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Florida Energy Systems Consortium

University of Florida

An Integrated Sustainable Transportation System

PIs: David Norton, Keith Duncan **Co-PI:** Shirley Meng

Description: The proposed vehicle, operating on biofuel while in transit and charged by the sun while parked, is the ultimate sustainable transportation system operating completely on renewable American energy resources. Moreover, the use of solid oxide fuel cells (SOFCs) rather than an IC engine in this hybrid vehicle results in a dramatic improvement in efficiency and reduction in emissions. SOFCs are the most efficient technology for converting energy from hydrocarbon fuels to electricity on a "well to wheels" basis. In contrast, the more conventional fuel cells require hydrocarbon fuels to first be converted to H_2, with resultant efficiency losses, followed by losses due to H_2 transport and storage. Therefore, on a system-basis SOFCs hold the potential for producing the least CO_2/kWh from conventional fuels, and if designed to operate on biofuel would in effect be carbon neutral and operating on a renewable resource. *If developed this vehicle would be a transformational change in transportation technology.*

Budget: $594,000
Universities: UF
External Collaborators: Solid-State Energy Technology, Inc., Lynntech, Inc., Planar Energy Devices, Inc., CFX Battery, Inc.

Executive Summary

The proposed vehicle, operating on biofuel while in transit and charged by the sun while parked, is the ultimate sustainable transportation system operating completely on renewable American energy resources. Moreover, the use of solid oxide fuel cells (SOFCs) rather than an IC engine in this hybrid vehicle results in a dramatic improvement in efficiency and reduction in emissions. SOFCs are the most efficient technology for converting energy from hydrocarbon fuels to electricity on a "well to wheels" basis. In contrast, the more conventional fuel cells require hydrocarbon fuels to first be converted to H_2, with resultant efficiency losses, followed by losses due to H_2 transport and storage. Therefore, on a system-basis SOFCs hold the potential for producing the least CO_2/kWh from conventional fuels, and if designed to operate on biofuel would in effect be carbon neutral and operating on a renewable resource. *If developed this vehicle would be a transformational change in transportation technology.*

In this project, we made significant gains in the science of energy conversion, from fundamental studies of the atomistic underpinning for materials properties to the engineering of the highest performance solid oxide fuel cells in the literature. Fundamental studies of the two most promising materials for solid electrolytes, using computational modeling, enabled us to determine the optimal potentials to use (the Gotte potential) in predicting materials properties for oxides of interest in this field. Moreover, from a molecular dynamics study of bismuth oxide we were able to confirm that dopant polarizability was the key feature in determining oxygen vacancy mobility in the fluorite system. Undergirded by these results we are now positioned to use our computational tools to further optimize the material properties of known oxygen ion conductors as well as develop new ones with superior performance.

We have also expanded the application of our previously developed continuum-level electrochemical model to describe and predict the performance of SOFCs as a function of electrolyte thickness. We were

able to show that, for maximum power density, mixed conducting electrolytes had an optimal thickness below which they were rapidly overwhelmed by electronic conduction and above which their ohmic losses grew. We also are the first ones to predict the drop in open circuit potential with decreasing thickness for these materials.

Our development of record conductivity materials also continued with the highest conductivity ceria based and bismuth oxide based materials reported. We further studied their stability and optimal temperature window for operation. In so doing we have established our institution as the clear leaders in this area.

We are also leading in the area of anode development as the first to develop SOFCs with anode functional layers, which enabled a quantum step in SOFC performance. By comparison, our work on cathode performance is set to take off. We have already developed one of the highest conductivity cathodes (a bismuth ruthenate-bismuth oxide composite) in the literature. However, our fundamental studies on the oxygen reduction reaction (ORR) have positioned us to break further ground towards making a significant performance jump using conventional cathode materials. We have used multiple techniques to investigate the factors governing the ORR and the results of those studies point to new electrode architectures that should both improve performance and increase stability (especially, with respect to chrome poisoning and secondary phase formation).

Finally, we have also found time to complete our research efforts in hydrogen production, which is critical for the realization of a future hydrogen economy. In addition, we moved forward with our work on sensors, by indentifying the factors affecting the sensing process and developing high selectivity sensors with high signal-to-noise ratios. This has garnered interest from industry, leading to collaborations with General Electric (GE) and Energy Management Solutions (aka EPS) and RedOx Fuel Cells.

This project has been completed.

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Biocatalytic Lignin Modification for Carbon Sequestration

PI: Jon Stewart
Students: Bradford Sullivan (postdoctoral fellow), Filip Boratynski (postdoctoral fellow)

Description: After cellulose, lignin is the second most abundant forma of carbon in plants. Lignin's complex structure makes it difficult to use this material in value-added products, and ahte vast majority of lignin is currently burned to provide energy for factory operations. While burning plant derived lignin does not add to global greenhouse gas levels, having options to remove lignin from the global carbon cycle would lead to diminished atmospheric CO2 levels. This could be accomplished by chemically altering lignin's structure to facilitate long-term terrestrial sequestration or using it in value-added products that would not be discarded immediately. We will use Nature's catalysts (enzymes) to tailor the chemical structure of lignin for both deep-well injection (by using lignin derivatives as drilling "muds") and for materials that can be used in building, packaging, and other manufactured products.)

Budget: $200,000
Universities: UF

Progress Summary

Bradford Sullivan joined this project as a postdoctoral fellow in February 2010 with extensive experience in both organic synthesis and in dioxygenase enzymes. To the best of our knowledge, no one has applied dioxygenases to lignin and/or lignin model compounds. Enzymes such as toluene dioxygenase offer the possibility of converting this renewable feedstock into valuable building blocks. In preliminary studies, Brad has applied toluene dioxygenase to model compounds derivable from lignin to create small molecule mediators required by laccases for lignin breakdown. Some reaction was observed. We are also setting up a collaboration between our lab and those of Steven Sherman and Charles Turick (Savannah River National Laboratory), who have developed a simple method for lignin extraction from a variety of soft materials such as switchgrass as well as woody tissues. This will provide us with the material for exploring ionic liquids and deep eutectic solvents for laccase-catalyzed lignin conversions. Filip Boratynski joined the project in September 2011 with a background in biocatalysis. He will be focusing on experiments using the lignin samples provided by our collaborators at Savannah River.

Funds leveraged/new partnerships created:

New collaborations		
Steven Sherman, Charles Turick (Savannah River National Laboratory)	Steve and Chuck have agreed to supply us with lignin samples prepared in their lab using a newly-developed extraction method. This product stream will be employed for enzyme-catalyzed reactions in our lab using safe, non-volatile solvents (ionic liquids and deep eutectic solvents)	No external funding yet for this work

Proposals						
Title	Agency	Reference Number	PI, Co-investigators and collaborators	Funding requested	Project time frame (1 year, 2 years, etc.)	Date submitted
Adapting Kernel Metabolism to Enhance Cereal Yield Under Adverse Conditions	USDA	2011-67003-30215	L. Curtis Hannah (P.I.), Tracy Hennen-Bierwagen (co-P.I.), Karen Koch (co-P.I.), Don McCarty (co-P.I.), Alan Meyers (co-P.I.), Mark Settles (co-P.I.), Jon Stewart (co-P.I.), William Tracy (co-P.I.)	$5M	5 years	June 2010
Improving Alkene Reductases for Applications in Asymmetric Synthesis	NSF	NSF 10-1	Jon Stewart (P.I.)	**497,851**	3 years	December 2010

Grants Awarded					
Title	Agency	Reference Number	PI, Co-investigators and collaborators	Period of Performance	Funding awarded
Adapting Kernel Metabolism to Enhance Cereal Yield Under Adverse Conditions	USDA	2011-67003-30215	L. Curtis Hannah (P.I.), Tracy Hennen-Bierwagen (co-P.I.), Karen Koch (co-P.I.), Don McCarty (co-P.I.), Alan Meyers (co-P.I.), Mark Settles (co-P.I.), Jon Stewart (co-P.I.), William Tracy (co-P.I.)	$5M	5 years
Improving Alkene Reductases for Applications in Asymmetric Synthesis	NSF	CHE-0615776	Jon Stewart (P.I.)	**497,851**	3 years

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Lignin makes up approximately 20% of the carbon fixed by plants [1] and must be separated from the cellulosic fraction in a number of processes including pulping and bioethanol production [2]. Traditional Kraft pulping chemically derivatizes lignin with sulfonic acid moieties, allowing it to be soluble under basic conditions, but also imparting a strong odor that makes it difficult to employ the lignin for any purpose other than combustion [3]. Steam treatment is typically employed in cellulosic ethanol processes, and this operation yields a lignin stream better suited to value-added uses [4]. It should be noted that sugarcane bagasse has a lower density of ortho-substitution, increasing its ability to be derivatized [5].

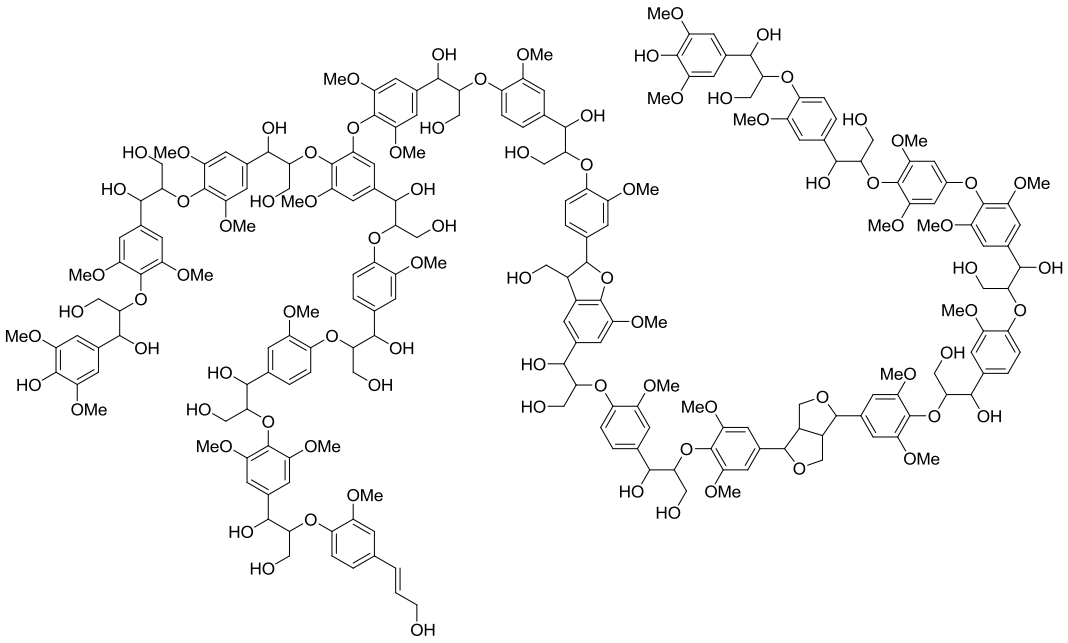
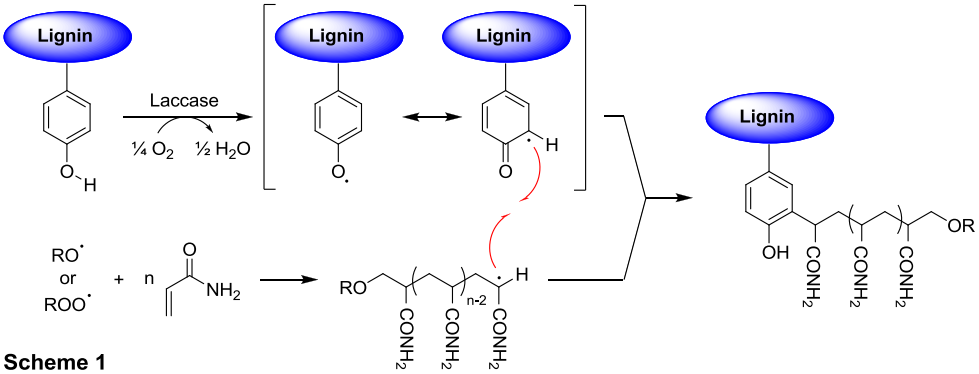


Figure 1: Typical lignin structure (re-drawn from http://www.dfrc.ars.usda.gov/ligninmodels.html).

Laccases are the best-known enzymes that accept lignin as a substrate. These multi-copper proteins are produced by a wide variety of species and play important roles in lignin degradation by white- and brown-rot fungi [6]. These enzymes mediate the four-electron reduction of O2 using lignin as the ultimate electron source. Because lignin can be highly crosslinked and interior portions are difficult to access by large proteins, laccases are paired with small molecule, diffusible electron carriers (mediators) [7]. Depending on reaction conditions, laccase / mediator systems can cross-link lignin internally, covalently add small molecules to lignin or degrade the lignin substrate [7-9]. We will focus on laccase-mediated molecular additions since these conversions can alter lignin properties in useful ways. To facilitate re-using laccases, these enzymes have been immobilized on a variety of solid supports (for a summary, see [9]).

Mai and co-workers have shown that polyacrylamide can be grafted onto lignin by simultaneous treatment with laccase and a small-molecule peroxide [10, 11]. The reaction is believed to proceed by by laccase-mediated radical formation within lignin. These radicals couple with radicals found at growing ends of polyacrylamide chains (Scheme 1). The resulting co-polymer had solubility properties suitable for use as deep-well drilling fluid. In addition to polymer grafting, laccase also cross-links the lignin into

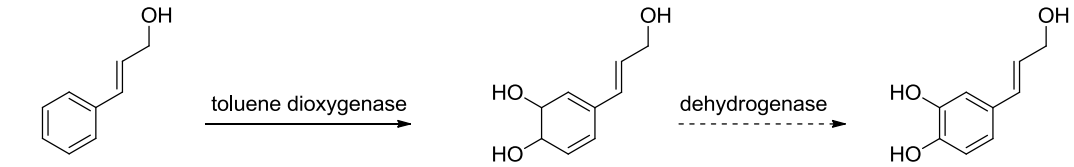
higher molecular weight assemblies, increasing its mechanical strength. These results suggest that other living radical polymerizations might also be amenable to lignin attachment.



Scheme 1

Non-covalent polymer blends represent an important means of using lignin for value-added products. Unfortunately, native lignin interacts poorly with existing materials. In an effort to solve this problem, Thielemans and Wool acylated kraft lignin in an effort to identify a derivative that dissolved in styrene [12]. While successful in this regard, only a limited number of acyl chains were examined in this study. This approach also depended on chemically synthesizing activated acyl derivatives (anhydrides, acyl chlorides). By contrast, lipases can utilize carboxylic acids directly and tolerate a wide variety of functional groups.

We are investigating the first step in the conversion of aromatic substrates into catechols by using cinnamyl alcohol as a model compound for lignin-derived materials. It appears that bacterial toluene dioxygenase does indeed accept cinnamyl alcohol and convert it to the corresponding diol. The next steps will be to combine this enzyme system with a dehydrogenase to yield the catechol in situ and to probe the possibility of oxidizing more complex lignin-derived materials. This can be combined with the polymer grafting approach described above to lower the costs of these materials even further.



cinnamyl alcohol 1,2-dihydrodiol catechol

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Combined Cooling, Heat, Power, and Biofuel from Biomass and Solid Waste

PI: William E. Lear Jr. **Co-PI:** Jacob N. Chung
Students: Elango Balu (PhD); Minki Kim (PhD); Uisung Lee (PhD)

Description: The goal of this project is to provide the underlying research and demonstration of a novel technology which would enable the economic utilization of dispersed biomass and solid waste resources to produce electric power, cooling, heat, and transportation fuels. This integrated gasification and power generation system combines University of Florida advances in high-temperature gasification, hydrogen generation and separation, and advanced gas turbine systems. Their integration is expected to result in significant improvements in the cost, emissions, feedstock flexibility, and water requirements, all in a relatively compact, modular plant system. This in turn will enable much greater utilization of renewable energy supplies, helping the development of a sustainable energy supply infrastructure.

Budget: $576,000
Universities: UF
External Collaborators: Siemens Power Generation, Florida Turbine Technologies, Energy Concepts Co., Nu-Power Technologies LLC, PlanetGreenSolutions Inc., LPP Combustion, LLC.

Progress Summary

The current project focus is in three areas: development of a system architecture and thermodynamic model, development of models and system-level experiments for the PoWER gas turbine unit, and exploration of the underlying science and demonstration of the high temperature steam gasification (HiTS) subsystem. These activities are structured in such a way as to allow stepwise research and development of the overall plant in outlying years.

The system architecture includes the full integration of waste heat and water produced in the gas turbine module with the gasification subsystem. This in turn allows efficiency gains, reducing the proportion of hydrogen utilized internally, and allows zero net usage of external water resources. A thermodynamic system model has been refined during the current year, and the architecture is suitable for inclusion of more complete subsystem models as their development continues. The PoWER and HiTS subsystem models have been further developed to include more detailed physics and, for the PoWER model, transient effects.

The PoWER system has been implemented as an experimental system in previous programs, and a demonstration-level plant is nearing completion. Early stage integration of the HiTS and PoWER subsystems includes operation of a Capstone C60 gas turbine engine on syngas from the developmental gasifier. Installation of the Capstone unit, including gas handling subsystem and load bank, has been accomplished. Some base test using Methane (CH_4) has been performed, and simulated syngas mixture test would be performed during this reporting period.

For HiTS, experiment using 15kW trailer gasification system was performed to enhance syngas quality so that we could supply the syngas to the microturbine ultimately. Conventional 4-cylinder engine was used instead of microturbine to check the validity at present. The engine output data was recorded via load

bank, and syngas composition was analyzed via gas chromatograph. The results show that the overall efficiency from biomass to electricity is mostly near 25%, which is close to the efficiency when the gasoline or natural gas used. In addition to that, bench-scale steam gasification system was also being tested using hydrogen and oxygen combustion to supply high temperature in oxygen free condition.

The Membrane reactor to be used alongside with the steam gasifier is designed to operate at 900°C to carry out the WGS reaction using MIEC (Mixed Ionic Electronic Conductivity) properties and in situ removal of H2 which helps in shifting the equilibrium to the right thus facilitating more H2 production and conversion of CO.

On the simulation side, equilibrium model for the gasifier was developed to predict the syngas quality with respect to reactor temperature, pressure, feedstock and steam to biomass ratio. The results were compared to other literature values, which are very close to theirs. The model outcome will be compared to the experimental result consecutively. Also, kinetic model which considers time effect will be studied for accurate prediction in the future.

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I. Experimental Facility

Trailer scale gasification system consists of a gasifier, cleaning system and an engine generator set with a load bank. The down-draft gasifier with the capacity of handling about 10 kg of biomass per batch will introduce syngas to the engine after cooling and cleaning stages. Ford DSG-423 four cylinder IC engine was operated at 1800 rpm to generate electrical power through the generator and the load was recorded at the load bank.

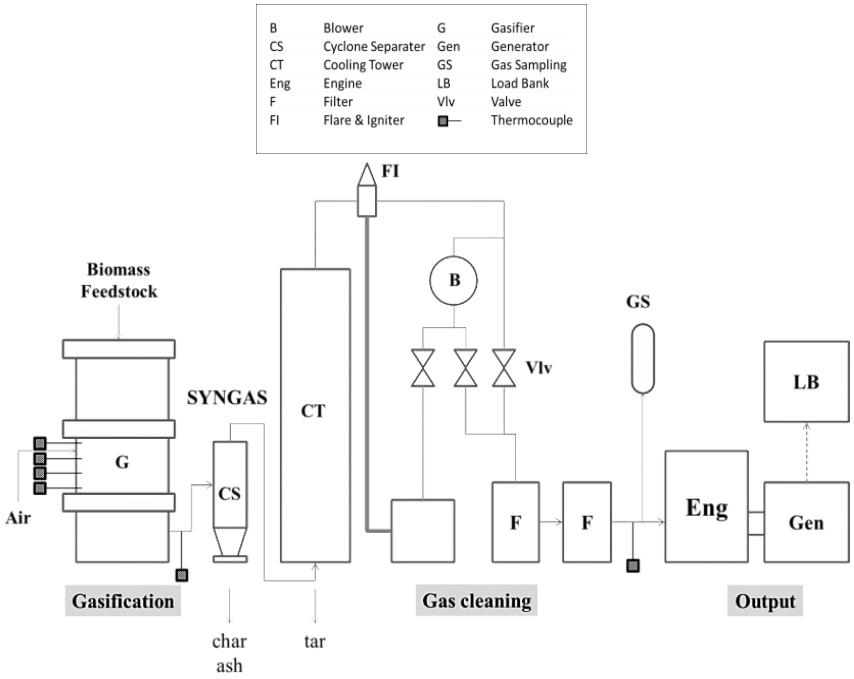

Figure 1: Schematic of experimental setup

II. Engine analysis

Energy consumption rates of the syngas could be calculated using measured syngas flow rate before it enters the engine. They were compared to the actual engine powers which were measured at the engine output using the generator and load bank to find engine efficiency. Before comparing the actual condition, stoichiometric air and fuel mass flow rates were calculated to check the equivalence ratio because if it is burned at the fuel-rich condition, excess syngas would not completely combusted. As it is found that all four syngas were combusted at fuel-lean condition, it is assumed there was enough air to burn all the syngas. Considering the efficiency using gasoline is around 30%, engine efficiencies using syngas from various feedstocks have quite reasonable values.

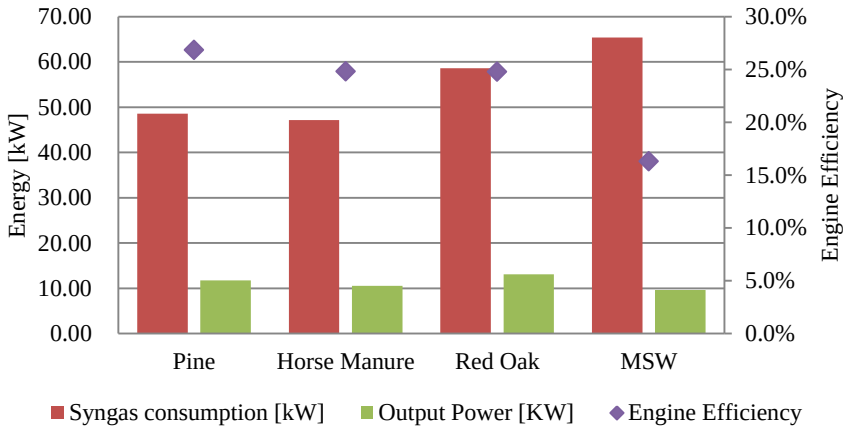

Figure 2: Engine efficiency (Energy input / Energy output)

III. Equilibrium Model

Biomass gasification is a series of chemical reactions to make synthetic gas which is useful form of energy. There are several types of biomass gasification models to predict gasification performance with given gasification condition such as temperature, pressure, feedstock, and oxidizing agent like air or steam. We have developed thermodynamic equilibrium model to predict the experiment result. Once we have feedstock chemical composition, amount of air and steam, temperature and pressure information, it is possible to determine the chemical composition and heating value of the syngas at the equilibrium state. These values could be compared to the actual experiment results.

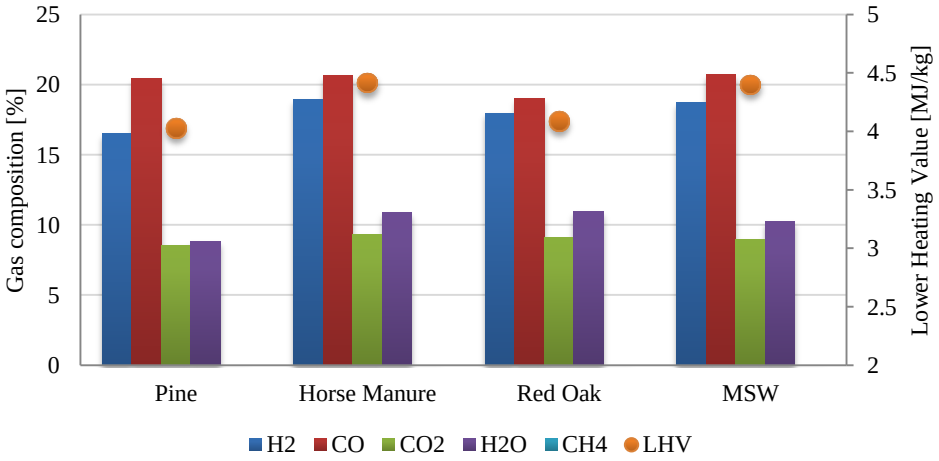

Figure 3: Equilibrium model prediction for the syngas composition and the lower heating value

IV. Steam gasification

Bench-scale high temperature gasification system was developed to check the steam gasification feasibility with municipal solid waste (MSW) and farm biomass waste. This system involves a thermal-chemical process that employs super-critical high-temperature steam to break down the feedstock to pure hydrogen-rich gaseous bio-fuels. Since the gasification agent is steam, the entire process is free of air and oxygen that traditionally produces air pollution effluents from incineration. The combustion of the hydrogen provides not only the steam as a product of the combustion but also provides an extremely high temperature, oxygen free environment for gasification. In addition part of the carbon monoxide produced may undergo a water shift reaction with the steam and produce additional hydrogen. Part of the hydrogen produced by the gasification is recycled back to the torch to maintain the gasification temperatures.

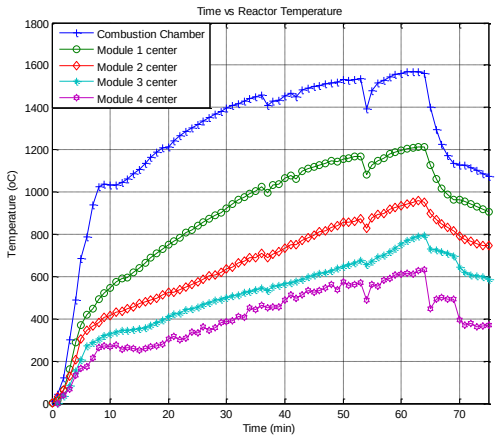

Figure 4: Reactor temperature with respect to time

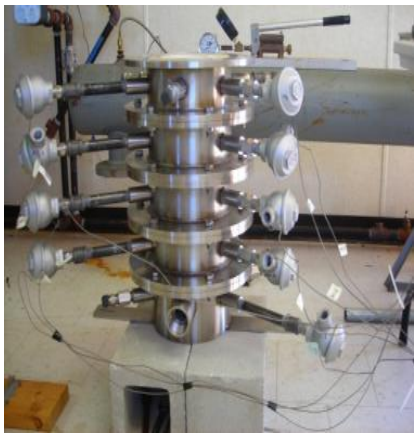

Figure 5: Bench-scale gasification system

V. Enhancing H_2 Yield Using SCZE Membranes

Syngas mixtures containing mostly H_2 and CO are typically generated at elevated temperatures via the conversion of biomass through steam gasification. The water-gas shift (WGS) reaction converts CO into CO_2 and provides additional H_2. To enhance H_2 yield further SCZE Membranes are being developed with the system in Fig 6.

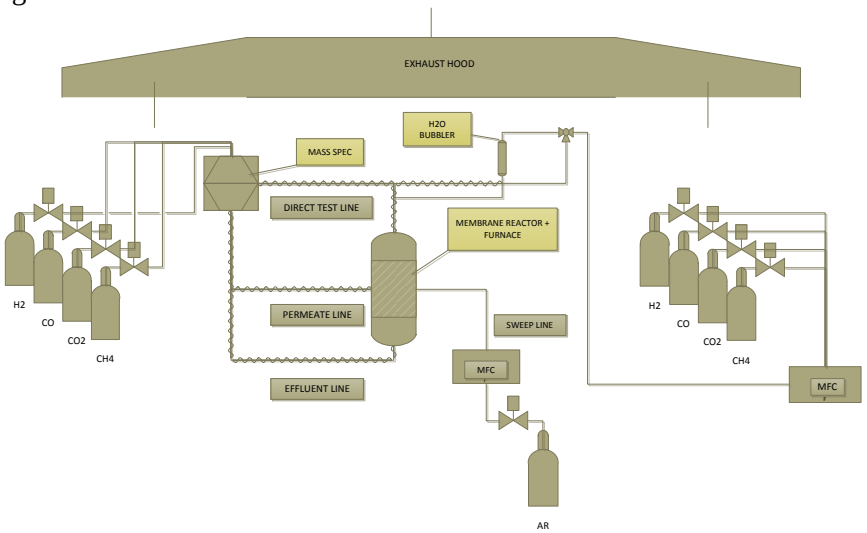

Figure 6: Experimental setup for H2 separation membrane

VI. Flameless Combustion Experiments and Modeling

The Power, Water Extraction, and Refrigeration (PoWER) system is the energy conversion subsystem to be eventually integrated with the steam gasification plant described above. One important feature of the PoWER system is that the combustion environment features high diluent concentrations, resulting in significantly reduced flame temperature. This in turn produces a flame characterized by very low soot production, highly-uniform temperature field, and low flame luminosity, so that the regime is termed flameless combustion. The low flame temperature reduces NOx without complex dry low-NOx technology; the low soot formation helps to reduce CO emissions. Overall, the primary regulated pollutants – NOx, particulates, unburned hydrocarbons, and CO – are simultaneously reduced to levels well below the current state of the art. At the same time, fuel flexibility is enhanced, making this system ideal for coupling to a biomass/MSW gasifier with a wide range of syngas compositions. This in turn makes the economics more attractive, as a single system is expected to be applicable in multiple applications with minimal or no modification.

Current activities have focused on coupling the output fuel stream of the gasifier to a modified, conventional microturbine in order to characterize the suitability of the various syngas variants for gas turbine operation. The gas turbine system is based on a Capstone C60™ microturbine (60kW) and multiple fuel sources, including methane, syngas, and a LPP Combustion, LLC gasified fuel skid, shown in Figure 7. The controls allow automatic, rapid switching between two gasified fuel paths, gasified liquid fuel (LPP) and biomass fuel. For test runs using stored syngas or other low-pressure fuel, we integrated a Copeland™ gas booster into the system. A Merlin Simplex portable load bank with 200 kW capacity is used to dissipate the electrical power as well as to control the engine output. As a parallel activity, integrated system modeling, PoWER(turbine), absorption refrigeration, and HiTS (gasifier), is continuing.

Figure 7: Micro-turbine test system

Integrated system modeling, gasification and PoWER system parts, is being simulated by using MATLAB® and C++. The system modeling architecture is shown in Figure 8. Three subsystem simulation programs are coupled to form the integrated plant model: turbocharger and microturbine system, vapor absorption refrigeration system (VARS), and HiTS.

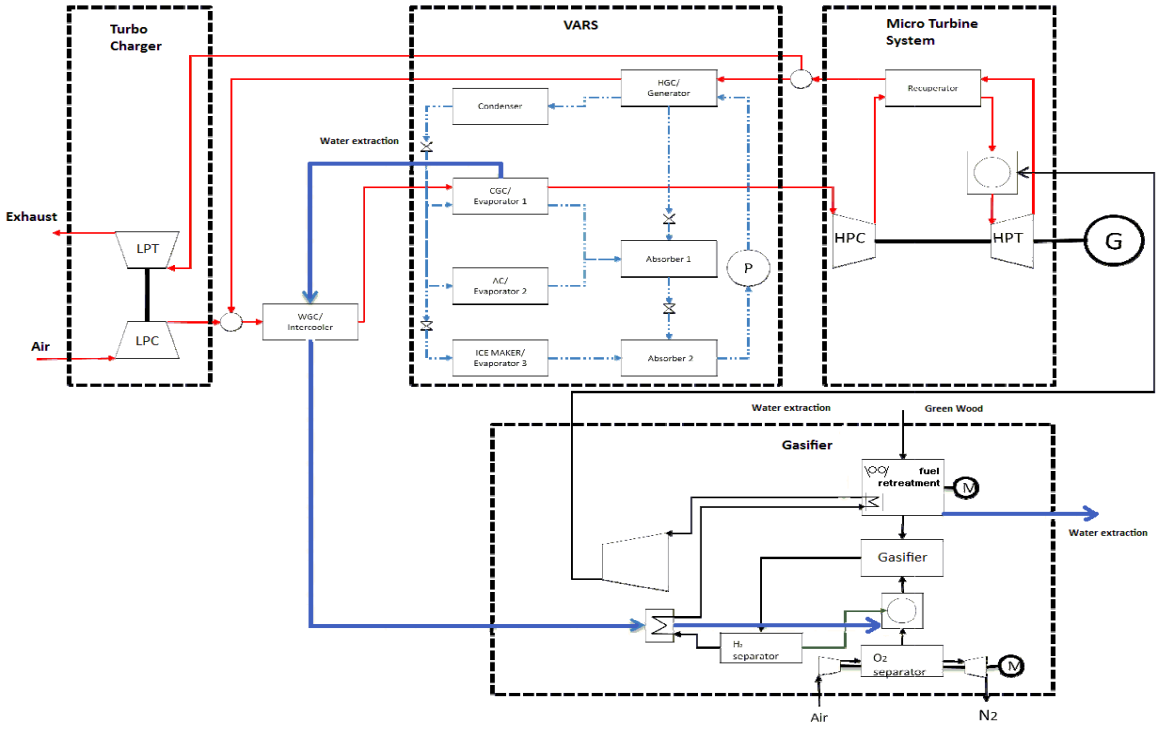

Figure 8: Integrated system modeling concept diagram

In the Gasifier simulation part, from biomass content, biomass flow rate, reactor design temperatures, component efficiencies and PoWER system water extraction are input data. Predicted temperatures, pressures and flow rates, energy flows, and syngas flow, temperature and compositions will be obtained as output data. Model chemical kinetics of the reactions in the gasifier have so far been made using an equilibrium assumption; the highly non-linear set of equations is solved by using MAPLE.

The modeling developments are steps along the path towards an integrated overall system simulation code. Such a code will allow determination of optimal flow path configuration to enable capture of waste heat and minimization of energy destruction, as well a parametric optimization for design purposes. The model is to be validated via interim experiments described above, so that the full plant design can be accomplished with confidence.

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Database Infrastructure for Integrative Carbon Science Research

PI: Sabine Grunwald **Co-PI:** Timothy A. Martin
Students: C.W. Ross (M.S.); X. Xiong (Ph.D.)
Technical staff: Brandon Hoover
Post-Docs: Nichola M. Knox

Description: Rising CO_2 concentrations in the atmosphere and effects on global climate change have been well documented, and future impacts are uncertain but potentially devastating. Florida's natural and agro-forest ecosystems have much potential to sequester carbon in biomass and soils due to unique climatic and landscape conditions. However, research gaps exist to accurately assess carbon pools and fluxes at coarse scales, ranging from county to the region and larger. The overarching objective of this project is to address these obstacles by developing a terrestrial carbon information system (called "TerraC") for the carbon science community, focused on ecosystems in Florida. The information system will be administered through the UF Carbon Resources Science Center (http://carboncenter.ifas.ufl.edu), a multi-disciplinary Center dedicated to research in support of enhanced agricultural and natural resource carbon management.

Budget: $199,440
Universities: UF
External Collaborators: Natural Resources Conservation Service-U.S. Department of Agriculture

Progress Summary

1) Database
The conceptual design for the Terra Carbon Information System (Terra C) has been completed and the database structure implemented in Structured Query Language (SQL). TerraC consists of a web-accessible database, meta data editors, and project wizard. The database hosts carbon and associated environmental data from the soils/geologic, atmospheric, vegetation, water, and whole ecosystem domains. A major amount of time was spent on testing, evaluation, and improvement to upload data into the database, which requires the use of a standardized data template. To accommodate a variety of different carbon data types (e.g. labile soil carbon, recalcitrant soil carbon, total soil carbon, carbon flux, and respiration rate), units of data (e.g. concentrations, contents, stocks, fluxes, CO_2eq., etc.), and spatial and temporal resolution of data the design of the database structure is divided into core and optional fields. The core fields are standardized to avoid duplication of carbon data entered into the TerraC database by different users and projects. Optional fields contain carbon data which are specialized in terms of their analytical methods and/or data collection protocol.

2) Web Design & Tutorials
The web site http://terraC.ifas.ufl.edu has been developed which provides access to the data engine, query tools, and tutorials. The latter ones provide step-by-step instructions how to use the system implemented in form of Adobe Presenter with voice over.

3) Carbon Datasets
Several site-specific carbon datasets have been identified and acquired from various sources. These carbon data are streamlined and documented in TerraC. Among them is the large, historic (~1965 to 1996) Florida Soil Characterization Dataset which contains about 1,300 soil samples and about 8,300+ horizons with 144 different soil physical, chemical, morphological, and taxonomic data which are

georeferenced. In this dataset 7716 samples have soil organic carbon measurements, belonging to 1252 profiles. Soil carbon has been measured based on Walkley-Black modified acid-dichromate method (mineral soils) and Loss on Ignition (organic soils), respectively. Other carbon data streamlined into TerraC include data from the Santa Fe River Watershed where various carbon pools (hot-water extractable (labile) carbon, recalcitrant carbon, total carbon, mineralizable carbon, and other biogeochemical properties were collected. We will continue to populate TerraC with carbon data representing various ecosystem types and ecosystem components over the next project phase.

4) Synthesis Analysis – Carbon Assessment / Capture

We continue to work on various prototype synthesis projects which utilize TerraC. For example, the Florida Soil Characterization Data has been synthesized with spectral data derived from visible/near-infrared diffuse reflectance spectroscopy to build a spectral carbon library for the State of Florida (Vasques et al., 2010). In another synthesis project, the soil carbon data in the Santa Fe River Watershed (FL) were fused with a large set of environmental factors to model the spatial distribution of soil carbon across the watershed in dependence of climate and land use change (Vasques et al., 2010). Similar synthesis analysis will continue in the next project phase.

References:

Vasques G.M., S. Grunwald and W.G. Harris. 2010. Building a spectral library to estimate soil organic carbon in Florida. J. Environ. Qual. 39: 923-934.

Vasques G.M., S. Grunwald, N.B. Comerford and J.O. Sickman. 2010. Upscaling of dynamic soil organic carbon pools in a north-central Florida watershed. Soil Sci. Soc. Am. J. 74: 870-879.

Funds leveraged/new partnerships created: By utilizing TerraC as a core structure for data warehousing and synthesis, it helped to leverage a new project funded by the United State Department of Agriculture (USDA) – National Institute of Food and Agriculture (NIFA) – Agriculture and Food Research Initiative (AFRI) Regional Project "Pinemap: Integrating Research, Education and Extension for Enhancing Southern Pine Climate Change" (2011-2016). This is a large-scale $20 million project with 50+ Co-PIs and Collaborators from 13 institutions (UF is the lead institution; PI: T.A. Martin; Co-PI: S. Grunwald) which supports 25+ students, 10+ Post-Docs, and staff members. The project goals are to create, synthesize, and disseminate the necessary knowledge to enable southern forest landowners to:

- harness pine forest productivity to mitigate atmospheric carbon dioxide
- more efficiently utilize nitrogen and other fertilizer inputs
- adapt their forest management approaches to increase resilience in the face of changing climate.

The TerraC system provides the data infrastructure for the Pinemap project. Since Pinemap funds a comprehensive monitoring program of ecosystem properties, many measurements related to the carbon cycle, will be streamed into TerraC populating the database and allow sharing of carbon and ecosystem data widely (constraint by the data sharing policy implemented in the Pinemap project).

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The overall goals of this project are to create a database infrastructure for the carbon science community, focused on ecosystems in Florida and the southeastern United States. The availability of this database will enable the analysis and synthesis of carbon data at multiple spatial and temporal scales. A short description of the TerraC Information System is provided.

What is Terra C?

The **Terrestrial Carbon (TerraC) Information System** is dedicated to advance terrestrial carbon science through sharing of carbon and environmental data. It provides information about carbon cycling as it relates to global climate and land use change. TerraC offers tools to upload, store, manage, query, analyze, and download data characterizing terrestrial carbon dynamics from various sources, including soils, plants/biomass, atmosphere, water, and whole ecosystems. The purpose of Terra C is three-fold: (i) advance terrestrial carbon science through sharing of carbon and environmental data; (ii) facilitate environmental synthesis; and (iii) enhance collaboration among researchers, scientists, and extension specialists through shared resources. Research projects involving carbon and related properties are many and spread across multiple disciplines and spatial and temporal scales. TerraC aims to integrate data from these widespread sources in a shared information system to facilitate cross-cutting analysis of carbon and environmental data, synthesis of carbon research, and enhance communication and collaboration among researchers. Data stored in TerraC conform to quality standards and can be shared privately among selected users or publicly with any user. Detailed information about the data sharing options available in TerraC is listed in the data sharing and usage policy.

Objectives of the Terra C Project

(1) *Build the Terra C Information System*: (i) Develop a coherent, searchable, and expandable database that integrates terrestrial carbon and associated environmental datasets, and (ii) provide information about carbon related to environmental stressors such as climate and land use change.
(2) *Data synthesis*: Synthesize multiple large carbon datasets to gain insight into carbon cycling and dynamics across various spatial and temporal scales; upscaling of site - specific carbon observations to landscape scales.
(3) *Geospatial outreach*: Build a 'GoogleEarth' application to deliver and share terrestrial carbon data in form of a Google carbon application.

Motivation

Rising CO_2 emissions in the atmosphere and effects on global climate change have been well documented, and future impacts are uncertain but potentially devastating. Florida's natural and agro-forest ecosystems have much potential to sequester carbon in biomass and soils due to unique climatic and landscape conditions. However, research gaps exist to accurately assess carbon pools and fluxes at coarse scales, ranging from county to the region and larger scales. The overarching objective of this project is to address these obstacles by creating a database infrastructure for the carbon science community, focused on ecosystems in Florida and the southeastern United States. The database engine of TerraC is administered through the UF Carbon Resources Science Center, a multi-disciplinary Center dedicated to research in support of enhanced agricultural and natural resource carbon management. The TerraC project aims to provide the framework to synthesize carbon and environmental data to facilitate meta-analysis, modeling of carbon dynamics and biogeochemical cycles, and to conduct applied and cutting-edge carbon science research.

TerraC in a Nutshell

TerraC provides a data engine which allows managing, archiving, sharing, editing, modifying, and querying carbon and associated environmental data. These data are derived from various projects and sources; thus, provide a wide array of different carbon measurements, in various ecosystems and geographic regions, and spatial and temporal scales. The Terra C data engine facilitates synthesis and modeling to gain better insight into carbon cycling from micro, plot, field, watershed, basin, large region, and global scales.

Data Sharing and Usage Policy

Data users submitting data to or use data from the TerraC Information System agree to abide by the terms and conditions explained in this document. Data users may be held responsible for any misuse that is caused or encouraged by failure to abide by this agreement.

Definitions

Project: Set of one or more datasets that contain carbon (and related) environmental data.
Dataset: Set of data comprised of one or more data fields that contain carbon (and related) data that is part of a single project.

Roles of users

Project owner (leader): Principal Investigator or person with similar credentials responsible for collecting and managing the original, quality controlled data generated by a specific project. The project leader needs to initiate a project before a dataset can be submitted to TerraC and is responsible for the quality of all datasets under his/her projects. The project leader controls the levels of data sharing and can assign one or more data managers to each of his/her projects.

Data contributor (or manager): User that has read/write access to a dataset in TerraC. The data manager has privileges to submit a new dataset to a project and access and modify existing ones in part or as a whole. The project leader needs to assign a user manager status before he/she can submit a new dataset or modify an existing one in a project.

Data user: User that can view a dataset in TerraC. The data user can read public datasets and also private datasets as long as he/she has been granted access to them by the project leader. The data user cannot submit a new dataset or modify existing ones unless he/she receives manager status from the project leader to a project.

Data sharing: Data stored in TerraC can be shared at three access levels. The access levels are chosen by the project leader to control access to their projects by different users. Different access levels can be assigned to different users, the level being project- and user-specific. Levels 1 and 2 mirror the roles of data user and data manager, respectively. Level 3 in the most restricted access level. *Levels of data sharing*:

Level 1 – Public with read-only access: Access to the data is open to all TerraC users. Any person that has a TerraC user account (i.e. data users) can view the data, but not modify it directly from the TerraC database. Only the project leader can modify/edit data.
Level 2 – Private read/write access: Access to the data is open to data managers who were assigned (approved) by the project leader to have permissions to view and modify/edit data directly from TerraC. *Private read/write access* is password-protected.
Level 3 – Private read-only access: Access to the data is restricted to the project leader and users selected by the project leader. Users can only view the data, but not modify it directly from TerraC.

The project leader controls the sharing of data in TerraC. He/she provides leadership for collaboration with new partners on behalf of the project teams. The project leader can switch sharing levels from Level 3 to 2 and 1, but not vice versa, meaning if the data are released to other users or the general public this right cannot be reversed.

Data users who are interested in to gain access to a specific protected dataset can contact the project

leader and negotiate agreement of data use of a specific project. The project leader may agree to share data with the data user to collaborate on a joint project, work on a co-authored research publication, or use them for other purposes.

Data usage: Data users are expected to use data obtained from TerraC to the highest level of professional integrity and ethics. Data users must abide by the following guidelines when distributing or publishing data obtained from TerraC:

Data sharing and usage in TerraC is governed by the **Attribution Non-Commercial Share Alike** license provided by Creative Commons (summary: http://creativecommons.org/licenses/by-nc-sa/3.0; legal code: http://creativecommons.org/licenses/by-nc-sa/3.0/legalcode), which observes the following rules:

Attribution: The data user must give credit to the project leader (or project) in the manner specified by him/her (but not in any way that suggests that the project leader endorses the data user or his/her use of the data);

Noncommercial: The data user may not use TerraC data for commercial purposes; data should be used for reserach and non-profit applications;

Share Alike: If the data is modified in any manner or used to derive other products, the data user may distribute the resulting work only under the same or similar license to this one;

Credits and publications derived from TerraC usage:

- The data user must inform or consult the project leader about his/her intentions to use the data for publication well in advance of submission of the publication; the project leader should be given the opportunity to read the manuscript and, if appropriate, be offered co-authorship;
- The data user must give credit to the project leader (or project), which can be in the form of co-authorship, citation, or acknowledgement, according to the requirements imposed by the project leader; any deviation from this rule must be formally agreed between the data user and project leader;
- The data user must cite or acknowledge TerraC as the data host used to obtain the data;
- Any modification to the data originally obtained from TerraC by the data user must be fully documented.

<u>Carbon Data and Associated Environmental Data</u>

(1) Core Data Fields:

- Identification number for each observation (SN)
- X coordinate (X) {Geographic Coordinate format (latitude/longitude in decimal degrees) with World Geographic Datum 1984, WGD 1984}
- Y coordinate (Y) {Geographic Coordinate format (latitude/longitude in decimal degrees) with World Geographic Datum 1984, WGD 1984}
- Sample date (DATE) {MM/DD/YYYY}
- Height or depth of measurement (Z) {in cm; below the soil surface negative numbers; above the soil surface positive numbers}
- Carbon measurements (variable names, data values, and meta data: analytical methods & units of measurement in Standard International Units)
- Biogeochemical or other environmental data (variable names, data values, and meta data: analytical methods & units of measurement in Standard International Units)

(2) Project Elements (meta data):

- Project title
- Project description (description of sampling design, sampling protocol, quality assessment, data constraints such as below detection limit treatment, missing values, etc.)
- Project owner (typically Principal Investigator of a research project; or Project Leader for agency lead project)
- Project contributor (optional)
- Project user (optional)
- Contact information (Project Owner)
- Funding source
- Project location (description of geographic location of project; size of project area)
- Project period (YYYY to YYYY)
- Link to project homepage
- Publications from project
- Acknowledgements

Data Quality and Standards

Data format: TerraC focuses on terrestrial carbon and related environmental data. Data submitted to TerraC must contain carbon data and have the following format:

- Be oriented in rows and columns, with cases (observations) listed in the rows and properties (attributes) listed in the columns;
- Carbon and other measured properties must be presented as variables in specific columns:
    - Each column must only contain properties measured using the same method; if the same property was measured using more than one method (e.g. total carbon vs. carbon fractions), each method must be presented as a separate column;
- Spatial coordinates (horizontal and vertical) and time stamps must be presented, whenever available, as variables in specific columns;
- Repeated measures (e.g., the same property collected at different times or replicated) must be treated as separate cases (i.e. listed in separate rows):
    - A column indicating that the cases are repeated measures of the same property must be included (e.g. using the same sample identifier for the repetitions);
    - A column indicating the number of the repetition (i.e. 1, 2, 3…) must be included;
- Quality assurance/quality control (QA/QC) data must not be included in the dataset, but instead in the metadata of the property it pertains to.

Metadata: Since the objective of TerraC is to share data among multiple users, it is critical that metadata are provided in detail for every project, dataset, and variable in a dataset. Upon creation of a new project, the project leader needs to provide information (i.e. metadata) describing project detail, including location, sampling design, contact information, objectives, and others. Upon submission of a new dataset, the project leader or data manager needs to provide metadata for dataset and for every variable in the dataset.

Data quality: It is the responsibility of the project leader to ensure that all data listed under a project in TerraC have passed QA/QC. The project leader provides information for each project's data about the type of QA/QC and adopted standards. The data managers can assist the project leader to meet QA/QC requirements. The TerraC team may quarantine suspicious data and request information from the project leader and/or data manager to assure quality of the data before making them available online. TerraC cannot be held responsible for mistakes in the data or inadequate data usage. Data that for some reason are restricted by funding agencies or imposed proprietary or legal rights (e.g. military projects, pending patents, projects funded by private companies, or other) should not be included in TerraC.

Fig. 1. Snapshot of the Terrestrial Carbon (TerraC) Information System website.

Fig. 2. Project setup in TerraC.

Fig. 3. Data setup in TerraC.

Fig. 4. User administration tools.

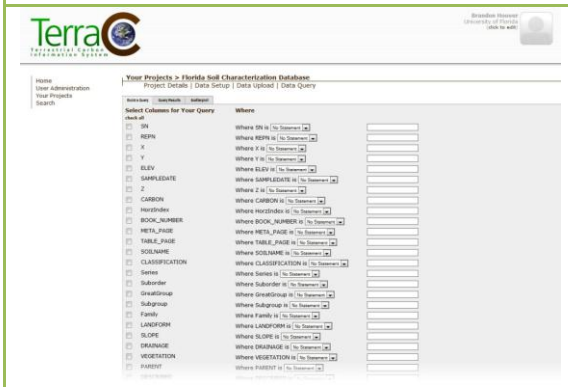

Fig. 5. Data query.

Fig. 6. TerraC tutorials.

Publications and Presentations from this Project:

Hoover B., N.M. Knox, S. Grunwald, T.A. Martin, X. Xiong, P. Chaikaew, J. Kim, B. Cao. 2011. Synthesis Tools for Carbon Assessment in Ecosystems. 2011. Florida Energy Systems Consortium (FESC) Summit, Gainesville, FL, Sept. 27-28, 2011.

Grunwald S., T. A. Martin, B. Hoover, G.M. Vasques, B. Zhong, and D.L. DePatieJr. 2010. Terrestrial carbon (TerraC) information system. 2010 Florida Energy Systems Consortium (FESC) Summit, Orlando, FL, Sep. 27-29, 2010.

Hoover B., G.M. Vasques, B. Zhong, S. Grunwald, T. A. Martin, and D.L. DePatieJr. 2010. The terrestrial carbon (TerraC) information system Vers. 1.0. 11th Annual Soil and Water Science Research Forum, Gainesville, FL, Sep. 10, 2010.

Grunwald S., T.A. Martin, G.M. Vasques and B. Hoover. 2009. Database infrastructure for integrative carbon science research. Florida Energy Systems Consortium Summit, Tampa, FL, Sept. 29-30, 2009.

University of Florida

Development of Biofuel Production Processes from Synthetic and Biomass Wastes

PI: Pratap Pullammanappallil
Students: Diane Chaulic (PhD), Zhuoli Tian (PhD), Gayathri Ram Mohan (MS), Nicholas Locastro (BS)

Description: With the ever-increasing price of petroleum and its finite supply, it is of high priority to develop domestic sources of transportation fuel, as well as other chemicals. Ethanol is an attractive alternate fuel that is being produced from corn starch. It is necessary to target other feedstocks for biofuel production and develop processes that have a minimal environmental impact. There is considerable ongoing research on developing processes and catalysts for conversion of biomass to biofuels like ethanol (called cellulosic ethanol process). But this project addresses other feedstocks with the following objectives: 1) development of biocatalysts for the conversion of waste biodegradable poly lactic acid based plastics to ethanol and 2) development of processes that processes for the production of additional fuels like biogas, bio-oil and biochar from the waste and byproducts of a cellulosic ethanol plant for the clean-up and reuse of these waste streams

Budget: $192,000
Universities: UF
External Collaborators: UCF

Progress Summary

Process development for biogasification and clean-up of cellulosic ethanol stillage

- Demonstrated that struvite (a slow release fertilizer containing ammonia and phosphate) can be recovered from the anaerobically digested stillage.
- A process was developed to recover struvite along with other organic carbonaceous residue remaining in the digested stillage.
- Showed that this process can be applied with or without prior anaerobic digestion of stillage.
- Estimated that sufficient phosphorous is contained in the recovered sludge to grow the biofuel crop. The application of this sludge to grow the bioenergy crop offsets the need for addition of phosphate fertilizer.
- Demonstrated that nanoceria enhances anaerobic digestion of biomass.

Process development for preparation of enzymes to saccharify pectin rich biomass feedstocks.

- Developed a process that can be implemented in the biorefinery to prepare biocatalysts for saccharification of pectin-rich biomass and a method for saccharifcation of such biomass. This process has applications for pretreating citrus pulp, sugar beet pulp, apple pomace, fruit and vegetable wastes etc prior to production of liquid fuels.

Biocatalyst development for conversion of waste PLA based plastics to ethanol

- An *E.coli* mutant was constructed that is incapable of utilizing lactic acid.
- Into this mutant a Lactate dehydrogenase (LDH) gene was inserted. Currently experiments are underway to verify the expression of this gene.

University of Florida

Development of Low-Cost CIGS Thin Film Hot Carrier Solar Cells

PI: Gijs Bosman **Co-PI:** Tim Anderson
Students: Yige Hu, PhD.

Description: PV has entered into a period of record growth. Most of the current production is based on crystalline Si technology. However, there are fundamental limits to the ultimate Si costs that may inhibit it from achieving the desired level of contribution to worldwide energy production. In contrast, thin-film PV technology can reach the desired outcome due to fast deposition rates and lower cost. Our study is focused on hot carrier solar cells for cell conversion efficiency improvement in a low cost, high throughput CIGS system. The rapid thermalizaton loss of hot photoexcited carriers interacting with the lattice can potentially be reduced through phonon engineering in the absorber layer; the subsequent extraction of the hot carriers may be realized through device engineering of energy selective contacts.

Budget: $ 126,112.00
Universities: UF

Progress Summary

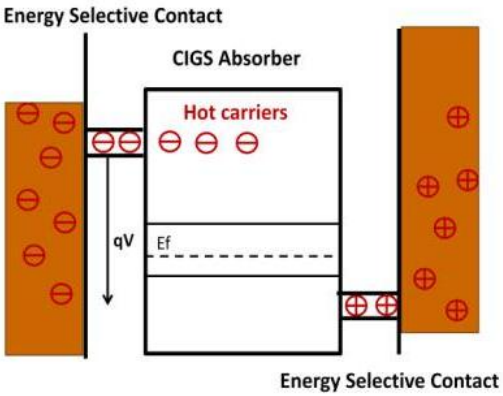

Figure 1: Schematic Presentation of A Hot Carrier Solar Cell

Hot carrier solar cells allow hot carriers to be collected before energy is lost to the lattice. This is accomplished by slowing carrier cooling in the absorber and collecting the carriers using energy selective contacts. This ultimately leads to both a higher open circuit voltage since the average energy of the collected electron is greater than the band gap energy. It also leads to a higher short circuit current, leading to an overall greatly improved efficiency. Phonon engineering in the absorber helps to increase the hot carrier lifetime. Photocurrent measurements as a function of applied bias were carried out on fabricated CIGS solar cell structures to characterize the hot carrier effect. The incident photon energy defines the initial hot carrier energy. The bias dependent electric field in the space charge region affects high-energy carriers differently than low energy carriers. For a given field strength, low energy, thermally

generated carriers will be directed to their traditional collecting contacts, but the hot carriers with randomly directed initial velocities may overcome the field effect and scatter into opposing contacts reducing the photocurrent in this way. Hence via a simple device physical model, a relationship between initial hot carrier energy, electric field in the space charge absorber region, and photocurrent has been established from which the relative density of hot electrons potentially can be determined from measured current voltage data. The current-voltage characteristics of a 20% efficiency CIGS solar cell under 455nm blue light and 633nm red light illumination were measured, respectively. Currently modeling efforts are underway to separate hot carrier effects from other device phenomena.

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The focus of this period is studying the hot carrier effect in the photocurrent-voltage characteristic of CIGS based solar cells. A simple model of the relationship of the hot carrier initial energy, electric field in the space charge region and the photo-current was developed. Simulation based on the model is presented for comparison with experimental data.

As shown in the figure 2, high energy photon excited electrons generated within the region of W-x1 to W have a 50% chance of going to the p region reducing the overall current; while those generated within the region of 0 to x1 will bounce from the conduction band Ec and subsequently be collected in the n region contributing to the photon current which can be written as

$$J_{opt} = q \times g_{op} \times x_1 + \frac{1}{2} \times q \times g_{op} \times (W - x_1)$$

$$= \frac{1}{2} \times q \times g_{op} \times (W - x_1)$$

where the photon generation rate g_{op} is assumed constant in the depletion region.

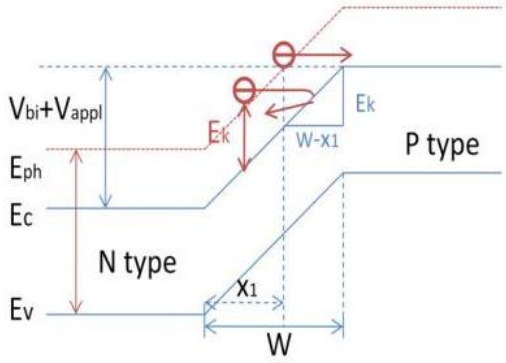

Figure 2: Band Diagram ff Hot Carrier Effect

The simulated reverse bias JV characteristic of a n-type ZnO and a p-type CIGS cell with 2.7eV incident photons based on this model is shown in figure 3. In low bias, hot carriers can overcome the barrier scattering to both contacts. Only half of them are collected on electron contact. Therefore the current density considering the hot carrier effect is half of the one without a hot carrier effect. As bias increases, more of the hot carriers bounce back from the E_C potential energy barrier and are collected via the n-side contact. Therefore the current density increases rapidly, as shown in figure 3 for reverse bias voltages larger than 0.5 V.

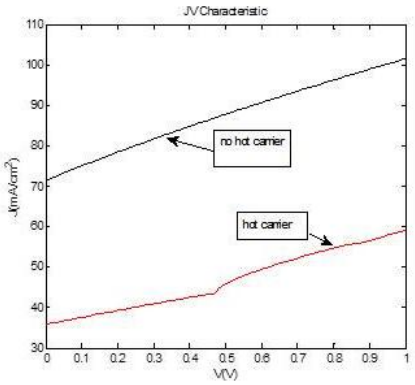

Figure 3: JV Characteristic of Hot Carrier Effect

A 19% efficient "champion" CIGS solar cell was illuminated with 455nm blue light and 633nm red light, respectively. In a parallel theoretical study, a n-ZnO/p-CIGS diode is simulated under the same condition. Figure 4 shows the photon current density versus voltage relationship of the experimental and simulation results. The photon energy of 455nm blue light is 2.7 eV, which is about 1.4 eV higher than the CIGS optical band gap and is able to generate high energy, hot electron-hole pairs. The photon energy of 633nm red light is only 1.9eV. The generated electron-hole pairs are closed to the conduction band edge and are more likely to relax as cold carriers. As shown, the experiment with blue light illumination reveals a rapidly increasing current density at high bias while the experiment with red light illumination does not show this effect. The trend of the experimental data matches with the simulated prediction. However, the optical current extraction needs to be better understood with respect to the reverse bias dark current since they are comparable parts in the total current. A study of the reverse bias dark JV characteristic will be carried out based on a space charge limited charge transport model. This will help improve the accuracy of the quantitative assessment in the future.

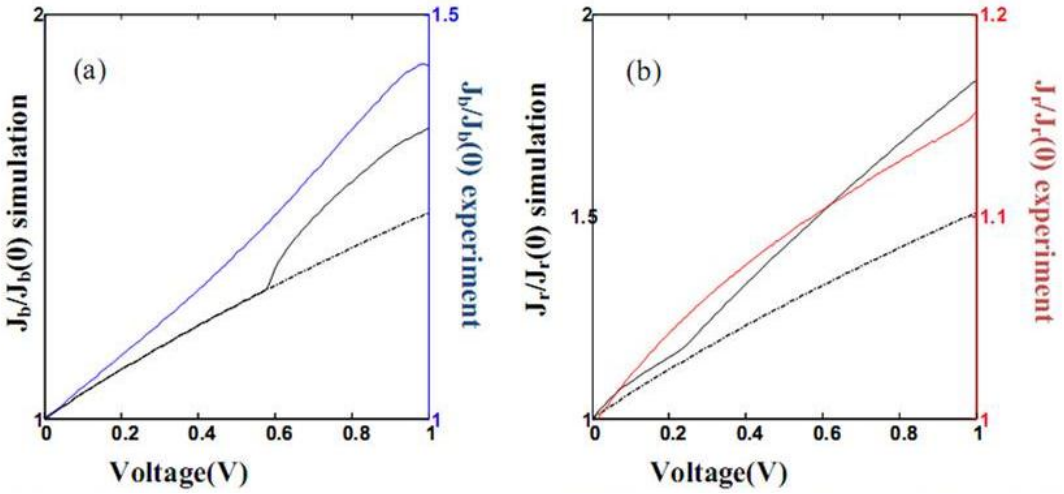

Figure 4: Reversed bias JV characteristics under (a) blue light illumination and (b) red light illumination. The current density on the y-axis is normalized to the current density value at V = 0. The blue line on (a) and the red line on (b) are the experimental data. They refer to the blue axis and the red axis respectively. The black solid line and black dash line are simulation results assuming photon generated carriers staying hot 100% and 0% respectively. Both refer to the black axis on the left.

FESC
Florida Energy Systems Consortium

University of Florida

Development of Novel Water Splitting Catalysts for the Production of Renewable Hydrogen

PI: Helena Hagelin-Weaver
Students: Justin Dodson (Ph.D.)

Description: This project focuses on the development of iron-based catalysts for the thermochemical splitting of water into hydrogen and oxygen. The thermochemical process of splitting water is particularly well-suited for the utilization of solar energy to provide the heat for the reaction and is a way to produce a renewable hydrogen fuel. As hydrogen is difficult to transport and store, producing hydrogen on site for power plants using proton exchange membrane (PEM) fuel cells or internal combustion engines to generate electricity or for the production of chemicals, such as liquid hydrocarbon fuels, is a very attractive approach. The project uses a two-step process in which water is passed over a reduced iron oxide to generate hydrogen while the oxygen is taken up by the oxygen-deficient iron oxide (Step 1: FeOx-1 + H2O FeOx + H2). In the second step the resulting iron oxide is heated to desorb oxygen and regenerate the oxygen-deficient iron oxide to close the catalytic cycle (Step 2: FeOx FeOx-1 + ½O2). The main objectives of the project are to develop mixed metal oxide catalysts that 1) will release oxygen at temperatures lower than 1500°C (Step 2), while still maintaining water-splitting activity (Step 1) and 2) are stable up to the temperature necessary for the oxygen desorption step.

Budget: $ 100,000
Universities: UF

Progress Summary

We have initiated the research and designed the reactor system (Figure 1), purchased a high temperature furnace and are in the process of purchasing a mass spectrometer (MS) for product analysis.

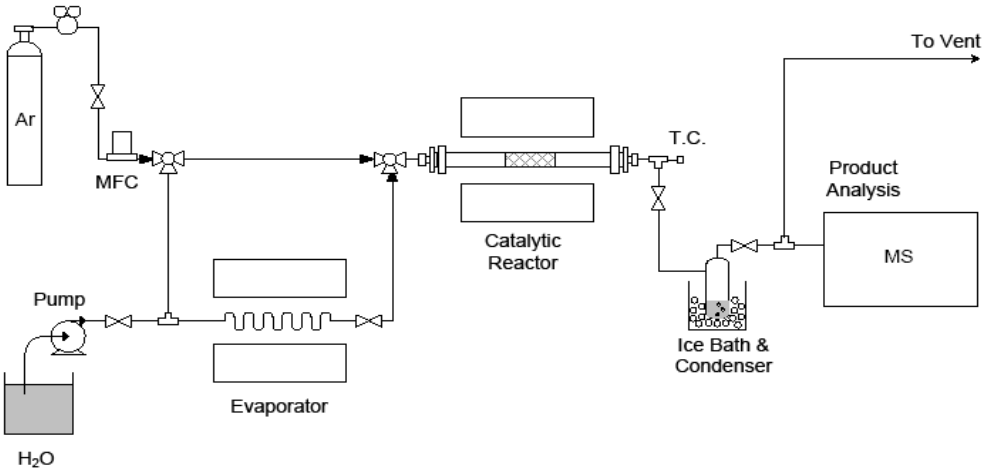

Figure 1: Drawing of reactor system for reaction studies on developed water-splitting catalysts (MFC = mass flow controller, T.C. thermocouple, MS = mass spectrometer).

University of Florida

Economic Impacts of Renewable Energy and Energy Efficiency Policies

PI: Theodore Kury
Students: Colin Knapp, Ph.D. (Post-doctoral Fellow)

Description: PURC is engaging in three new research projects that will provide important information for policy makers in Florida. The projects are:

Economic and Job Impacts of State Renewable Energy and Energy Efficiency Policies

This project will provide empirical estimates of state renewable energy and energy efficiency policies on economic development and jobs. Proponents of state and federal policies promoting renewable energy and energy efficiency policies often assert that the policies will have positive impacts on jobs, specifically the so called green jobs.

Electric Grid Impacts of State Renewable Energy and Energy Efficiency Policies

This project will provide an estimate of the impacts of renewable energy policies on the electric grid. It will fill a gap in the literature for Florida, which as to date focused on the impacts on electricity generation.

Effects of Energy Commodity Profit Margins on Effectiveness of Energy Efficiency Programs

This project will test an assumption that is built into many state energy policies and that is held by many policy makers at the national level, namely that utilities would improve consumer energy efficiency practices if utility prices were decoupled from utility profits.

Budget: $150,000.00
Universities: UF

Progress Summary

Work has continued on evaluating the effects of Renewable Portfolio Standards (RPSs) on state-level employment. These policies have become a popular policy in state capitals across the country. As of 2010, 36 states and the District of Columbia had adopted programs which fall under the RPS umbrella. The reasons often cited for the adoption of these programs include; increasing the share of electricity generation from renewable sources, thus lowering greenhouse gas emissions and reducing the threat of global climate change; increasing security by moving towards national energy independence; and creating job growth by dedicating expenditures towards industries or technologies not represented within a state's current mix of employment opportunities. These outcomes are supported by a vast *ex ante* literature which forecasts results using input-output analysis and economic forecasting models.

The purpose of this project is to approach the employment claim from a purely *ex post* perspective and measure the effect an RPS has on state-level employment. Initial results suggest a best-case scenario where every job created by an RPS is equally offset by job losses elsewhere in the state. Alternative specifications suggest a worsening employment situation with net job loss in those states which adopt an RPS. Additional results suggest that RPSs do not significantly increase the amount of energy generated from renewable sources in these states. This appears because the establishment of these guidelines is done with little enforcement of realistic and intermediate targets, making the policy an 'empty promise'. The effectiveness of alternate programs, such as mandatory green power purchasing programs, suggests that

the 'field of dreams' mentality that surrounds RPSs may be misguided and other options might exist which help satisfy some of the same goals.

2011 Annual Report

Initial work on the effect of renewable portfolio standards (RPS) has been completed. This includes the literature review, data collection, and data analysis concerning the effect of RPS implementation on state-level employment. An initial version of the results was presented during a seminar given to Ph.D. students studying regulation at the University of Florida on April 19, 2011. Feedback was received and incorporated into the project. The updated report on this project is in revision and new results will be presented during the 2011 FESC Summit. The paper associated with this project will be targeted for publication in a peer-reviewed journal such as *The Journal of Regulatory Economics*. Following submission of the peer-reviewed article, attention will be given to the remaining projects outlined in the description.