 and 4	top	3.1	73.9	23.0	0.88	7.42	0.35
	middle	3.0	70.1	26.9	0.90	8.97	0.43
	bottom	4.2	61.1	34.7	0.89	8.26	0.64
130124 and 5	top	1.70	77.1	21.2	0.93	12.5	0.30
	middle	2.20	65.7	32.1	0.94	15.60	0.52
	bottom	3.1	70.7	26.1	0.89	8.42	0.41
130213 and 6	top	4.2	64.4	31.5	0.88	7.50	0.35
	middle	3.7	65.6	30.7	0.89	8.29	0.52
	bottom	4.4	63.4	32.3	0.88	7.34	0.58

The sewage sludge biochar produced by these runs was grouped according reaction conditions and sent to 6 different laboratories for analysis. Three of these laboratories are accredited by the EPA (Hazen, FQlabs, and Test America), one (ADSC) is widely used by university researchers, one is a UH lab, and one is a lab at U. Ghent. The UH lab had little experience with sewage sludge so its results are not listed. We await results from U. Ghent. The analyses we received are listed in the Table below. The heavy metals are listed in mg/kg dry feed or charcoal. Copper and nickel concentrations in the sewage sludge charcoal are too high for Belgium regulations while molybdenum is a problem for USA and State of Hawaii tresholds.

		Lab	FC experiment	As	Cd	Cu	Pb	Hg	Mo	Ni	Se	Zn	Cr	B	Mn
sewage sludge	feed	ADSC	121114	0.02	0.89		11.84	99.60	0.18	11.58	4.49	671.3	33.29		
	feed	FQlabs	130213	5.5	0.35	348	5.07	0.43	8.95	30.7	5.9	963	42.3		
	feed	Hazen	121213	4.66	3.2	346	14	0.28	9	27	8.58	1,030	65.0		
	feed	Test America	130124	4.5	1	270	13	0.99	6.8	18	6	700	36		
	feed	Ugent	121120												
	charcoal	ADSC	121114	0.05	1.26		19.01	22.00	0.33	35.13	5.99	1,529	54.40		
	charcoal	FQlabs	130213	12.0	2.05	916	27.4	≤ 0.36	19.8	75.8	10.8	2,470	108		
	charcoal	Hazen	121213	7.66	9.1	1,000	52	0.01	19.6	70	19.1	2,940	178		
	charcoal	Test America	130124	7.8	2.3	700	36	≤ 0.020	23	68	9.4	1,900	110		
	charcoal	Ugent	121120												

These results enabled us to calculate depletion ratios as discussed above. Values of these ratios are given in the Table below.

Depletion ratios (heavy metals organized from low to high boiling point) together with the average temperature of the exhaust gasses of the flash carbonization equipment during carbonization.

Laboratory	Hg [%]	As [%]	Se [%]	Cd [%]	Zn [%]	Pb [%]	Cu [%]	Cr [%]	Ni [%]	Temperature [°C]
TestAmerica	99.3	43.3	48.7	24.8	11.2	9.4	15.2	0.1	-24.00	195.5
Fqlabs	71.1	26.3	38.1	-98.0	13.3	-83.0	11.0	13.7	16.50	208.6
Hazen	98.8	44.4	24.8	3.9	3.5	-26.0	2.3	7.4	12.40	456.3

Regulations limit the amount of each heavy metal present in sewage sludge biochar that can be added to the soil. Analyses by the three laboratories enabled us to calculate the maximum amount of sewage sludge biochar that can be added to the soil based on its content of each heavy metal as given by the three laboratories. These amounts are listed in the Tables below for the USA and the EU.

Table 8: Annual dry sludge application rate in metric tons per hectare per year in the USA[a] (metric ton/ha/year).

Laboratory	As	Cd	Cu	Pb	Hg	Ni	Se	Zn
A[b]	256	792	104	405	42500	300	532	71
B	261	209	75	288	85000	300	262	48
C	167	905	79	536	2125	269	463	55
Average	218	419	84	385	5930	289	382	56

[a] EPA regulations 40 CFR 503.48 Table 4.
[b]A=TestAmerica, B=Hazen, C=FQLabs.

Table 9: Annual dry sludge application rate in metric tons per hectare per year in the EU[a] (metric ton/ha/year).

Laboratory	As	Cd	Cu	Pb	Hg	Ni	Se	Zn
A[b]	nr[c]	63	17	405	5000	43	nr[c]	15
B	nr	16	12	288	10000	43	nr	10
C	nr	71	13	536	250	38	nr	12
Average	nr	331	13	385	698	41	nr	12

[a]EU Directive 86/278/EEC
[b]A=TestAmerica, B=Hazen, C=FQLabs.
[c]nr=not regulated by the EU.

Somewhat surprisingly, the zinc content of the biochar is the limiting factor for its addition to the soil in both the USA and the EU. Nevertheless, the potential addition of 10 mt/ha/yr of biochar to the soil is an attractive proposition.

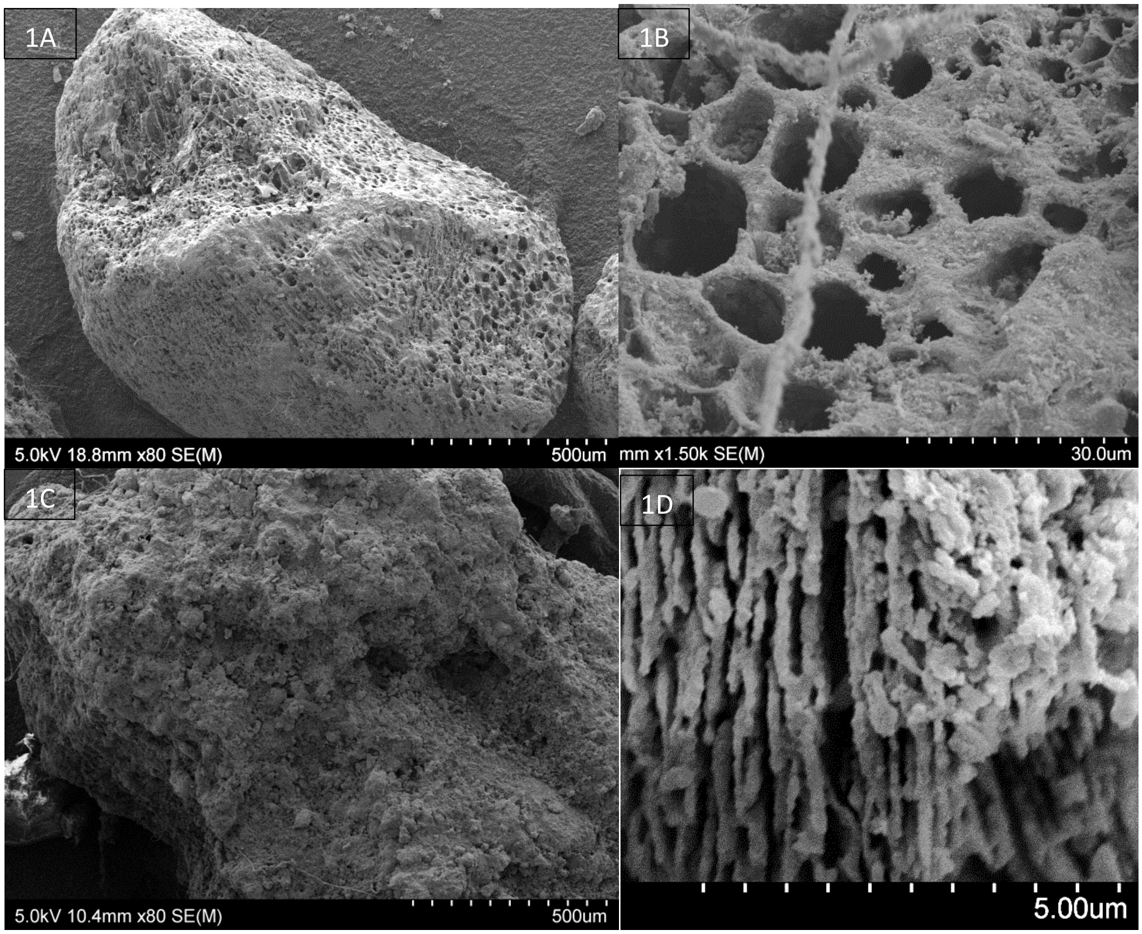
Beyond the analyses discussed above, to support the work of Dr. Deenik, we collaborated with chemists of the Hungarian Academy of Sciences (HAS) to obtain GC-MS and ICP-AES analyses of the extractives of untreated and treated HK SS. The HAS chemists extracted the charcoals using ultra-pure water, acetone, and hexane solvents. The water extract cannot be injected into the GC-MS; consequently its solutes were methylated, dissolved in hexane and analyzed. Unfortunately, not all the soapy residue of methylation dissolved in the hexane.

Recognizing that both the untreated and treated biochars had similar positive effects on the growth of corn, we identified extractives that were present in both biochars. For example, sterane compounds were detected in the acetone and hexane extracts of the untreated biochar, but these were not present in the treated biochar; consequently they are probably not responsible for the positive effects. Small amounts of long chain acids were detected in the water extracts of both the treated and untreated charcoals; consequently these could be responsible for the positive effects.

However, the ICP-AES analysis accounted for about 60% of water extracted mass from the untreated biochar, and a similar fraction of the treated biochar. Recognizing that the ICP-AES analysis detects only cations, and that anions (e.g. Cl) must also be present in large quantities, it is likely that inorganic compounds dominate the composition of the extracts. As expected, substantial amounts of Ca, K, Mg, Na and S were detected by ICP-AES. Other elements are listed in the detailed report that has been distributed to all WESS participants.

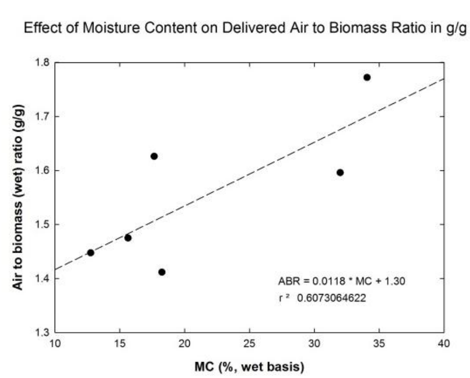
In light of the above findings, it is probable that the favorable effects of the sewage sludge charcoals on plant growth are due to their high content of minerals.

We are currently acquiring scanning electron microscope images of the biochar materials as a means to visually assess differences in the biochar materials. So far we have acquired approximately 60 images from soil samples collected from the third harvest. The next step will be to image the original biochar particles prior to their mixing with soil. Preliminary inspection of the images indicate clear differences in porosity and pore structure between the CC and SS biochars. The CC biochar shows clear porous structure reflecting structural properties of the original biomass (Fig 1A&B). The SS biochar, on the other hand, shows no clear porous structure at low magnification (Fig 1C), but at high magnification it shows a distinct layered structure suggesting high potential surface area (Fig 1D). We are planning to conduct surface area analysis of the biochar materials to quantify differences in surface area.



The Quantachrome instrument was repaired using Federal funds. The repair was successful and the instrument now reproduces its measurements when new. Everyone who expressed interest received training on the use of the instrument by the Quantachrome technician. A protocol has been developed to protect the instrument from contamination during sample analysis. A surface area analysis of macshell charcoal was recently completed.

We completed a series of tests on the effects of airflow, moisture content, and pressure on the carbonization of HK SS in the lab-scale Flash Carbonization™ (FC) reactor. The chief finding was the suitability of HK SS for carbonization. When the proper carbonization conditions (this refers to conditions of Flash Carbonization) are employed, the HK SS was easily carbonized to a high quality charcoal. Issues related to SS moisture content, and the unusual exotherm associated with its carbonization, which previously led to ash fusion issues, were overcome by a proper control of airflow. Treated and untreated HK SS charcoals are undergoing greenhouse pot trials as soil amendments to enhance the growth of corn, along with similar ongoing greenhouse trials with corn cob biochar.



We also carbonized waste food solids separated from the waste trap grease collected at PBI. Unfortunately, the solids are oil soluble and therefore full drying of the solids was not achieved at elevated temperature (100°C). Consequently, a poor biochar was achieved as the oil in the sample interfered with the flash carbonization process, yielding a poorly carbonized soft biomass that was unsuitable as biochar. As such, direct carbonization of this solid waste is not likely although it could be blended with other materials, even contributing to the combustion process.

Task 7: *Characterize the fundamental properties of soils supporting high bio-oil productivity from Jatropha crops*

The first objective of the work at the Maui Pilot Test Site was to identify factors that contribute to the unusually high yield produced by Jatropha curcas at the Kula Agricultural Park. Jatropha accessions collected in Hawaii were planted at Poamoho Research Station in January of 2007 and at the Kula Agricultural Park in May of 2010. Poamoho Research Station is located on the North Shore of Oahu Island at 700 foot elevation. The Kula Agricultural Park is located on the leeward side of Mount Haleakala on Maui Island at 1500 foot elevation. The soil series at Poamoho Research Station and Kula Agricultural Park are Wahiawa (very-fine, kaolinitic, isohyperthermic, Rhodic Haplustox) and Keahua (fine, kalonitic, isohyperthermic, Ustic Haplocambid), respectively. Soil samples were collected at the start of the experiment to a depth of 6 to 8 inches. Irrigation and fertilizer were applied to both fields. Seed were collected as fruit matured during the first 10 months after planting. Soil pits were excavated in September, 2011, to observe root growth, and collect soil samples to analyze for chemical and physical properties. Chemical analyses were performed by the Agricultural Diagnostic Service Center, College of Tropical Agriculture and Human Resources, University of Hawaii.

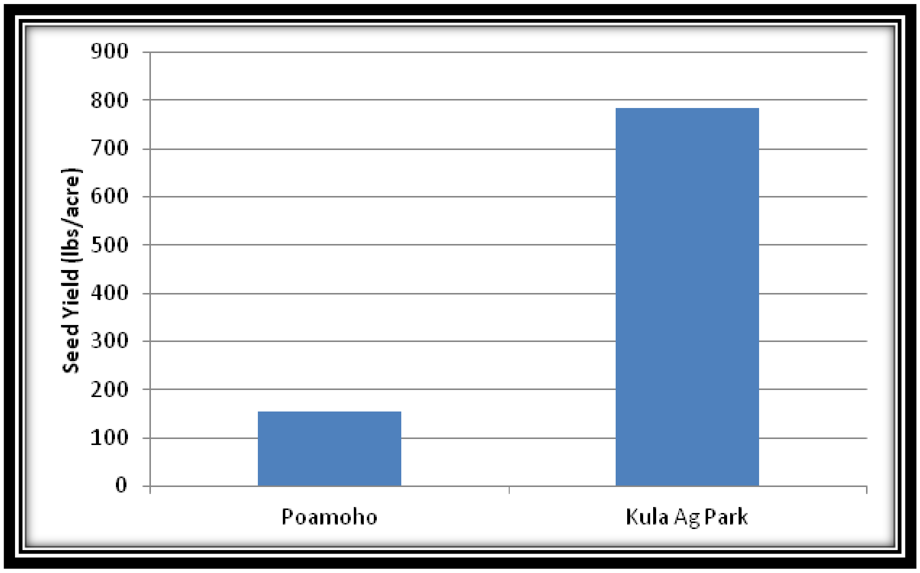
Seed yield was much higher at Kula Ag Park compared to Poamoho Research Station at 10 months after planting (Figure 1). Seed yield at Kula and Poamoho were 784 and 154 lbs/acre, respectively.

During the first 10 months of growth, solar radiation was virtually equal at the two locations, but temperature and rainfall were more favorable at Poamoho than Kula Ag Park (Figures 2 to 4). The daily average total global solar radiation was 478 and 472 cal cm^{-2} at Poamoho and Kula Ag Park (Figure 2). Average air temperature was higher at Poamoho (75 F) than Kula Ag Park (72 F) (Figure 3). Total rainfall was greater at Poamoho (15 inches) than Kula Ag Park (7 inches). In addition, supplemental irrigation at Poamoho was greater than Kula Ag Park, 24 and 4 inches, respectively. Temperature and rainfall at Poamoho seemed more favorable for plant growth at Poamoho than Kula Ag Park, but was contrary to the yield results.

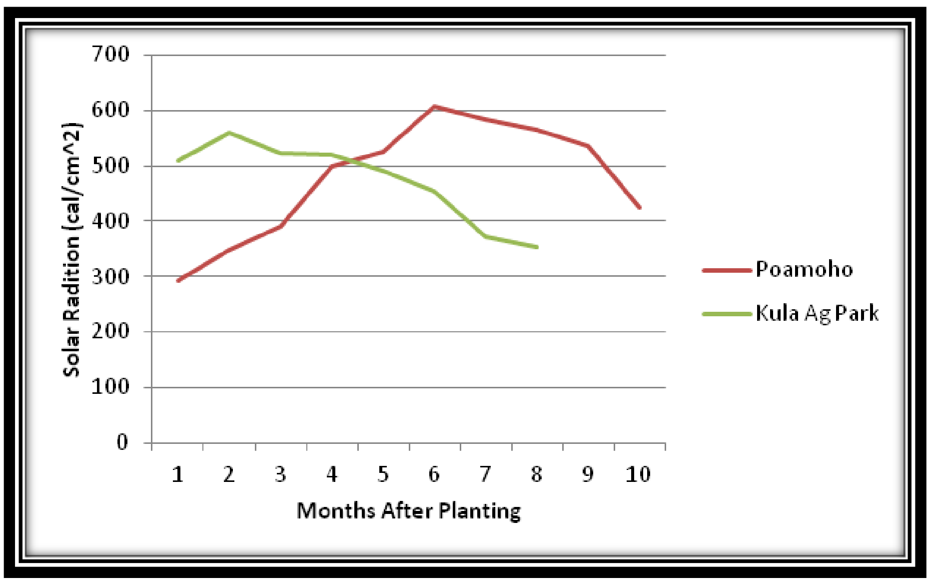
The nutrients phosphorus, potassium, and calcium in soil decreased over time (Figures 7 to 9). The decrease is likely due to uptake by the Jatropha tree and leaching losses. The elapsed time between initial and final soil sample collection was 56 months at Poamoho and 17 months at Kula Ag Park. In Figures 7 to 9, each µg/g of nutrient on the vertical axis represents 1.95 and 1.75 lbs of nutrient in the top 6.7 inches of soil across an acre at Poamoho and Kula Ag Park, respectively. Phosphorus, potassium, calcium and magnesium in an acre was reduced by 1103, 453, 2115, and 184 lbs at Poamoho, and 299, 56, 523, and 190 lbs at Kula Ag Park. The low rainfall and irrigation at Kula Ag Park suggests that the removal of nutrients is mainly by root uptake. The quantity of nutrients removed from the top 6.7 inches indicates these nutrients are required in significant quantities, especially for phosphorus and calcium, for Jatropha growth and yield.

The soil properties bulk density and effective cation capacity were more favorable at Kula Ag Park than Poamoho. Soil bulk density, a measure of soil porosity and compaction, at both sites ranged from 1.02 to 1.33 g cm^{-3} (Figure 5). These values are within the normal range for cultivated clay and silty clay soils. At both depths the bulk density is lower at Kula Ag Park suggesting that roots may penetrate this soil more readily. The effective cation exchange capacity, a measure of the reservoir of soil nutrients, was approximately three times greater at Kula Ag Park than Poamoho (Figure 6). This suggests that the soil at Kula Ag Park creates a larger reservoir for nutrients and would be less likely to lose nutrients to leaching.

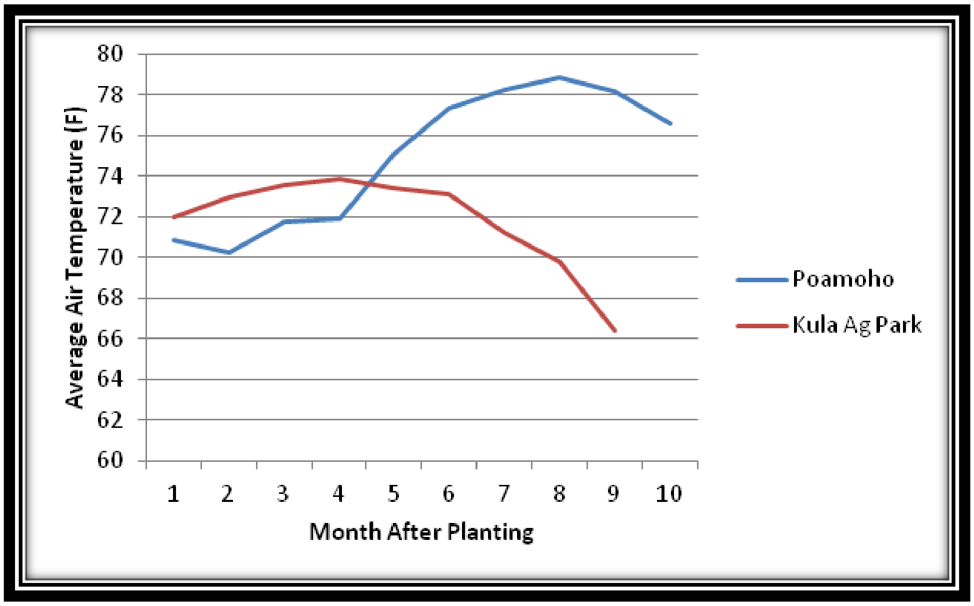
The main factors related to greater Jatropha curcas seed yield at Kula Ag Park soil fertility, effective cation exchange capacity, and soil bulk density. Because of their significant reduction in soil, phosphorus and calcium seem to be important in Jatropha seed production. Other nutrients, such as potassium and magnesium, are required as well. Effective cation exchange capacity produces a greater reservoir to hold nutrients and prevent leaching. Low bulk density may play an important role as to allow root penetration and/or to increase porosity that enhances water drainage or holding capacity.



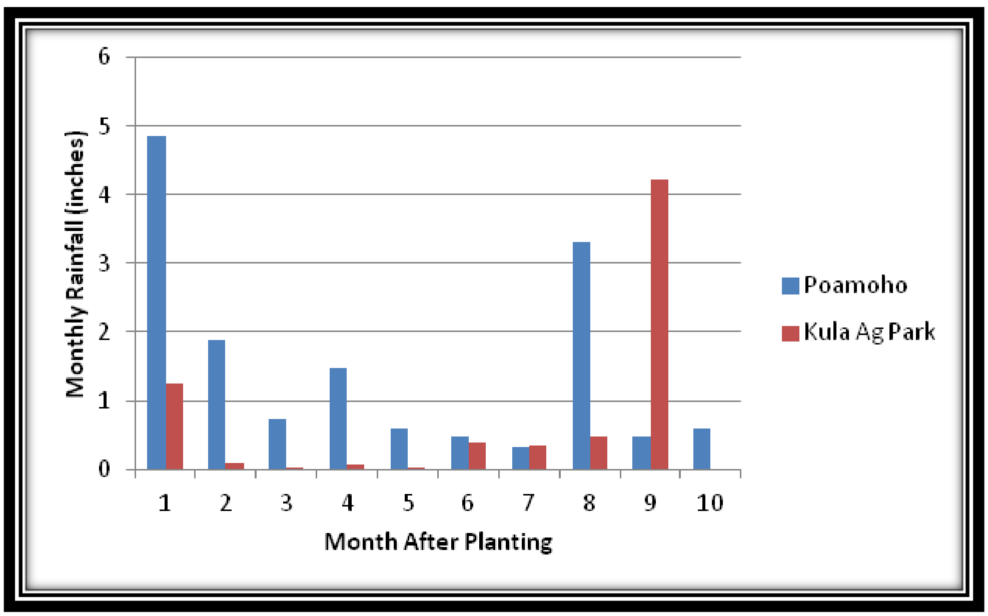
Jatropha curcas seed yield 10 months after planting at Poamoho Research Station (Oahu) and Kula Agricultural Park (Maui).



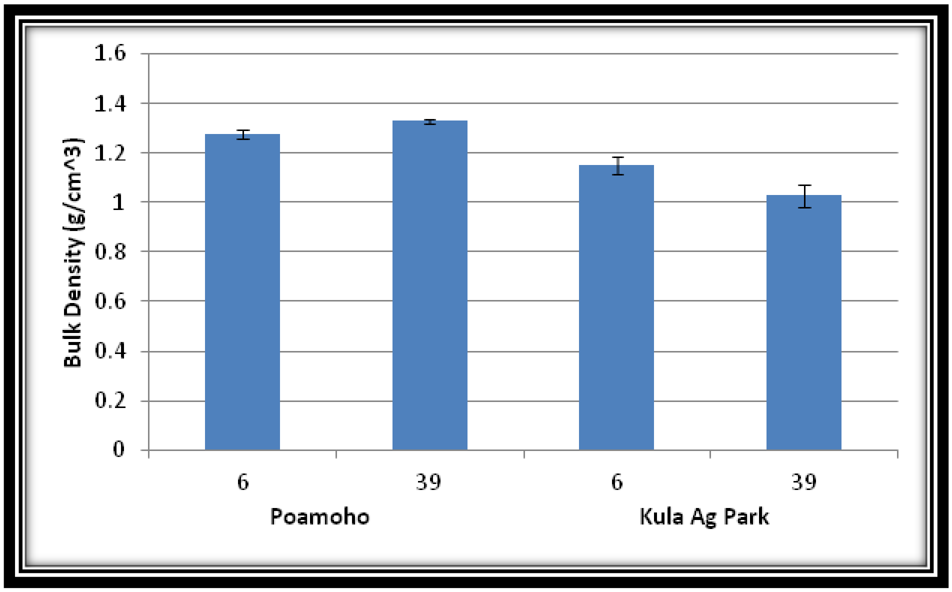
Average daily total global solar radiation over 10 months after planting Jatropha curcas at Poamoho Research Station (Oahu) and Kula Ag Park (Maui).



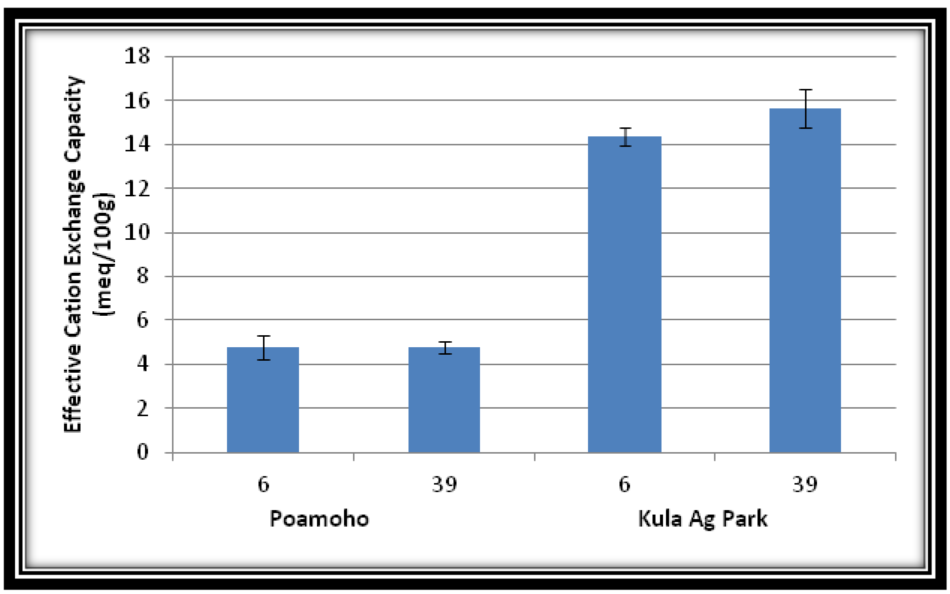
Average daily air temperature at Poamoho Research Station (Oahu) and Kula Ag Park (Maui) during the first 10 months of Jatropha curcas growth.



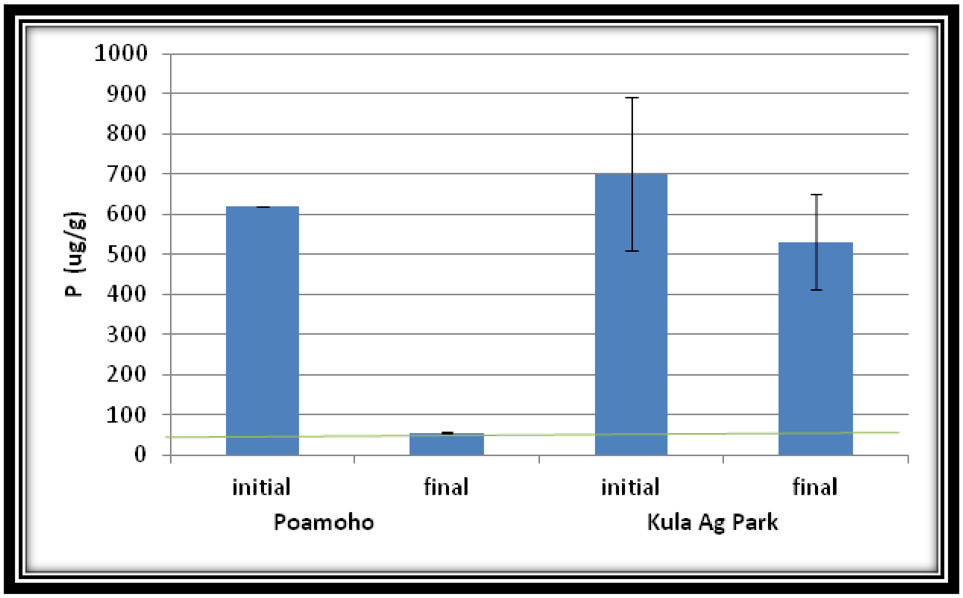
Monthly total rainfall at Poamoho Research Station (Oahu) and Kula Agricultural Park (Maui) recorded during the first 10 months after planting Jatropha curcas. Poamoho and Kula Ag Park received 14.8 and 6.9 inches of rain, respectively.



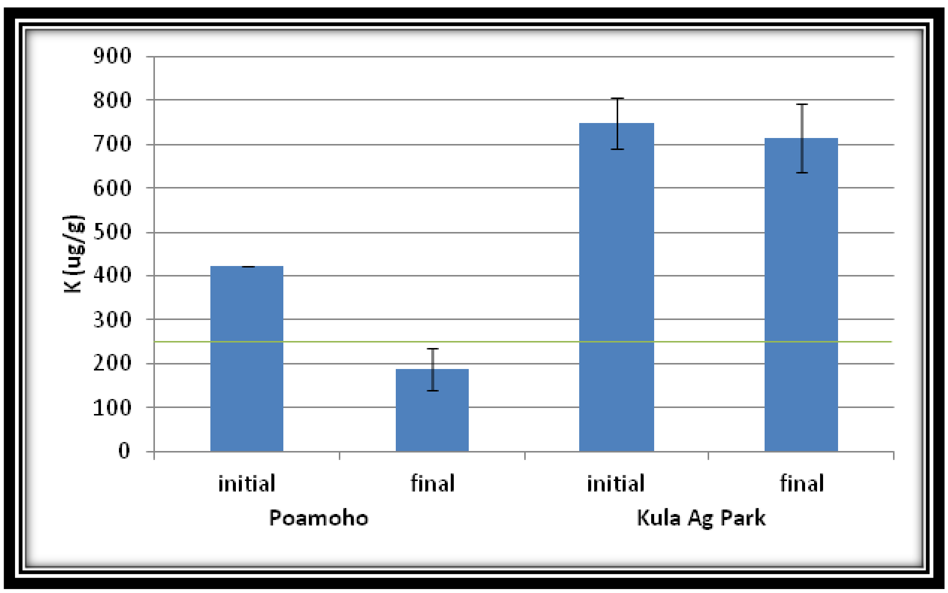
Soil bulk density from two depths (6 and 39 inches) at two locations (Poamoho Research Station and Kula Agricultural Park) where Jatropha curcas were grown. Error bars are +/- one standard deviation of the mean.



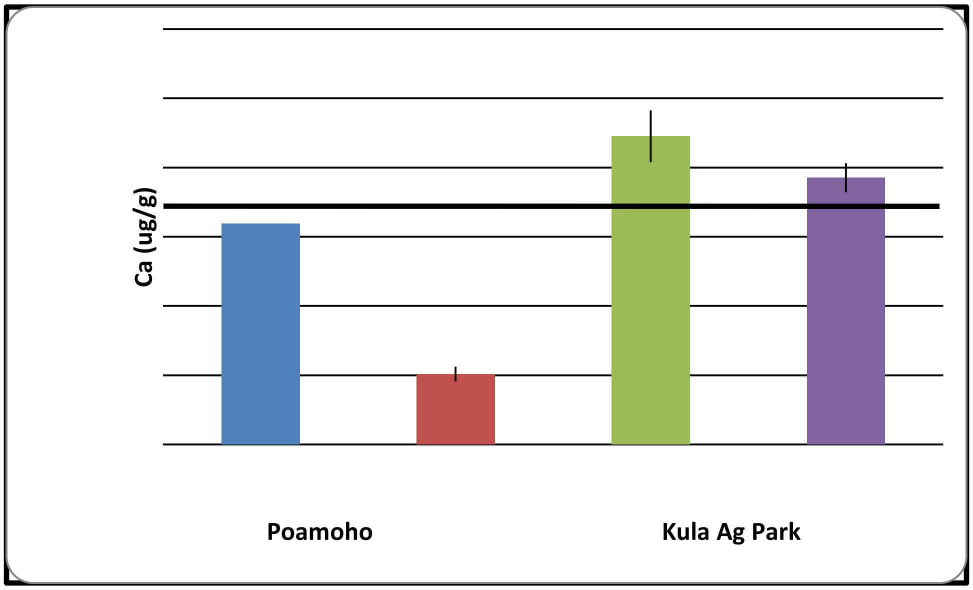
Cation exchange capacity of soil at two depths (6 and 39 inches) at two locations (Poamoho Research Station and Kula Agricultural Park). Error bars are +/- one standard deviation of the mean.



Soil phosphorus concentration at 6 inch depth at two locations (Poamoho Research Station and Kula Ag Park) at the time of planting Jatrohpa curcas (initial) and September, 2011 (final). The time elapsed between the initial and final samples was 56 months at Poamoho, and 17 months at Kula Ag Park. The green line represents the sufficiency threshold for plant growth. Error bars are +/- one standard deviation of the mean.

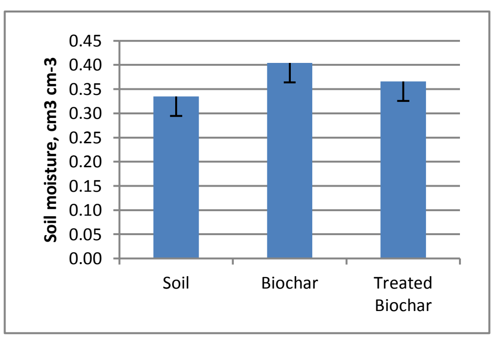


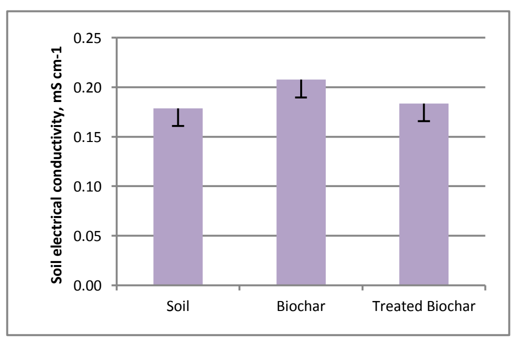
Soil potassium concentration at 6 inch depth at the time of planting Jatropha curcas (initial) and September, 2011 (final). Time elapsed between initial and final was 56 months at Poamoho and 17 months at Kula Ag Park. The green line represents the sufficiency threshold for plant growth. Error bars are +/- one standard deviation of the mean.



Soil calcium concentration at 6 inch depth at the time of planting Jatropha curcas (initial) and September, 2011 (final). Time elapsed between initial and final was 56 months at Poamoho and 17 months at Kula Ag Park. Error bars represent +/- one standard deviation of the mean.

The application of biochar to the Wahiawa soil series in the irrigation trial at Poamoho research station increased both the soil moisture content and the electrical conductivity, a measure of ions in the soil. It remains to be seen whether these changes in the soil characteristics translates into increased seed yield from Jatropha curcas.





Future Plans

To continue to correlate which of the properties described above can be duplicated by addition of biochar to poor soils.

Task 8: *Evaluate anaerobically treated biochar as a base material to make Terra Preta soils*

Corn growth in soils amended with SS char (A) and CC char (B).

A series of greenhouse pot experiments were conducted at the CTAHR Magoon Greenhouse facility to test the effects of various biochars added to two soils on corn seedling growth. The first phase comprised a series of two experiments testing the effects of untreated and anaerobically treated CC and SS biochars on the growth of corn seedlings in an infertile Oxisol. By growing three cycles of corn plants in succession in the same biochar-amended soil, we were able to investigate biochar effects on soil properties and plant growth as a function of time. The second phase of experiments was conducted to address the following two objectives: 1) to evaluate the effect of three biochar materials on plant growth in a fertile Mollisol, and 2) to determine the effect of removing water soluble components of biochar materials on plant growth. With respect to objective 1, we hypothesized that the biochar effect would be less significant in the fertile soil and for objective 2 we hypothesized that water soluble components of the biochars containing mineral nutrients are responsible for the positive effects of biochar on plant growth.

Experiment 1: corn cob biochar

The first experiment evaluated the effect of anaerobically treated and untreated corn cob (CC) biochar with and without fertilizer on corn seedling growth in an acid, infertile Oxisol. The effects of CC biochar were mixed. Biochar alone showed no improvement in corn seedling growth in all three crops cycles compared with the control (Fig. 1). Both the untreated and treated biochars in combination with fertilizer increased plant growth by approximately 50% as compared to treatment solely with fertilizer in the 1st crop. However, the positive effect disappeared with the 2nd crop. In the 3rd crop, the untreated biochar + fertilizer doubled biomass production compared with fertilizer alone, while the treated biochar had no significant effect on plant growth compared with fertilizer alone. Contributions to improved plant growth in the first cropping cycle are best explained by a biochar liming effect and improved nutrient availability to the growing plants. Increases in soil pH from CC biochar applications were significantly correlated with dry matter accumulation, and CC biochar significantly increased the availability of soil P, K, and Ca (Fig. 2). Increases in extractable P and K translated directly into significantly higher plant uptake compared with the fertilizer alone control. Whether the biochar was treated prior to application or not was less important. In the 3rd crop cycle, where the untreated biochar + fertilizer doubled biomass production, plant growth benefits were best explained by the persistence of the liming effect with a significant detoxification of soil Mn. With each cropping cycle, soil pH in the control+fertilizer pots dropped from a mean of 6.20(±0.02) to 4.91(±0.13) by the end of the 3rd crop cycle. Acidification of this soil increases the solubility of soil Mn reserves creating toxic levels of soil Mn. There was significant non-linear decrease in extractable soil Mn as pH decreased in non-biochar amended soils (Fig. 3a). High dry matter in the biochar soils was significantly correlated with the reduction in soluble Mn (Fig. 3b).

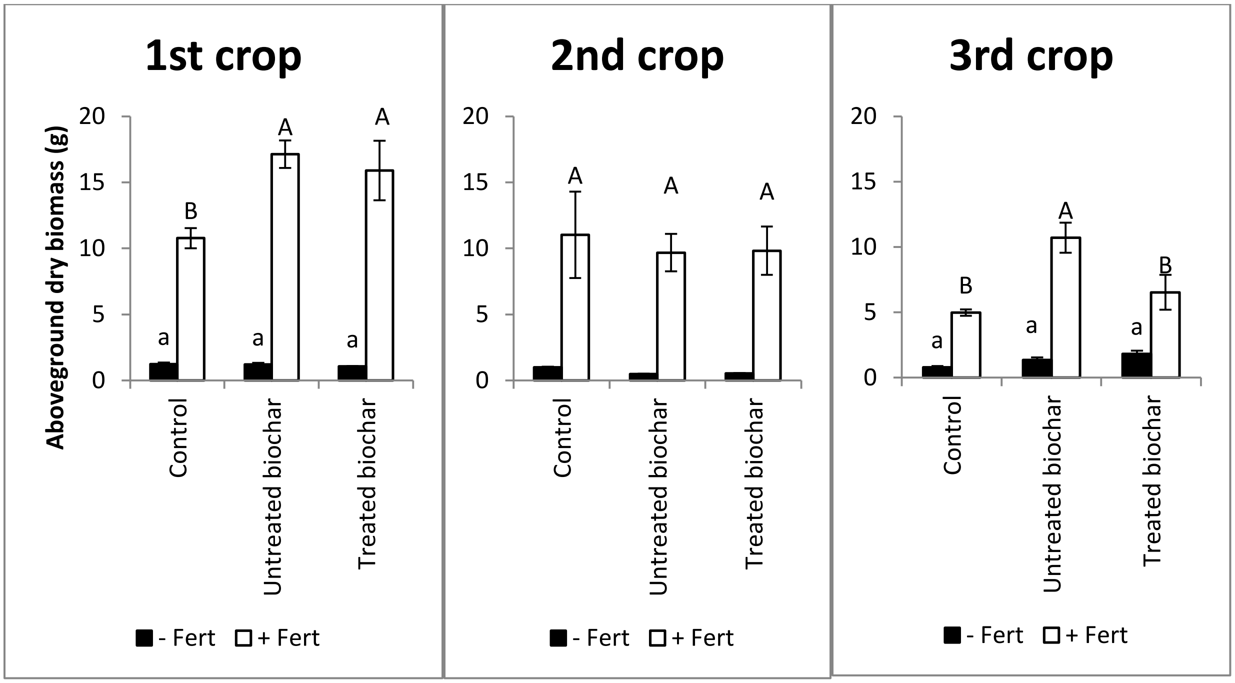


Figure 1. CC biochar treatment effects on corn seedling growth in an infertile Oxisol. Bars represent the mean of four replicates, bars are the standard error of the mean, and the bars with the same letter are not statistically different (P<0.05).

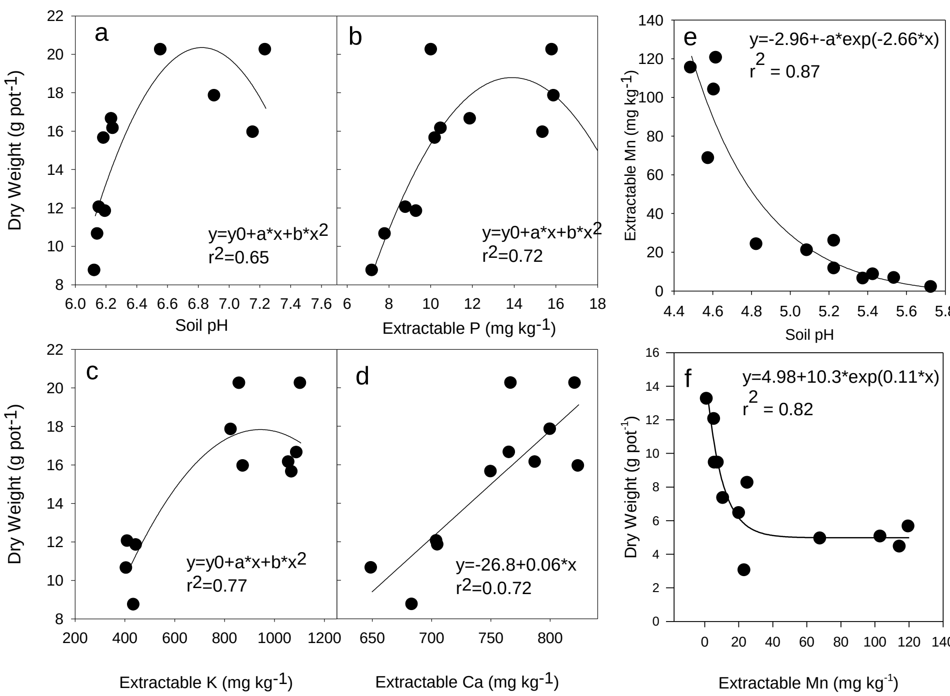


Figure 2. In the first crop cycle CC biochar induced increases in soil pH (a), extractable P (b), extractable K (c), and extractable Ca (d) and the associated effects on corn dry matter. In the 3rd crop cycle corn growth increases were explained by the biochar liming effect and its direct reduction of soil Mn solubility (e, f).

Experiment 2: sewage sludge biochar

In the SS biochar trial, the treated and untreated biochars together with fertilizer improved plant growth over and above fertilizer or biochar alone in the first and third crop cyles (See image below) with only the the treated biochar enhancing growth in the second cycle. In the first crop, untreated biochar alone performed as well as fertilizer, but the positive effect disappeared in the second and third crops, where biochar alone performed no differently than the control. The largest effects were seen in the first and third crop cycles, where the combination of both biochars with fertilizer improved biomass by more than two-fold in the first crop and a striking three-fold in the third crop cycle. Biochar increased K, Mg, and Ca availability in the soil in the first planting cycle, and measured increases in these nutrients translated into direct increases in their uptake by the growing corn plants compared with the fertilizer only treatment (Fig. 4). Soil P increased significantly with the treated biochar treatment, which may explain the added growth. Increased nutrient availability and uptake were a result of the direct elemental contributions from the high ash content of the biochar combined with the biochar liming effect, which was most significant in the treated biochar treatment. In the second planting cycle, the liming effect persisted in both biochars

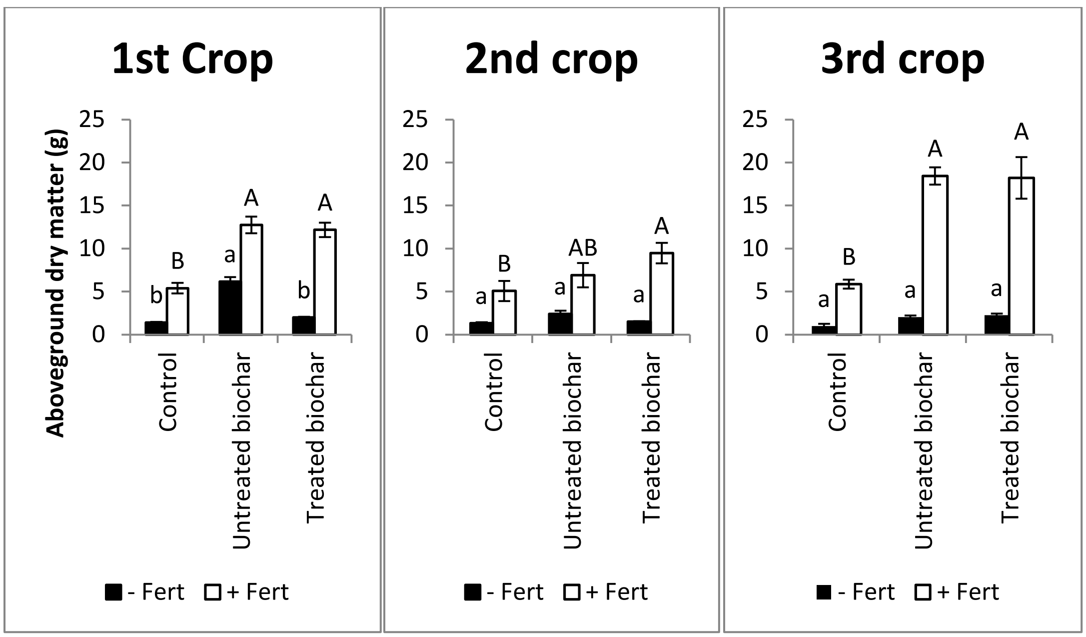


Figure 3. SS biochar treatment effects on corn seedling growth in an infertile Oxisol. Bars represent the mean of four replicates, bars are the standard error of the mean, and the bars with the same letter are not statistically different (P<0.05).

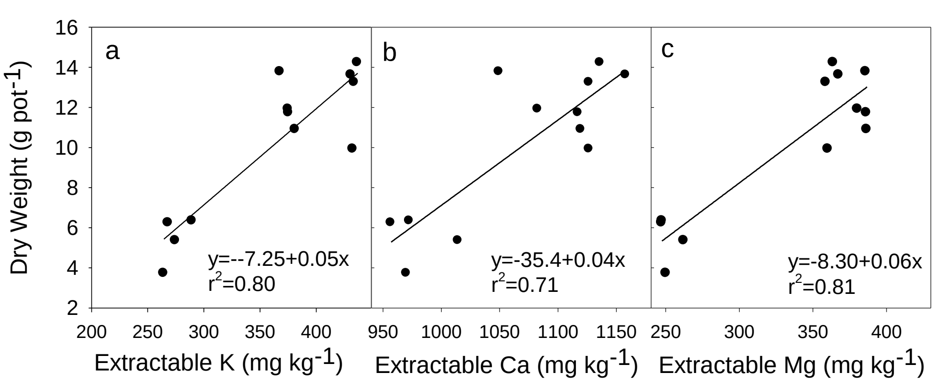


Figure 4. Biochar effects on corn dry matter yield extractable as function of soil K (a), Ca (b), and Mg (c) in the first planting cycle.

with the treated biochar maintaining the highest pH. Both biochars continued to provide increased P and Mg availability in the soil compared with the control. While biochar showed significant improvements in these key soil chemical properties, they were not significantly correlated with crop growth or plant nutrient uptake. Corn Mn uptake, however, was significantly reduced in the treated SS bin improved tolerance to Mn toxicity. We speculate that maintenance of pH above 6.0 in the treated SS bichar treatment reduced the negative effects of Mn toxicity. The high yields recorded in the biochar amended soils in the third crop show a clear relationship with the biochar liming effect, which prevented soil acidification, increased P, Ca, and Mg availability, and dramatically reduced the debilitating effects of Mn toxicity. In the absence of biochar, soil pH dropped to 4.9 with significant declines in soil nutrient availability and a significant increase in soil Mn solubility (Table 1), which resulted in poor corn growth

Table 1. Sewage sludge biochar effects on soil pH and extractable nutrients in an infertile Oxisol after the third cropping cycle .

Treatment*	pH	P	K	Ca	Mg	Mn
		mg kg^{-1}				
Control	4.91b	15.6b	160b	662b	160b	52.1a
Untreated BC	5.79a	58.8a	393a	850a	272a	16.3b
Treated BC	6.01a	52.4a	347a	911a	339a	0.55b

*all treatments are in combination with fertilizer

despite the application of conventional fertilizer. Increased corn growth in the biochar amended soils was significantly correlated with maintenance of pH above 5.5 (Fig 5a) and increased extractable soil P and Mg (Fig. 5b&c). More importantly, the biochar amended soils significantly reduced soil Mn solubility protecting corn plants from the tendancy of these soils to be severely limited by their tendency towards Mn toxicity (Fig. 6). The agricultural potential of the Wahiawa soil is severely limited unless pH is

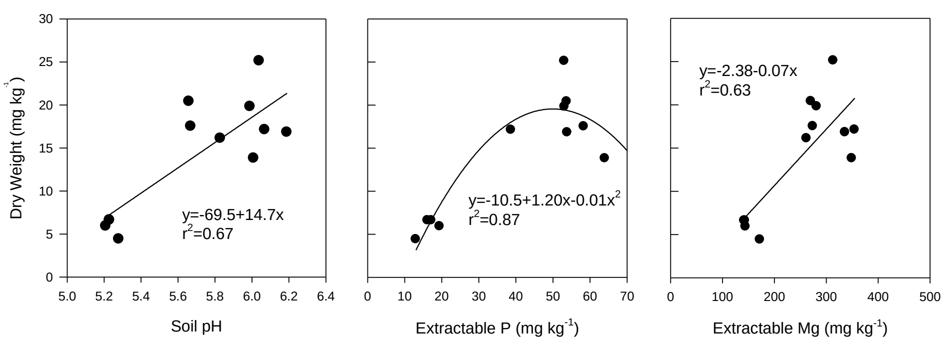


Figure 5. Sewage sludge biochar improvements on soil pH (a), extractable P (b), and extractable Mg (c) in relation to corn dry matter production.

managed to eliminate the negative effects of Mn toxicity. The SS biochar effectively mitigated the negative effects of Mn toxicity by maintaining higher pH in the soil, which reduced Mn in corn tissue below toxic concentrations and promoted corn growth (Fig. 6).

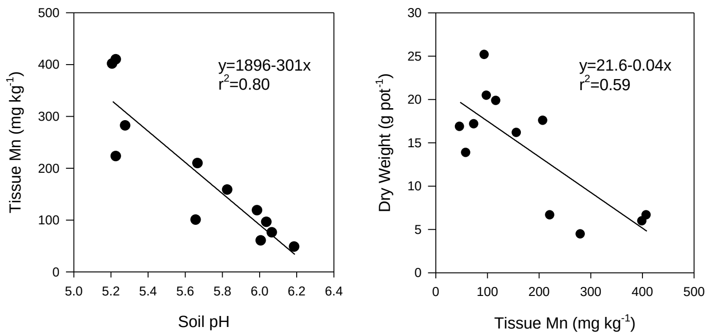


Figure 6. Increases in soil pH with SS biochar application and its effect on decreasing Mn uptake in corn plants (a) and increased corn growth as Mn in tissue is limited (b).

Our success (flash carbonization efforts) in efficiently converting toxic sludge into a more stable non-toxic material combined with the greenhouse work that showed dramatic improvements on plant growth and soil properties demonstrates that the char form of sewage sludge as a soil amendment is potentially ground breaking in terms of solving the current dilemma of sludge disposal facing the State of Hawaii. The persistence of the growth response to the fertilized biochar provides compelling evidence that carbonizing sewage sludge may be a solution to the current dilemma of sludge disposal facing the State of Hawaii, the nation and, indeed, the planet. While growth response to CC biochar was not as dramatic as the effect of SS biochar, the persistence of the positive effect suggests that *carbonization of agricultural waste products may be desirable* especially when positive growth responses are coupled with the C sequestration potential of these kinds of biochars.

Experiment 3: Biochar amendment of a fertile Mollisol

The first phase of greenhouse trials focused on evaluating the use of biochars to remediate an acid infertile Oxisol. A follow-up experiment was designed to address the following two objectives: 1) to evaluate the effect of three biochar materials on plant growth in a fertile Mollisol, and 2) to determine the effect of removing water soluble components of biochar materials on plant growth. With respect to objective 1, we hypothesized that the biochar effect would be less significant in the fertile soil and for objective 2 we hypothesized that water soluble components of the biochars containing mineral nutrients are responsible for the positive effects of biochar on plant growth.

Procedures

The Mollisol (Waialua series, very fine, mixed superactive, isohyperthermic, pachic, haplustolls) was collected from the CTAHR experiment station located in Waimanalo. The soil is a productive, fertile soil composed primarily of high activity clays with near neutral soil reaction, high cation exchange capacity, high base saturation, and low phosphorus fixation capacity. Three biochars made from three different waste streams were obtained: a sewage sludge from from the Hawaii Kai waste water treatment plant, corn cob waste from the corn seed industry on oahu, and wood trimmings from a commercial wood mill in Canada. The sewage sludge and corn cob were converted to biochar utilizing the flash carbonization process and the wood chip biochar was produced using a screw auger pyrolysis unit Diacarbon in Vancouver Canada.

The experiment consisted of three biochar treatments (untreated biochar, biochars extracted with cold water, and biochars extracted in a hot water bath at 80°C) and two fertilization regimes (+ nitrogen and potassium fertilizer and 0 fertilizer). The cold and hot water extracts for the biochars were collected and frozen for future analysis. Biochars were added to the soil at a 2% (w/w) application rate, N was added at 200 mg N kg^{-1}, and K at 360 mg kg^{-1}. Treatments were compared against two controls, the soil with no amendments and the soil with N and K fertilizers without biochars. All treatments were replicated three time s for a total of 60 experimental units.

Results from scanning electron microscopy show clear differences in the physical structure of the three biochar materials. The corn cob biochar (a) showed the largest pore sizes, but exhibited considerable fragmentation. The wood chip biochar (b) showed intermediate pore size and the sewage sludge biochar displayed the smallest pore size. Extracting the biochars

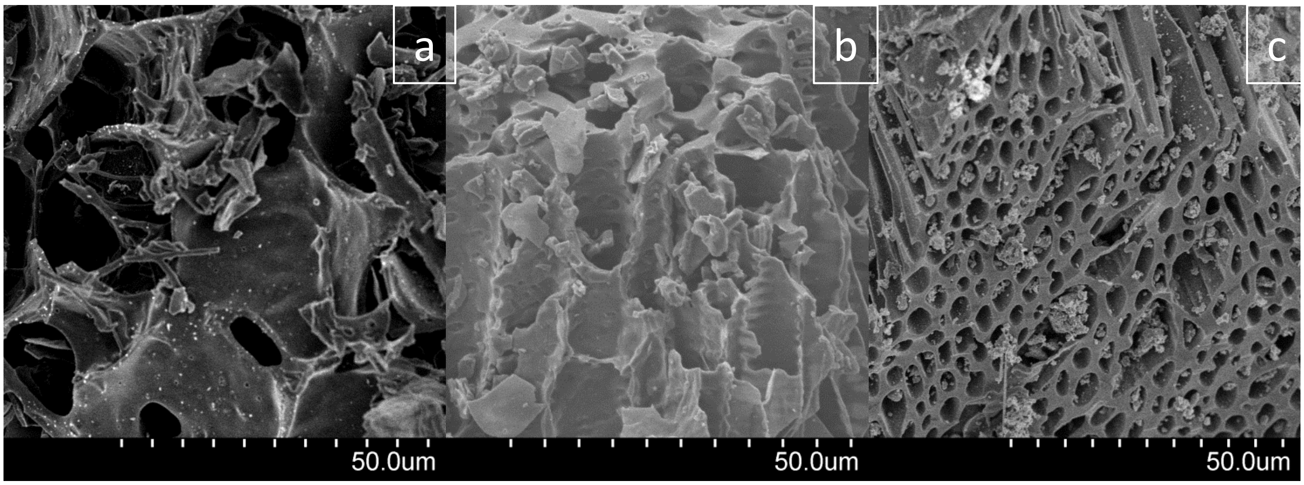


Figure 7. Scanning electron images of the corn cob (a), wood chip (b), and sewage sludge (c) biochars.

in cold and hot water had small, but measurable effects on the relative distribution of volatile matter, ash and fixed carbon of the three biochar materials (Table 2). Extractions in both cold

Table 2. Extraction effect on biochar volatile matter, ash, and fixed carbon content.

Determination	Untreated			Cold H_2O			Hot H_2O		
	CC	WC	SS	CC	WC	SS	CC	WC	SS
Volatile Matter	12.0	5.47	4.47	13.2	6.65	5.74	12.9	7.25	7.95
Ash	7.16	1.84	70.6	3.98	1.19	67.8	4.41	2.11	66.1
Fixed Carbon	80.8	92.7	24.9	82.9	92.2	26.4	82.7	90.6	25.9

CC = corn cob, WC = wood chip, SS = sewage sludge biochars; all values in %

and hot water decreased ash content and increased volatile matter content for the corn cob and sewage sludge biochars. The largest changes occurred in the corn cob biochar where extracting with cold water and hot water decreased ash content by 45% and 38% respectively. We expected the hot water extraction to remove more ash than the cold water extraction, but this was only supported for the sewage sludge biochar, but the difference was very small. For the wood chip biochar, the cold water extraction removed ash compared to the untreated biochar, but the hot water extraction resulted in an unexplained increase in ash and volatile matter content compared to the untreated biochar.

Untreated biochar amendments to the fertile Mollisol had no effect on corn growth with or without fertilizer additions compared with the controls (Fig. 2). These results agreed with the hypothesis that a fertile soil does not benefit from biochar amendments in the same way that an infertile soil does. Additions of fertilizer produced significant improvements in growth, but there was no added benefit of applying biochar in combination with fertilizer. Figure 2b suggests that the wood chip biochar performs less well than the sewage sludge and corn cob biochars with an overall negative effect on corn growth. Treating the biochars with either a hot or cold water extraction did not have a significant effect on corn growth (Fig. 2), except with the hot water extracted sewage sludge biochar combined with fertilizer, which produced a small, but significant improvement on corn growth compared with the fertilized control (Fig. 2c).

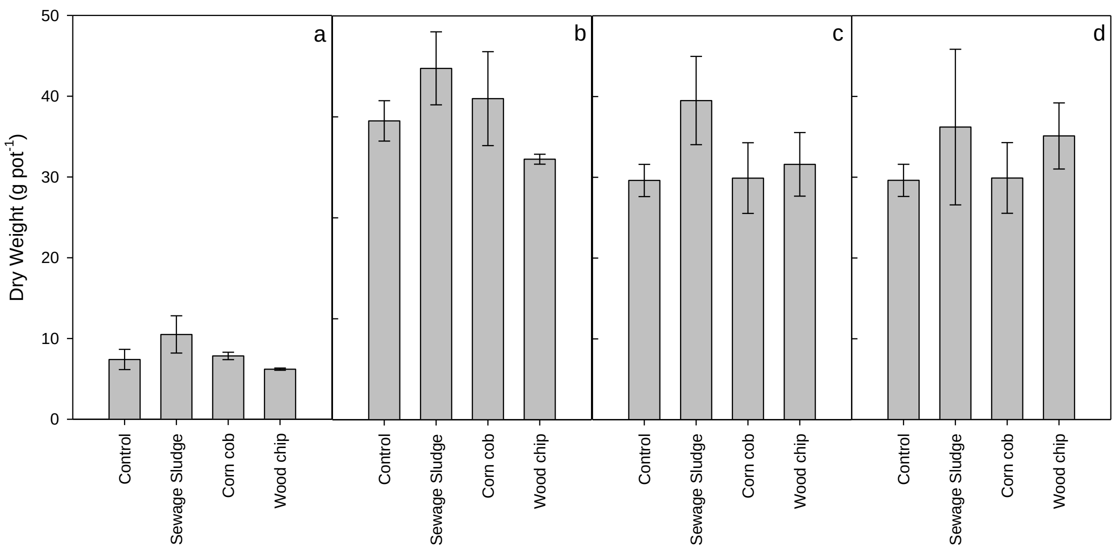


Figure 8. Corn above ground biomass response to untreated biochar without fertilizer (a), with fertilizer (b) and hot water (c) and cold water (d) extracted biochars combined with fertilizer.

Extracting the biochars with cold water had no effect on corn growth compared with the controls. The small positive effect of hot water extraction on the sewage sludge biochar did not persist into the second planting cycle. Results from the second planting cycle showed no effect of any of the biochars on corn growth.

Water Retention Properties of Biochars

A laboratory study was conducted to characterize the water retention properties of eight different biochars produced from different feedstocks under varying pyrolysis conditions. The experiment was designed to test the following two hypotheses: 1) biochar volatile matter can be used as a predictor of water retention capacity, 2) biochar effects on soil water retention are more significant in a coarsely textured soil than a finely textured soil. In relation to hypothesis 1, we know that materials with high surface area have high water retention capacities. We also know that biochar materials created at increasing temperatures exhibit increasing surface areas and volatile matter is related to the temperature at which the biochar was created. Given these relationships we would predict that biochars with low volatile matter content would exhibit high surface area and high water retention potential whereas high volatile matter biochars would have lower surface areas and lower water retention potential. The benefit of confirming such a hypothesis would be that volatile matter determinations are routine laboratory procedures that are low cost, relatively simple procedures that can be performed rapidly.

Procedure

The experiment included a range of eight biochars produced from different feedstock utilizing different pyrolysis conditions. The sewage sludge biochar and the biochars made from corncobs were produced using the Flash Carbonization process developed at the Hawaii Natural Energy Institute at the University of Hawaii (Antal et al., 2003). The Kiawe biochar was made from Kiawe (*Prosopispallida*) wood and produced on the island of Maui in a traditional kiln. The eucalyptus biochar was made in a traditional kiln according procedures used by Thai farmers. The gasification biochar was made from *Leucaena* *leucocephala* wood via a gasification procedure (Turn et al., 1998) at temperatures of 850°C. Two biochars were made from wood scraps from the lumber industry. The first (wood1) was made in a screw-auger continuous flow slow pyrolysis reactor by Diacarbon Energy Inc. a commercial pyrolysis company in Canada, and the second (wood2) was made using a traditional pit method by Hawaii Biochar Products, LLC in Hilo, Hawaii. Biochars were ground to pass a 2 mm sieve and proximate analysis was performed to determine volatile matter, as content, and fixed carbon according to the methods outlined in ASTM D1762-84 (1990a) and ASTM E1756-95 (1990b). All biochar materials were analyzed for surface area using BET (N_2 gas adsorption) by Micrometrics Analytical Services (Nocross, GA). Assuming that 99% of the biochar materials are comprised of micropores that restrict N2 gas entry during analysis, data from Micrometrics Analytical Services were corrected accordingly (De Jonge and Mittelmeijer-Hazeleger, 1996). Scanning electron microscope (SEM) Hitachi S-4800 was used to analyze biochar porous structure. Biochar effects on water holding capacity was determined using the pressure desorption method utilizing pressurized chambers, ceramic extractor plates, and retainer rings to hold the biochars and soil/biochar mixtures. Water characteristic curves with fixed pressures at -10, -33, -100, -400, and -1500 kPa were run for each biochar and for biochar soil mixtures at three rates (0, 2, and 4%). Water retention results for all treatments were expressed as volumetric water content (θ_v), which was calculated as gravimetric water multiplied by bulk density. Differences in water retention potential for the eight biochars were tested by ANOVA and mean separation was achieved using Tukey's HSD post-hoc test with Minitab 16 software. Significant biochar and soil effects and their interactions were tested by two-way ANOVA and Tukey's HSD pot-hoc test was used to compare specific treatments.

Results

Volatile matter content for the eight biochar materials ranged from a low of 2.22% for the gasification biochar created at very high temperature (>900°C) to a high of 35.8% for the eucalytptus biochar created in a traditional kiln at an unknown temperature (Table 4). Images from scanning electron microscopy provided some evidence for differences in porosity and pore size distribution. The plant feedstock biochars all showed similar pore structure (Fig. 8) with the exception of the kiawe biochar, which showed a distinct absence of pores (Fig 8e). The pore distribution of all the plant-based biochars (except the kiawe biochar) suggest high surface area and a high potential to absorb and retain water. The sewage sludge biochar exhibited a lack of distinct pores, but the rough surface and presence of deep cavities also indicate potential for high

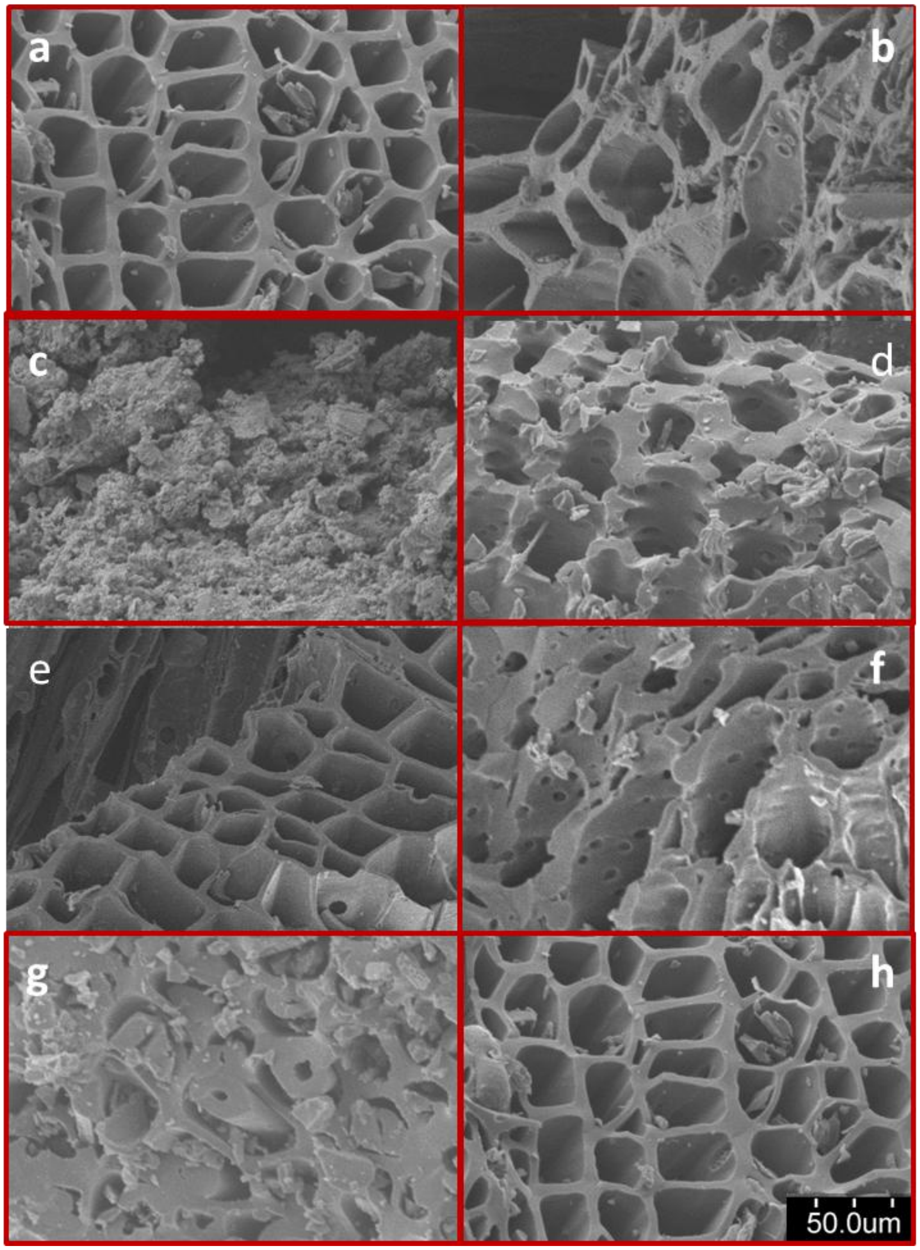


Figure 8. Scanning electron micrographs of the eight biochars arranged in order of increasing volatile matter all captured at 1000X magnification: gasification (a), wood2 (b), sewage sludge (c), low VM corn cob (d), wood1 (e), medium VM corn cob (f), kiawe (g), and eucalyptus (h).

surface area (Fig. 8c). Regressing VM content on surface area indicated a non-linear inverse relationship (Fig. 9), but biochars with VM contents between 5 and 10% showed widely varying surface area bringing into question the robustness of the relationship.

Table 4. Results of proximate analysis and surface area for the eight biochars.

Biochar	Volatile Matter % dry weight	Ash	Fixed Carbon	Surface Area $m^2\ g^{-1}$
Gasification	2.22	18.1	79.7	360
Wood2	5.47	1.84	92.7	133
Sewage Sludge	7.10	59.8	33.2	551
Low VM Corn Cob	7.68	5.19	87.1	21.6
Wood1	10.9	31.2	57.9	56.4
Medium Corn Cob	21.8	4.39	73.8	49.1
Kiawe	23.9	1.17	75.0	36.5
Eucalyptus	35.8	2.35	61.9	148

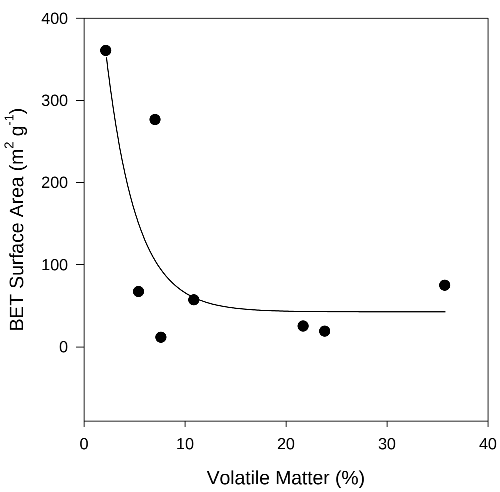


Figure 9. The relationship between VM content and surface area for 8 biochar materials.

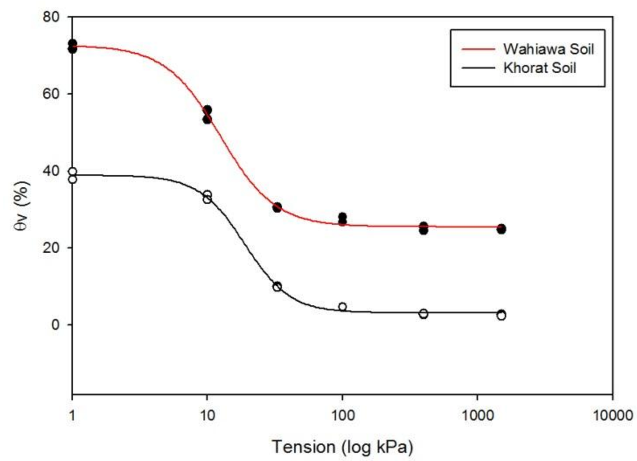
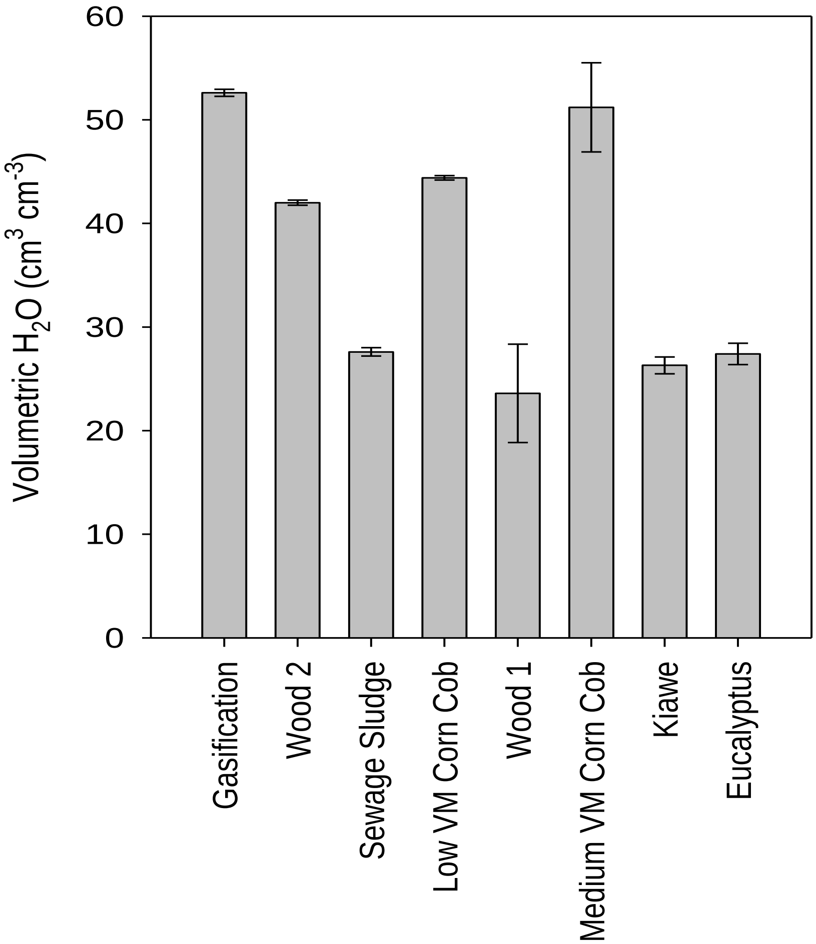


Figure 10. Water release curves for the clay (Wahiawa) and sandy (Khorat) soils.

The clay-rich soil showed significantly higher water retention properties than the sandy soil (Fig. 10). Higher water retention in the clay soil is explained by differences in surface area for the two soils. The clay soil had surface of 46.9 $m^2\ g^{-1}$, which was more than 40 times higher than the sandy soil at 1.22 $m^2\ g^{-1}$. Water holding capacities measured at -33 kPa of the biochars ranged from a high of 52.6 $m^3\ m^{-3}$ for the gasification biochar to a low of 23.6 $m^3\ m^{-3}$ for the kiawe biochar (Fig. 11). Our method of measuring water holding capacity allowed for the quantification of biochar bulk density, which is typically inversely correlated with porosity. Biochar bulk density ranged from 0.129 to 0.829 with the gasification biochar with the lowest bulk density showing the highest water holding capacity, but sewage sludge with the highest bulk density did not show the lowest water holding capacity. Neither VM content nor surface area were significantly correlated with water holding capacity. These results suggest that routine laboratory measurements do not capture the complexities of biochar water retention properties.

Figure 11. Water holding capacities of the eight biochar materials measured at -33 kPa.



Overall, biochar amendments significantly increased water holding capacity of both soils at both rates (Fig. 7). The hypothesis that biochar effects on water holding capacity would be higher in the sandy soil compared to the clayey soil was not supported. When the biochar data were pooled by soil, mean increase in water holding capacity in the sandy soil was 17.2% and 19.4% for the clayey soil compared with the control. Within soils, however, there were significant differences in water holding capacity depending on biochar type. In the sandy soil, the gasification and eucalyptus biochars applied at 2% showed the largest increases in water holding capacity, 32 and 28% respectively, whereas the sewage sludge biochar did not have a significant effect on water retention compared with the control (Fig. 7a). In the clayey soil, surprisingly, the sewage sludge biochar produced the largest effect on water retention with an increase of 27% while the gasification biochar showed a 23 % increase in water retention (Fig. 7b). It is unclear at this point why the sewage sludge biochar showed opposite behavior in the two soils. Using the morphological features provided by the SEM images, it appears that the biochars with a more distinct pore structure (gasification, eucalyptus, and wood1) had the most pronounced effect on increasing water retention in the sandy soil, but in the clayey soil the biochars with a less distinct pore structure (sewage sludge and kiawe) were more effective at increasing water retention. This observation suggests that the mechanism controlling water retention is different in the two soils.

Doubling the biochar from 2% to 4% was more effective at increasing water retention in the sandy soil with wood 2 (12.6%), wood 1(12.2%), and sewage sludge (11.3%) biochars showing the largest increases, medium VM corn cob (9.2%), eucalyptus (9.0%), and kiawe (8.3%) showing intermediate increases, and the gasification (4.3%) and low VM corn cob biochars (2.1%) showing the least improvements. Nonetheless, in the sandy soil doubling the rate had positive effects on water retention, but the question remains whether these increases justify the high rates of biochar application (approximately 80 tonnes per ha at 4%). Doubling the biochar application rate in the clayey soil was less effective in producing positive effects on water retention. Overall, biochars increased water retention by an average 3.1% compared with a mean increase of 8.6% in the sandy soil. The most notable difference was that doubling application rate for the kiawe and wood 1 biochars reduced water retention by 4.1% and 4.7%, respectively in the clayey soil. On the other hand, doubling the rate increased water retention in the sewage sludge by 9.9%, by 8.7% in the medium VM corn cob and gasification biochars.

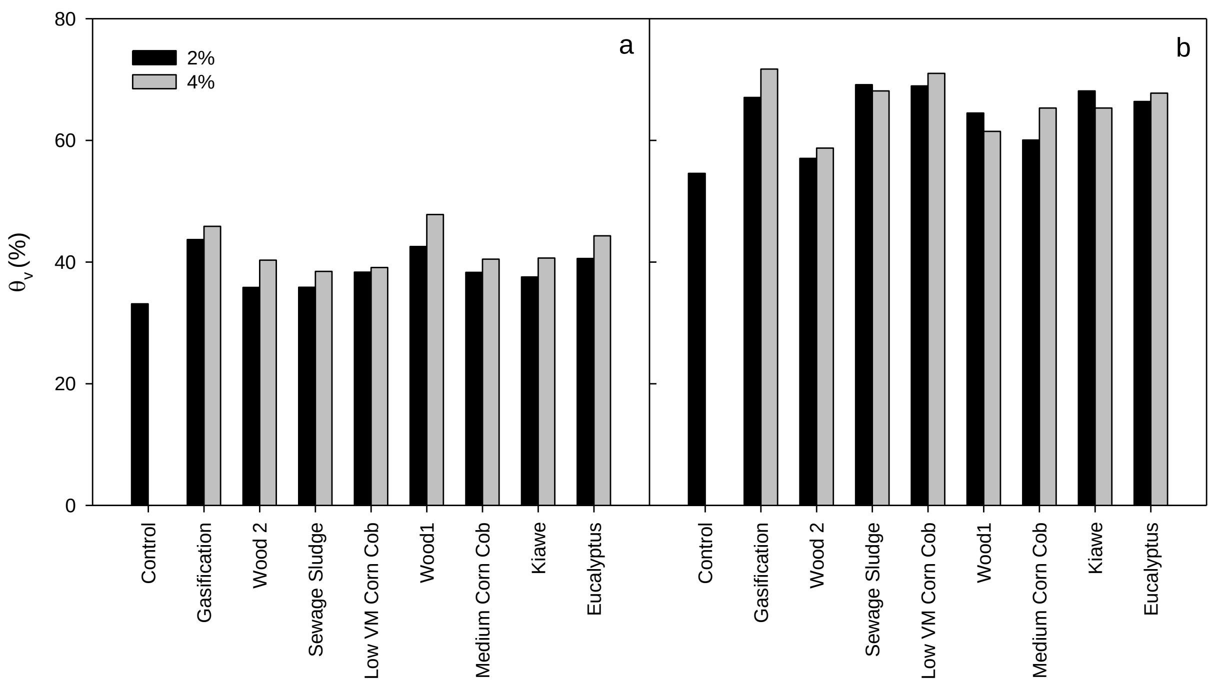


Figure 12. Biochar effects on soil water holding capacity in a sandy Ultisol (a) and a clayey Oxisol (b).

Biochar application to both soils showed a significant increase in plant available water (PAW), but the magnitude of increase was different in the two soils, and the biochars behaved differently depending on which soil they were added to (Fig. 13). Biochar showed the greatest improvement in PAW in the clay soil; mean increase in PAW in the biochar treatments where PAW was significantly different than the control soil was 46.2% in the clay soil compared with 20.6% improvement in the sandy soil. In the control clay and sandy soil, PAW expressed as depth was 4.46 and 4.59 cm, respectively; amended with gasification biochar PAW increased by 1.3 cm in the sandy soil and in the clay soil amended with the SS biochar the increase was 2.5 cm. Translated into volume, the biochar an increase of 130,000 and 250,000 L of PAW per ha in the sandy and clay soils, respectively. Such improvements in water holding capacity acquire added significance as water requirements for food production rise in an increasingly uncertain environment.

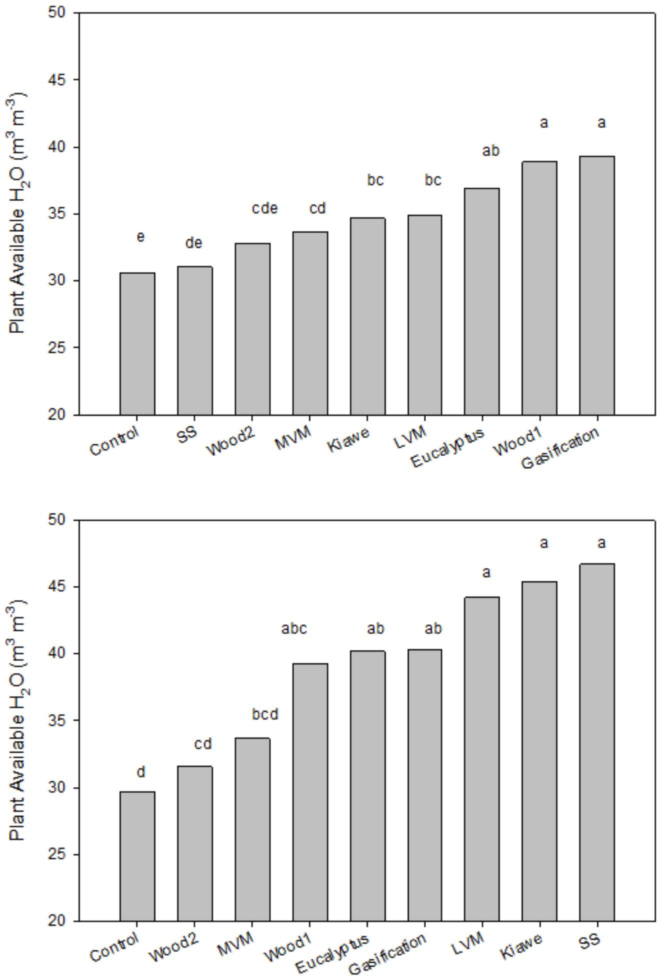
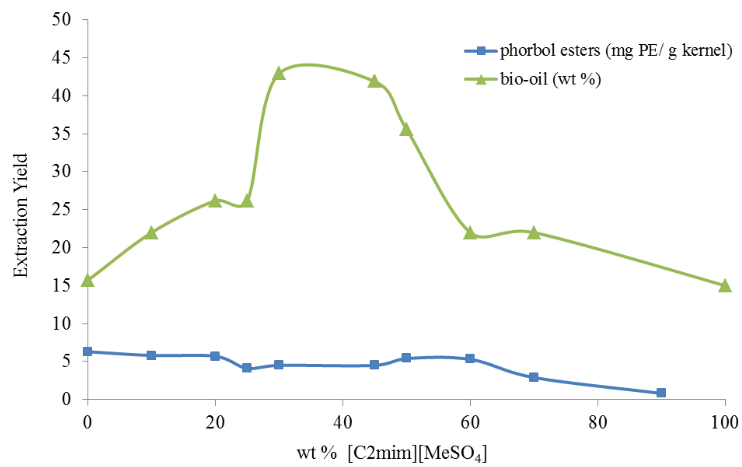
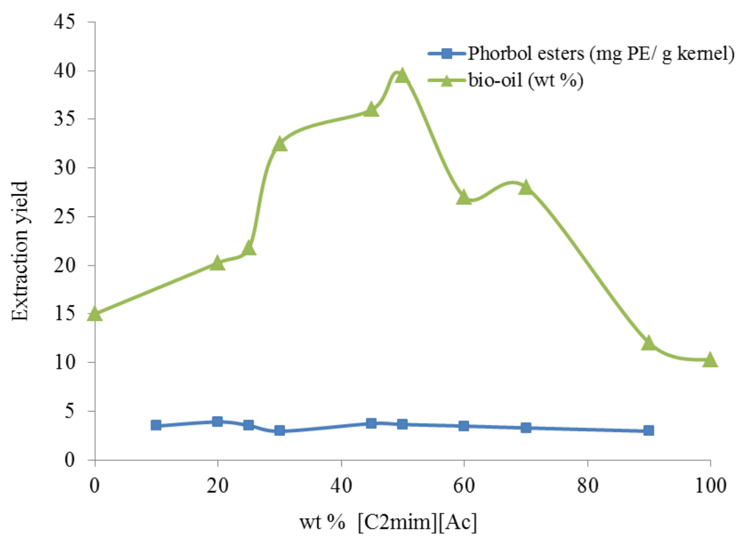


Figure 13. Gains in PAW due to biochar amendments to Sandy (top) and clay (bottom) soils.

Task 9: *Characterize the capacity of amphiphilic extraction solvents to detoxify delipified Jatropha meal, thus providing an additional value stream as an animal or fish feed*

This work evaluated and expanded the applicability of ionic liquid-polar co-solvent systems to extract phorbol esters from bio-oil containing biomass. Both EMIM[$MeSO_4$]-MeOH and EMIM[Ac]-MeOH co-solvent systems were found to effectively extract both bio-oil and phorbol ester in a extraction single step. The extracted phorbol esters remained soluble in the co-solvent due to a shared amphiphilic nature with the ionic liquid and hydrogen bonding. The extracted bio-oil separated to its own immiscible phase and the protein remained with the biomass. The high protein low phorbol ester content of the extracted biomass suggests that the co-solvent treated kernel biomass has improved potential as an animal feed. These results have been published in the Journal of Separation Science and Technology.





We also, in collaboration with a mainland company (SuGanit) that has contracted Dr. Cooney to evaluate the potential of the co-solvent system above to both extract bio-oils from safflower biomass, but also to "pretreat" the biomass such that efficient enzymatic hydrolysis of the de-lipified biomass can be executed to produce simple sugars. Safflower seeds are high in both bio-oil and carbohydrates. Although pretreatment with either the co-solvent or pure ionic liquid yielded comparable hydrolysis kinetics and fermentable sugar yields on *safflower* whole seeds, the addition of alcohol to the ionic liquid was necessary to optimally recover both bio-oil and fermentable sugars. The ionic liquid [C2mim][Ac] was far more effective than [C2mim][$MeSO_4$] with optimum processing conditions occurring at a co-solvent concentration of 70-30 wt% of [C2mim][Ac] to methanol and a processing temperature of 120^oC. Under these conditions the majority of the bio-oil was extracted and 25.4 wt% (*safflower*) and 14.3 wt% (*jatropha*) of the whole seed biomass was recovered as fermentable sugars. The recovery of fermentable sugars from the carbohydrate fraction was as high as 74 % and 78 % for *jatropha* and *safflower* seeds, respectively, when using [C2mim][Ac] co-solvent. A preliminary theoretical analysis of two potential oil seed processing pathways using the co-solvent system suggested that the co-recovery of bio-oil, fermentable sugars and a protein rich meal can recover a majority of the energy contained in the original biomass – a result that improves upon the traditional approach of solely extracting bio-oil. *Our results have been published in the International Journal of Chemical Engineering* a provisional patent on the subject has been submitted to the US Trade and Patent Office.

Task 10: *Develop one capstone course in Engineering that addresses the WESS concept*

WESS funds have been used to retype past mathematical lectures on *Thermodynamics with Applications*, and *Chemical Kinetics with Applications*. The advanced graduate course on chemical thermodynamics with applications to fuel cells, (2012S) will be taught next term by Dr. Antal. The course is being offered through the mechanical engineering department.

A new course, CEE 491 Sustainability Systems Analysis will be taught annually starting in Fall of 2013. The course will serve two purposes. First, it will satisfy a need in the CEE department to augment its undergraduate program with courses that address sustainability. As part of their accreditation process CEE graduates must take at least one course that addresses sustainability. To date the Department has offered two courses which have expressed sustainability views that align with classic Civil Engineering (i.e. sustainable transportation systems, re-use of concrete). This course will add a sustainability course (and thus choice to the environmentally minded Civil Engineers) that addresses environmental engineering, particularly with respect to water and its recycling. The course will use the WESS concept as the working model.

Course Description: This course will introduce students to the concept of sustainability analysis from a systems cycle perspective. Emphasis will placed upon the interplay that occurs between the conceptualization of a sustainability cycle based in sound science principles that speak to the thermodynamic and resource potential of the process cycle and the realization of a commercial process that satisfies sound engineering and market feasibility analysis. A number of case studies that address the nexus between water, energy, and soil sustainability will be introduced and analyzed from a systems perspective using appropriate scientific, engineering, and regulatory metrics.

Task 11: *Support Global Environmental Science Undergraduates conducting WESS research*

Six GES students, Jeremy Bascunana, Emile Meder, Ryan Lopez, Erika Mizokuchi, Ken Lewis, and Bryan Chinaka, have worked on WESS related projects. Ryan Lopez, Jeremy Bascunana, and Bryan Chinaka have completed senior theses based on their research and have graduated. Jeremy Bascunana examined the effects of various biochars on water retention in two soils. He graduated in December 2012 and is applying to graduate programs in Sustainable Development. Ryan Lopez completed his GES senior thesis on anaerobic digestion in December 2011 and is now attending graduate school at the University of New Mexico. Emile Meder worked on biochar production in the first year of WESS funding. The WESS program Fellowships were readvertised to GES students last summer and three additional students were funded. Erika Mizokuchi is working with Dr. Susan Crow on the effects of biochar amendments on soil cation exchange capacity and fertility. She will graduate in Summer, 2013.

Ken Lewis is working with Dr. Michael Cooney on a senior thesis investigating high rate anaerobic digestion of grease trap waste. Bryan Chinaka worked with Dr. Steven Matsutani investigating the use of gas hydrates in water purification and desalination and graduated in May 2013.

Task 12: *Submit one REU proposal targeting the WESS concept, for future GES students*

In collaboration with Sea Grant, a concept proposal has been submitted to the Castle Foundation to support the transfer of STEM students from Kapiolani Community College to the University of Hawaii at Manoa. The transfer students would transfer directly into GES or the Geology and Geophysics undergraduate program (note: an agreement has actually been worked out between the Department of Geology and Geophysics and KCC wherein STEM KCC students graduating from KCC with and Associates Degree in Natural Sciences (who followed a concentration in physical science) and a GPA minimum of 2.0 will be accepted into the G&G program with junior status). The concept proposal would seek to fund the tuition of up to 6 students as well as allotting a 500 dollar education stipend per semester.

Task 13: *Create business-friendly master agreements that can be used as templates between the UH and any potential host test site that would be recruited into the WESS program*

We have executed a model Omnibus Agreement between the University of Hawaii and Pacific Biodiesel.

Future plans

Task 14: *Develop comprehensive business plans, fundraising portfolios, and economic analyses that enable the UH administration to solicit funds to create a WESS research industry in Hawaii*.

WESS hired an independent consultant to help ghost write a model Master Plan to implement the WESS concept at the Waialee Livestock Station. The Master Plan modeled three with stakeholders in industry (PBI, Naked Cow, RGP), the University Admin (CTHAR, VCRGE), and key community (Dean of the Hawai'inuiakea School of Hawaiian Knowledge) and environmental groups (North Shore). This plan, if completed and agreed to by all key stakeholders, will become a template for discussion as to how an integrated Tech Park could be operated.

The PACE program funded 4 graduate students (2 business, 1 Law, and one postdoc) during the Summer of 2011 to develop an business plan that evaluates the production, harvesting, and processing of jatropha oil seeds. This project has looked at integrating a growth plantation adjacent to an oil-seed processing plant, and evaluated the business viability over a 30 year operating period, using reasonably optimistic productivities. The group has also evaluated two processing streams: one that considers only mechanical extraction of the bio-oil with no secondary use of the toxic seed-cake, and a second that looks at solvent extraction applied to the toxic-seed cake so as to produce a viable animal feed.

Future Plans

Task 15: *Establish a permanent and neutral administrative group within HNEI, that can manage interdisciplinary research projects and proposals between UH faculty, industry, government, the private sector, and all combinations thereof*

APPENDICES

Hazen Research, Inc.
4601 Indiana Street
Golden, CO 80403 USA
Tel: (303) 279-4501
Fax: (303) 278-1528

Date: May 17, 2012
PROJ. # 009-444
CTRL # E3/12
REC'D 05/01/12

Hawaii Natural Energy Institute
Dr. Michael Antal
1680 East-West Rd. POST 109
Honolulu, Hawaii 96822

Sample Number: E3/12	-1	-2	-3	-4	-5
Sample Identification:	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Moisure, %	3.00	17.22	3.19	9.16	3.49
Arsenic (As Received), mg/kg	15.8	5.62	14.9	0.16	0.54
Arsenic (Dry Basis), mg/kg	16.3	6.79	15.4	0.18	0.56
Mercury (As Received), mg/kg	0.02	0.44	0.10	<0.01	0.57
Mercury (Dry Basis), mg/kg	0.02	0.53	0.10	<0.01	0.59
Selenium (As Received), mg/kg	15.0	7.10	15.3	<0.05	0.86
Selenium (Dry Basis), mg/kg	15.5	8.58	15.8	<0.05	0.89

Gerard H. Cunningham
Fuel Laboratory Manager

Hazen Research, Inc.
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Date	May 25 2012
HRI Project	009-444
HRI Series No.	E3/12-1
Date Rec'd.	05/01/12
Cust. P.O.#	

Hawaii Natural Energy Institute
Michael J. Antal
1680 East-WestRd, Post 112C
Honolulu, Hawaii 96822

Sample Identification
Sample 1 Top/Middle
Sludge Charcoal
-

Reporting Basis >	As Rec'd	Dry	Air Dry
Proximate (%)			
Moisture	3.00	0.00	3.00
Ash	71.23	73.43	71.23
Volatile			
Fixed C			
Total			
Sulfur	4.290	4.423	4.290
Btu/lb (HHV)			
Btu/lb (LHV)			
MMF Btu/lb			
MAF Btu/lb			
Ultimate (%)			
Moisture	3.00	0.00	3.00
Carbon	24.54	25.30	24.54
Hydrogen	0.11	0.12	0.11
Nitrogen	2.04	2.10	2.04
Sulfur	4.29	4.42	4.29
Ash	71.23	73.43	71.23
Oxygen*	<0.01	<0.01	<0.01
Chlorine**			
Air Dry Loss (%)			
Forms of Sulfur,as S,(%)			
Sulfate			
Pyritic			
Organic			
Total	4.29	4.42	
Water Soluble Alkalies (%)			
Na2O			
K2O			

Lb. Alkali Oxide/MM Btu=
Lb. Ash/MM Btu=
Lb. SO2/MM Btu=
Lb. Cl/MM Btu=
As Rec'd. Sp.Gr.=
Free Swelling Index=
F-Factor(dry),DSCF/MM Btu=

Report Prepared By:

Gerard H. Cunningham
Fuels Laboratory Supervisor

* Oxygen by Difference.
** Not usually reported as part of the ultimate analysis.

An Employee-Owned Company

Extraction of char samples

Char samples:
Hawaii kai SS untreated 4
Hawaii kai SS treated

Solvents:
Acetone
Hexane
Water

Extraction:
3g of treated or 5 g of untreated char sample was extracted in a Soxhlet apparatus during 6 hours, using 120ml or 150ml of solvents.
Blank extraction sample was prepared in case of each solvent by extraction of a clean thimble. The calculated mass loss of char and blank samples are summarized in table 1.

		Before extraction		After extraction	
		Cellulose thimble (g)	Sample (g)	Sample + Cellulose thimble (g)	Extracted mass (%)
Hawaii kai SS untreated 4	Water (150 ml)	2.1505	5.0055	6.6083	7.65
	Acetone (150 ml)	2.1880	5.0074	7.0825	1.57
	Hexane (150 ml)	2.3551	5.0021	7.2526	1.42
Hawaii kai SS treated	Water (120 ml)	2.0642	3.0039	4.9303	2.72
	Acetone (120 ml)	2.0171	2.9998	4.9619	1.10
	Hexane (120 ml)	2.0257	3.0092	4.9684	1.32
Blank	Water (120 ml)	2.4312	0	2.3870	1.82
	Acetone (120 ml)	2.3017	0	2.2742	1.19
	Hexane (120 ml)	2.1961	0	2.1754	0.95

Table 1. Calculated extraction mass loss of char samples and blank experiments

Analysis of acetone and hexane extract
About 60ml of extract was evaporated to 3ml by rotary evaporator at the solvent boiling point under atmospheric pressure. The concentrated solutions were directly analysed by GC/MS.

Analysis of water extract
As water as a solvent is not suitable for GC analysis, we had to change the solvent for analysis. Furthermore, the methylation of carboxylic acids was done for easier GC analysis.

The water solvent was totally evaporated by rotary evaporator at 35°C heating bath temperature under vacuum. Before the evaporation few drops of concentrated NaOH solution was added to the water extract to prevent the evaporation of organic acids.
($R\text{-}COOH + OH^- = R\text{-}COO^- + H_2O$)
15ml methanol and 3ml of 10% HCl containing methanol were added to the yellowish waxy/soapy residue [K.Ichihara, Y.Fukubayashi, Preparation of fatty acid methyl esters for gas-liquid chromatography, Journal of Lipid Research Volume 51, 2010, 635-640]. It was wortexed and incubated at 40°C for 16 hours. Unfortunately the solid residue did not dissolved completely. After cooling to room temperature, 5 ml of hexane and 5 ml of water were added for extraction of methylesters. The tube was vortexed, and then the hexane layer was analyzed by GC/MS directly.

GC/MS experiments
Analysis of the extracted samples was performed with a GC/MS (Agilent Techn. Inc. 6890 GC / 5973 MSD) using Agilent, DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 m film thickness). 1ul sample was injected to a column in splitless injection mode. The GC injector was kept at 300°C. The GC oven was programmed to hold at 40°C for 1 min and then increase to 280°C at a rate of 10°C min^{-1}. The mass spectrometer operated at 70 eV in the EI mode. The mass range of 25-800 Da was scanned.

ICP-AES experiments
ICP-AES analysis of water extracts were performed on a Spectro Genesis ICP-OES (simultaneous spectrometer), with axial plasma viewing and optical-plasma-interface (OPI) in a wavelenght range 175-775nm, 15 linear CCD detector system. The resolution were 0,029 nm, the generator frequency 27,12 MHz and a plasma power 750–1700W (changeable).
The water extract of the char samples and blank experiment was analysed directly by ICP-AES.

Results of GC/MS experiments

Fig. 1-3 shows the GC/MS total ion chromatograms of the extracts. The peaks originating the contamination of solvents, thimble etc. are signed “X” on the chromatograms. (These peaks are exists in the blank samples).

Extracts of untreated char
The GC/MS chromatogram of the acetone and hexane extract of the untreated sample are very similar (Fig. 1). The main component of these samples are the hydrocarbon isomers. Due to the large number of the isomers they are appearing as two “hump” on the baseline of the chromatogram (unresolved peaks). Beside the hydrocarbons, acetamide and few sterane compound also appear in both extract.
In the chromatogram of the water extract of untreated char, linear chained saturated (hexadecanoic acid methyl esther) and unsaturated methylesthers (octadecenoic and nonadecenoic acid methyl esters) appear. These are the methyl esthers of fatty acids originates from char.