

# **THE SCIENCE AND ENGINEERING FOR A BIOBASED INDUSTRY**

A compilation of the multistate, multidisciplinary, cooperative  
accomplishments of past and present objectives for S-1041.

Program Proceedings

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Edited by

Kent Rausch  
Vijay Singh  
Mike Tumbleson



# **THE SCIENCE AND ENGINEERING FOR A BIOBASED INDUSTRY**

## **Symposium Schedule**

Tuesday, August 7, 2012

- 08:00 Overview of the National Institute of Food and Agriculture (NIFA)  
Sonny Ramaswamy, Director, NIFA/USDA
- 08:30 Bioenergy Research and Development Initiative (BRDI) Program Review  
Peter Arbuckle, BCE/NIFA/USDA
- 08:50 Sustainable Bioenergy Production  
Ganti Murthy, Oregon State University  
Andy Hashimoto, University of Hawaii
- 09:50 Implementing Systems Methodologies for a Sustainable Biobased Economy  
Lindsay Anderson, Cornell University
- 10:20 Break
- 10:50 Biomass Feedstocks Supply Logistics  
Al Womac, University of Tennessee
- 11:20 Education: Bioenergy and Sustainable Technology  
Distance Education Graduate Certificate  
Julie Carrier, University of Arkansas
- 11:50 Bioenergy/Bioproduction and Processes:  
Summary of Research Activities of S-1041  
Bernie Tao, Purdue University
- 12:20 Thermochemical Conversion and Revision of Objective 2  
Roger Ruan, University of Minnesota
- 12:50 Discussion for rewrite  
Julie Carrier, University of Arkansas

## Table of Contents

	Page
BIOMASS RESEARCH AND DEVELOPMENT INITIATIVE (BRDI) PROGRAM REVIEW Peter Arbuckle                      BCE/NIFA/USDA	1
SUSTAINABLE BIOENERGY PRODUCTION G. S. Murthy                      Oregon State University Andy Hashimoto                      University of Hawaii	3
IMPLEMENTING SYSTEMS METHODOLOGIES FOR A SUSTAINABLE BIOBASED ECONOMY Lindsay Anderson                      Cornell University	19
BIOMASS FEEDSTOCK SUPPLY LOGISTICS Al Womac                      University of Tennessee	21
EDUCATION: BIOENERGY AND SUSTAINABLE TECHNOLOGY DISTANCE EDUCATION GRADUATE CERTIFICATE Julie Carrier                      University of Arkansas	25
BIOENERGY/BIOPRODUCT PRODUCTION AND PROCESSES: SUMMARY OF RESEARCH ACTIVITIES OF S-1041 Bernie Tao                      Purdue University	27
THERMOCHEMICAL CONVERSION AND REVISION OF OBJECTIVE 2 Roger Ruan                      University of Minnesota	29
HYBRID THERMOCHEMICAL-BIOCHEMICAL PROCESSING FOR BIORENEWABLE ALCOHOL PRODUCTION USING <i>Alkalibaculum bacchi</i> Hasan Atiyeh                      Oklahoma State University	31
FOULING RATES OF SYNTHETIC THIN STILLAGE Ravi Challa                      University of Illinois	33
AUTOHYDROLYSIS OF <i>Miscanthus x giganteus</i> FOR THE PRODUCTION OF XYLOOLIGOSACCHARIDE (XOS): PRODUCT CHARACTERISTICS AND RECOVERY Ming-Hsu Chen                      University of Illinois	35

## Table of Contents (cont.)

MICROWAVE ASSISTED PYROLYSIS OF MICROALGAE FOR RENEWABLE BIO-OIL PRODUCTION Zhenyi Du University of Minnesota	37
BIO-OIL FROM SWITCHGRASS PYROLYSIS: UPGRADE TO TRANSPORTATION FUEL BY HYDROGENATION AND CATALYTIC TREATMENT Tahmina Imam Texas A&M University	39
COMPARISON OF MONOSACCHARIDE PRODUCTION FROM PRETREATED <i>Miscanthus</i> OF VARYING PARTICLE SIZE Esha Khullar University of Illinois	41
TECHNOECONOMIC ANALYSIS AND ENVIRONMENTAL IMPACT OF ETHANOL PRODUCTION FROM PERENNIAL RYEGRASS STRAW Deepak Kumar Oregon State University	43
CHEMICAL COMPOSITION OF LIGNOCELLULOSIC FEEDSTOCKS FROM PACIFIC NORTHWEST CONSERVATION BUFFERS Deepak Kumar Oregon State University	45
UNDERSTANDING AND ENHANCING ALKALINE AND OXIDATIVE CHEMICAL PRETREATMENTS FOR THE PRODUCTION OF CELLULOSIC BIOFUELS THROUGH IMPROVED CHARACTERIZATION Muyang Li Michigan State University	47
PRODUCTION OF BIOPOLYOLS AND POLYURETHANES FROM LIGNOCELLULOSIC BIOMASS AND CRUDE GLYCERIN Yebo Li Ohio State University	49
BIOBASED ENERGY EDUCATIONAL MATERIAL EXCHANGE SYSTEM (BEEMS) Yebo Li Ohio State University	51
VINASSE CONVERSION INTO AQUATIC FOODS VIA FUNGAL FERMENTATION Saoharit Nitayavardhana University of Hawaii	53
EFFECT OF FERTILIZATION AND GROWING SEASON ON CONSERVATION RESERVE PROGRAM (CRP) PASTURELAND AS A BIOFUEL FEEDSTOCK Tucker Porter Montana State University	55

## Table of Contents (cont.)

IMPACT OF TREATED EFFLUENT WATER USE IN CELLULOSIC ETHANOL PRODUCTION	Divya Ramachandran	University of Illinois	57
PRODUCING FURFURAL FROM BIOMASS IN AN INTEGRATED BIOREFINERY	Troy Runge	University of Wisconsin	59
EFFECT OF STEAM INJECTION LOCATION ON BIOMASS GENERATED PRODUCER GAS IN A FLUIDIZED BED GASIFIER	Ashokkumar Sharma	Oklahoma State University	61
GREEN PROCESSING OF TROPICAL GRASSES FOR BIOFUEL AND BIOPRODUCTS	Devin Takara	University of Hawaii	63
BIOBASED CONCRETE SEALANT	Bernard Tao	Purdue University	65
BIOMATERIALS AND BIOPROCESSING RESEARCH AT KANSAS STATE UNIVERSITY	Praveen Vadlani	Kansas State University	67
CLEMSON SUSTAINABLE BIOREFINERY	Terry Walker	Clemson University	69
BIOWINOL: CAPTURING RENEWABLE ELECTRICITY AND CARBON DIOXIDE FOR TRANSPORTATION FUEL	Mark Wilkins	Oklahoma State University	71
PRODUCTION OF FERMENTABLE SUGARS FROM EASTERN RED CEDAR	Mark Wilkins	Oklahoma State University	73
ESTABLISHMENT OF A THREE STAGE SOLID SUBSTRATE CULTIVATION FOR SOLVENT PRODUCTION USING CORN STOVER	Julia Yao	University of Kentucky	75
BIOMASS TO LIQUID HYDROCARBON PROCESS VIA CATALYTIC CONVERSION ON CARBON ENCAPSULATED IRON NANOPARTICLES	Fei Yu	Mississippi State University	77
<b>Author and Affiliation Index</b>			<b>79</b>

## **BIOMASS RESEARCH AND DEVELOPMENT INITIATIVE (BRDI) PROGRAM REVIEW**

Peter W. Arbuckle

BCE/NIFA/USDA, 1400 Independence Avenue SW, Washington, DC 20250  
(202-401-5741) parbuckle@nifa.usda.gov

Reauthorized by section 9001(a) of the Food, Conservation and Energy Act (FCEA) of 2008 (Pub. L. 110-246), the Biomass Research and Development Initiative (BRDI) fills an important gap in the continuum of technology development and commercialization supported by USDA and other federal programs. While meeting the requirements of section 9008(e) of FCEA, USDA has shaped the program to be a source of bridge funding for developing and emerging technologies to cross the “economic valley of death”. The program intent is to help develop and demonstrate technologies that meet the congressionally defined objectives to the point they might attract additional private or public financing to scale up and/or produce commercial quantities of biomass based energy and/or materials.

Using the FCEA, section 9008, as a guide, NIFA tracks award statistics that measure program performance relative to program administration requirements and program objectives defined by section 9008(e)(6). Over the life of the program, BRDI has met the requirement that each technical area, Feedstock Development, Biofuels and Biobased Product Development, and Biofuels Analysis, receive not less than 15% of available funds. BRDI also has fostered consortia awards averaging more than four collaborators per award. The program has attracted a diversity of applicant types from a number of locations. A typical BRDI award includes at least four collaborating organizations; the program has involved an average of 18 states per year.

In the early years of the BRDI program, grants were focused narrowly to address specific technical challenges and new product development issues. The program now supports larger and more comprehensive projects, which requires awardees to develop new products and technologies in the context of the supply chain and target markets; therefore, projects must address all three technical areas. The program has adopted an overarching theme of sustainability to foster desirable outcomes, by requiring awardees to address environmental, economic and social implications of the technology throughout its life cycle.

Progress toward the objectives of FCEA, section 9008, are monitored and documented through a series of independent project reviews administered through the University of Nebraska-Lincoln (UNL). UNL coordinates project reviews through site visits conducted by technical experts from the Multi-State Committee on Science and Engineering for a Biobased Industry and Economy (S-1041) and the USDA Agricultural Research Service (ARS). Project outputs and incremental progress toward program objectives are illustrated through the project reviews included in this report. BRDI technology priorities are broad and not prescriptive. Trends in BRDI investment are driven largely by trends in biomass based energy and materials markets. The program affords the flexibility for the balance of investment to shift toward technical challenges of increasing importance in the market. Project results provide anecdotal indications of industry progress and program impact.





# **SUSTAINABLE BIOENERGY PRODUCTION**

Ganti S. Murthy<sup>1</sup> and Andy Hashimoto<sup>2</sup>

<sup>1</sup>Biological and Ecological Engineering, Oregon State University, Corvallis, OR 97331  
(541-737-6291) murthyg@onid.orst.edu

and

<sup>2</sup>Molecular Biosciences and Bioengineering, University of Hawaii at Manoa,  
Honolulu, HI 96822  
(808-956-7531) andrew.hashimoto@hawaii.edu

## **ABSTRACT**

There is wide spread agreement that bioenergy systems must be sustainable. Also, there is general agreement that sustainability encompasses aspects of economics, environment and social/community. The challenge is to determine the appropriate indicators for the three aspects of sustainability, especially the environmental and social/community impacts. A discussion on sustainability metrics especially focused on the environmental and technoeconomic aspects will be presented. We will present details of some of the important global initiatives for sustainable bioenergy certification. We will discuss our methodology to address sustainability in our Biomass Research and Development Initiative (BRDI) project titled “Conversion of High Yield Tropical Biomass into Sustainable Biofuels”. We will discuss the rationale for the choice of the methodology and its relation to sustainability metrics. We will include a more general discussion on life cycle assessments and sustainability indicators. We hope to stimulate a robust discussion within S-1041 of appropriate sustainability indicators for the US, while at the same time being linked to global sustainability indices and indicators.

## **INTRODUCTION**

There is wide spread agreement that bioenergy systems must be sustainable. Also, there is general agreement that sustainability encompasses aspects of economics, environment and social/community. Although various definitions of sustainable systems have been proposed, a common notion of sustainability is defined as, “development that meets the needs of the present without compromising the ability of the future generations to meet their own need” (Brundtland Report, 1987).

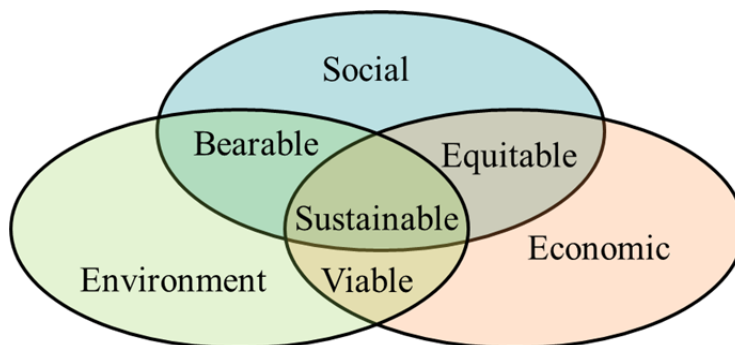
The objective is to present different assessment tools with a particular focus on economic and environmental aspects of bioenergy sustainability. A discussion will be presented to justify the methodological choices proposed to address sustainability in our recently funded Biomass Research and Development Initiative (BRDI) project titled “Conversion of High Yield Tropical Biomass into Sustainable Biofuels”.

## SUSTAINABILITY ASSESSMENT

A sustainable approach to bioenergy can be found at the intersection of all three aspects of sustainability namely, economic, environmental and social/community (Fig. 1). Thus it is important to have metrics to evaluate objectively and quantitatively sustainability. Many methodologies have been described to assess these three aspects of sustainability. However, much of the progress in the bioenergy sustainability assessment has been focused on economic and environmental aspects. In general, all three aspects of sustainable bioenergy must be considered (technoeconomic viability, environmental sustainability and social/community aspects) to evaluate a bioenergy processes.

### Economic Aspects of Sustainability

Economic aspects of sustainability can be refined further to include technical feasibility to demonstrate the influence of various technological alternatives available. For example, as demonstrated in our recent work, different pretreatment processes such as dilute acid, dilute alkali, hot water and steam explosion represent various technological choices available to produce the same biofuel (cellulosic ethanol) and have varying tradeoffs in terms of technical feasibility, economic viability and environmental impacts (Kumar and Murthy, 2011). Similarly, in the context of corn ethanol, it would mean the differences in technical feasibility and economic viability of using dry grind corn ethanol vs wet milling process to produce fuel ethanol.



**Figure 1. Aspects of Sustainable Bioenergy (Adapted from Adams, 2006).**

Technical feasibility and economic viability of a process/product is assessed using integrated technoeconomic analyses that often involve development of process models to conduct detailed mass and energy balances and perform economic calculations. Commercial software such as Aspen, SuperPro and Bioprocess simulators are used for process model development and conducting technoeconomic analyses. Accuracies of these factored estimates

are up to  $\pm 30\%$  and they are useful to compare process alternatives (Perry's Chemical Engineer's Handbook, 1997).

## Environmental Aspects of Sustainability

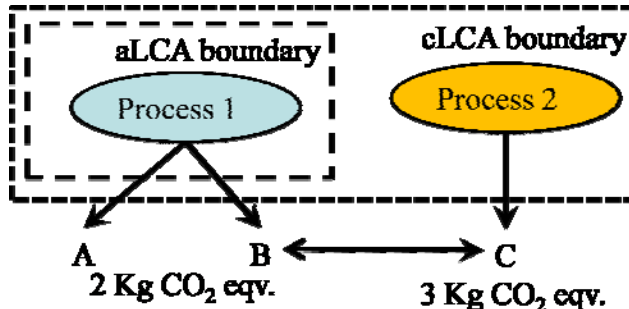
Methods to compare impacts of different products/processes on environment can be classified into process oriented metrics and environmental pressure oriented metrics. While process oriented metrics, such as life cycle assessment, are useful to assess competing technologies, environmental pressure oriented metrics, such as sustainable process index, are useful for assessing resources depletion. Life Cycle Assessment (LCA) is a tool to assess the potential environmental impacts and resources used throughout a product's life cycle, ie, from raw material acquisition, via production and use phases, to waste management (ISO, 2006). LCA is a comprehensive assessment and considers all attributes or aspects of natural environment, human health and resources (ISO, 2006). Special emphasis is placed in the LCA methodology to avoid problem shifting, for example, from one phase of life cycle to another or from one environmental problem to another. A classic example of problem shifting is hydrogen cars; although hydrogen cars themselves do not produce CO<sub>2</sub> emissions and may seem environmentally friendly, the picture is altered when viewed from a life cycle perspective that accounts for emissions from combustion of natural gas used to produce hydrogen.

LCA is divided into four stages: goal definition and scoping, life cycle

inventory, life cycle impact assessment and life cycle interpretation. There are two variants of LCA that answer different questions related to environmental sustainability. Attributional LCA (aLCA) is defined by its focus on describing the environmentally relevant physical flows to and from a life cycle and its subsystems. Consequential LCA (cLCA) is defined by its aim to describe how environmentally relevant flows will change in response to possible decisions (Curran et al, 2005; Earles and Halog, 2011). In other words, aLCA is used to answer the question: What are the total emissions from the process during the life cycle of the product?

### **Text box 1: Comparison of aLCA and cLCA**

Consider two processes, 1 and 2 which produce the products A, B and C. Assume that process 1 produces a coproduct B that can replace C on a 1:1 basis.



GHG Emissions for process 1:

aLCA: 2 Kg CO<sub>2</sub> eqv.

cLCA: -1 Kg CO<sub>2</sub> eqv. (2-3 as B replaces C).

It is important to note that while aLCA GHG emissions can never be negative, cLCA can have negative GHG emissions due to the inclusion of indirect effects. In the above example, replacement of a GHG intensive process (process 2) with a 'greener' process (process 1) results in net lower *marginal* emissions.

While cLCA is designed to answer the question: What is the change in total emissions from the process during the life cycle of the product? (Brander et al, 2006). An example to demonstrate differences between aLCA and cLCA is provided in the Text box 1.

The different focuses of aLCA and cLCA also is reflected in the use of average and marginal data in aLCA and cLCA, respectively (Tillman, 2000, Finneveden et al, 2009). In aLCA, average data for a system representing the average environmental burdens for producing a unit of the good and/or service in the system are used. In cLCA marginal data, which represent the effects of a unit change in the product/service output on all of the processes in an economy, are used to assess the consequences (Ekvall and Weidema, 2004).

Another major difference of importance between aLCA and cLCA is in the selection of system boundary. Many contrasting conclusions from LCA studies in the literature can be explained on the basis of system boundary selection and coproduct allocation methods (Wang, 2005). Therefore, it is of critical importance to select the system boundary on a rational, quantitative basis. An objective method that uses repeatable and verifiable quantitative criteria to delineate the system boundary in aLCA, called relative mass, energy and economic value (RMEE) method, was proposed by Reynolds (2000). Similarly, Schmidt (2008) proposed an objective method for delineating the system boundary in cLCA for agricultural systems. The system delineation in cLCA is even more important as the magnitude of uncertainties due to various interactions of socioeconomic factors is higher compared to aLCA. A comparison of differences between the aLCA and cLCA is presented in Table 1.

### **Summary of Global Initiatives to Assess Bioenergy Sustainability**

With increasing awareness and agreement on the need for sustainable bioenergy, various initiatives have been proposed and regulations have been enacted around the world. Recently, Dam et al (2011) provided an excellent review of the global efforts towards certification of sustainable bioenergy. Of more than 67 ongoing initiatives around the world, comparisons among the three major initiatives Renewable Fuel Standard II, RFS-II (US), European Union-Renewable Energy Directive, EU-RED (Europe) and Roundtable on Sustainable Biofuels, RSB (Europe) are presented in Tables 2 and 3.

One of the challenges with many of these initiatives is there is no clear distinction maintained between the aLCA and cLCA methodologies. Lack of such clear delineation often leads to metrics that can neither be classified as aLCA nor cLCA. For example, US RFS II uses aLCA (average data) for most of the LCA but also includes the indirect land use change (ILUC) which is an attribute of cLCA methodology. Use of ILUC by Searchinger et al (2008) to evaluate GHG emissions and subsequent critique of their analyses demonstrates the need for having clearly defined methodologies for performing LCA.

Recently Global Bioenergy Partnership (GBEP) formulated a set of 24 sustainability indicators that cover all three aspects of sustainability. GBEP indicators were developed in consultation with over 127 countries and UN, and hence were designed to have wide applicability to various bioenergy systems. Progress towards sustainability was designed to be assessed by measuring improvement in the metrics and therefore avoiding any contentious hard limits for various proposed metrics.

Table 1. Differences between aLC and cLCA (directly quoted from Brander et al, 2009).

	Attributional LCA (aLCA)	Consequential LCA (cLCA)
Question the methods aims to answer	What are the total emissions from the processes and material flows directly used in the life cycle of a product?	What is the change in the total emissions as a result of a marginal change in the production of a product?
Application	aLCA is applicable for understanding the emissions directly associated with the life cycle of a product.	cLCA is applicable for informing consumers and policy-makers on the change in total emissions from a purchasing or policy decision
System boundary	The processes and material flows directly used in the production, consumption and disposal of the product.	All processes and material flows which are directly or indirectly affected by a marginal change in the output of a product.
Marginal or average data	aLCA tends to use average data, e.g. the average carbon intensity of the electricity grid.	cLCA tends to use marginal data e.g. the marginal carbon intensity of the electricity grid.
Market effects	aLCA does not consider the market effects of the production and consumption of the product.	cLCA considers the market effects of the production and consumption of the product.
Allocation methods	aLCA allocates emissions to coproducts based on either economic value, energy content, or mass.	cLCA uses system expansion to quantify the effect of coproducts on emissions.
Non-market indirect effects	aLCA does not include other indirect effects.	cLCA should include all other indirect effects, such as the interactions with existing policies or the impact of R&D on the efficiency of the production of other products.
Time scales	aLCA aims to quantify the emissions attributable to a product at a given level of production at a given time.	cLCA aims to quantify the change in emissions which result from a change in production. It is necessary to specify the time-scale of the change, the means by which the change is promoted, and the magnitude of the change.
Uncertainty	aLCA has low uncertainty because the relationships between inputs and outputs are generally stoichiometric	cLCA is nearly always highly uncertain because it relies on models that seek to represent complex socio-economic systems that include feedback loops and random elements.

Table 2. GHG emissions criteria in three sustainable bioenergy initiatives (data from Dam et al, 2011).

Initiative	GHG Emissions Criteria	Functional unit	Scope	Allocation	Default values	ILUC	LUC	Selected time period
US RFS-II	Conventional biofuels: 20% Advanced biofuels: 50% Biomass-based diesel: 50% Cellulosic biofuel: 60% lifecycle GHG threshold (below gasoline)	GHG reduction (%) compared to fossil fuel	Renewable fuels	Displacement method	Results provided by the EPA	Yes	Yes	100 year with 2% discount rate OR 30 year with 0% discount rate
RSB	Biofuel shall have lower GHG emissions than the fossil fuel baseline and shall contribute to the minimization of overall GHG emissions. The threshold (10, 40 and 70% is under discussion) will be set at the conclusion of the test period	g CO <sub>2</sub> eq/MJ	Biofuels	Guidelines under development	Criteria for acceptable default values under development	?	Yes	Based on IPCC methodology
EC-RED	At least 35% GHG emission reduction compared to reference fuel Rising to 50% on January 2017 to 60% in 2018 for biofuels and bioliquids produced in installations in which production started on or after January 2017	g CO <sub>2</sub> eq/MJ	Biofuels and bioliquids	Based on energy content	Typical and default values	No	Yes	Annualized emissions based on 20 years

Table 3. Other criteria in three sustainable bioenergy initiatives (data from Dam et al, 2011).

Initiative	Biodiversity	Soil Quality	Water quality and quantity	Other environmental factors	Social aspects of workers and local communities
US RFS-II	No (except new plantings)	No	No	No	No
EC-RED	Yes (partially)	No	No	No (Except good farming practices)	No
RSB	Yes	Yes (partially)	Yes (partially)	Yes	Yes

## METHODOLOGIES FOR SUSTAINABILITY ASSESSMENT IN THE PROJECT

Overall goal of the sustainability assessment in the project is to guide the development of advanced biofuel production supply chain, with special emphasis on:

- 1) Supporting informed decision making of the project participants on approaches to improving sustainability metrics for a biorefinery enterprise in Hawaii by providing timely data driven guidance using an existing suite of tools for measuring and estimating economic, environmental and social impacts and
- 2) Adapting the framework of the Global Bioenergy Partnership 24 Sustainability Indicators (GBEP, 2011) to provide a systematic evaluation of the impact of biofuel production in the Hawaiian Islands.

To achieve this overall goal, the sustainability assessment in the project covers three important sustainability aspects. Detailed methodology for each of these aspects is presented below.

### Technoeconomic aspects of sustainability

Analyses of costs and returns for energy crop production, coproducts (front end derived juice as nutrient supplement, lignin for hydrogen production) and advanced biofuels will be performed. Annual equivalent costs and revenues will be calculated to account for the time value of money (Tran et al, 2011). Break even prices of energy crops, coproducts and advanced biofuels will be used as indicators of economic viability of the production/processing operations. The economic value of sequestering carbon will be measured using: 1) historical stock market prices of carbon and 2) estimating the energy value (\$/Btu) of carbon stock. The environmental value of carbon balance will be integrated into the economic analysis and results will be



analyzed along with results of energy accounting to determine the cost effectiveness of advanced biofuel production from energy crops.

Comprehensive technoeconomic analyses will be performed for conversion of energy crops to advanced biofuels using some of the most common pretreatment technologies (dilute acid and hot water). Process models incorporating feedstock handling, conversion to advanced biofuel, coproduct and wastewater handling will be developed. Detailed chemical oxygen demand (COD) and energy calculations will be performed for waste streams following organic acid recovery to determine the potential for methane production. Tradeoffs in capital, energy and water use exist in complex systems and will be dependent on several factors such as age at harvesting, pretreatment methods, fermentation parameters and factors governing thermochemical conversion of organic acids to advanced biofuels. Age at harvest is a critical factor in determining the ease of processing, product yields and overall net energy balance. Using process models developed in this task, various tradeoffs in capital costs, energy and water use and impact on product yields, production cost and net energy balance will be examined at different stages of growth of biomass. This will be used to guide decisions on determining appropriate harvest age and operational details for processing energy crops into advanced biofuels.

### **Environmental Aspects of Sustainability**

Despite their suitability to compare environmental impacts at individual farm and firm levels, aLCAs are unsuitable for understanding indirect effects of large scale production of biofuels as influenced by interaction effects and policy initiatives. cLCAs are designed to account for these interactions and thus are suitable to investigate environmental impacts of different policy choices, technology adoption behaviors of farmers and interaction effects. Differences between the aLCA and cLCA is important and can be a valuable source of information to different stakeholders if used properly. In the context of bioenergy and specifically this project, we envision that aLCA could be used by individual producers to assess the environmental impacts of their biofuel process compared to standard fuels such as gasoline. The cLCA performed as part of this project could be a useful aid in formulating policies as this method considers both direct and indirect effects of a process.

Therefore, we will conduct both aLCA and cLCA (Figs. 2 and 3) to provide different sets of information useful to both individual bioenergy processors and policy makers. Similarly, keeping in view that sustainability often is defined using different metrics in various initiatives, we have taken a data centric approach which will ensure that any postfacto assessment can be performed. Important questions such as overall net energy value (NEV) of advanced biofuels, use of fertilizers and pesticides, natural resources such as fresh water, impact on GHGs, NO<sub>x</sub> emissions, eutrophication, acidification and long term sustainability will be addressed in the

aLCA. These metrics are similar to the bioenergy sustainability indicators suggested by the Global Energy partnership. As discussed earlier, the GBEP sustainability indicators for bioenergy consist of 24 metrics to assess sustainability that consider various environmental, social and economic factors. Fifteen of these metrics will be measured in this project while four metrics are not relevant for the current scenario. Five metrics will be relevant for large scale implementation of the proposed technologies but will be measured to a limited extent, or not measured, as there will be insufficient data to measure the metrics with confidence (Table 4).

### **Social and Economic Aspects of Sustainability**

The Hawaii State IMPLAN (Impact Analysis for PLANning) model will be used to determine short and long term impacts on island communities. Evaluation over time is important to analyze structural changes that may occur in local communities. To examine more aggregate economic impacts from biofuels production (such as Napier grass), a computable general equilibrium (CGE) model is used to estimate statewide impacts (Coffman et al, 2007). The CGE model can be calibrated from an IMPLAN based social accounting matrix (SAM) (Holland et al, 2007). The CGE framework is appropriate for Hawaii since the State has a small, open economy.

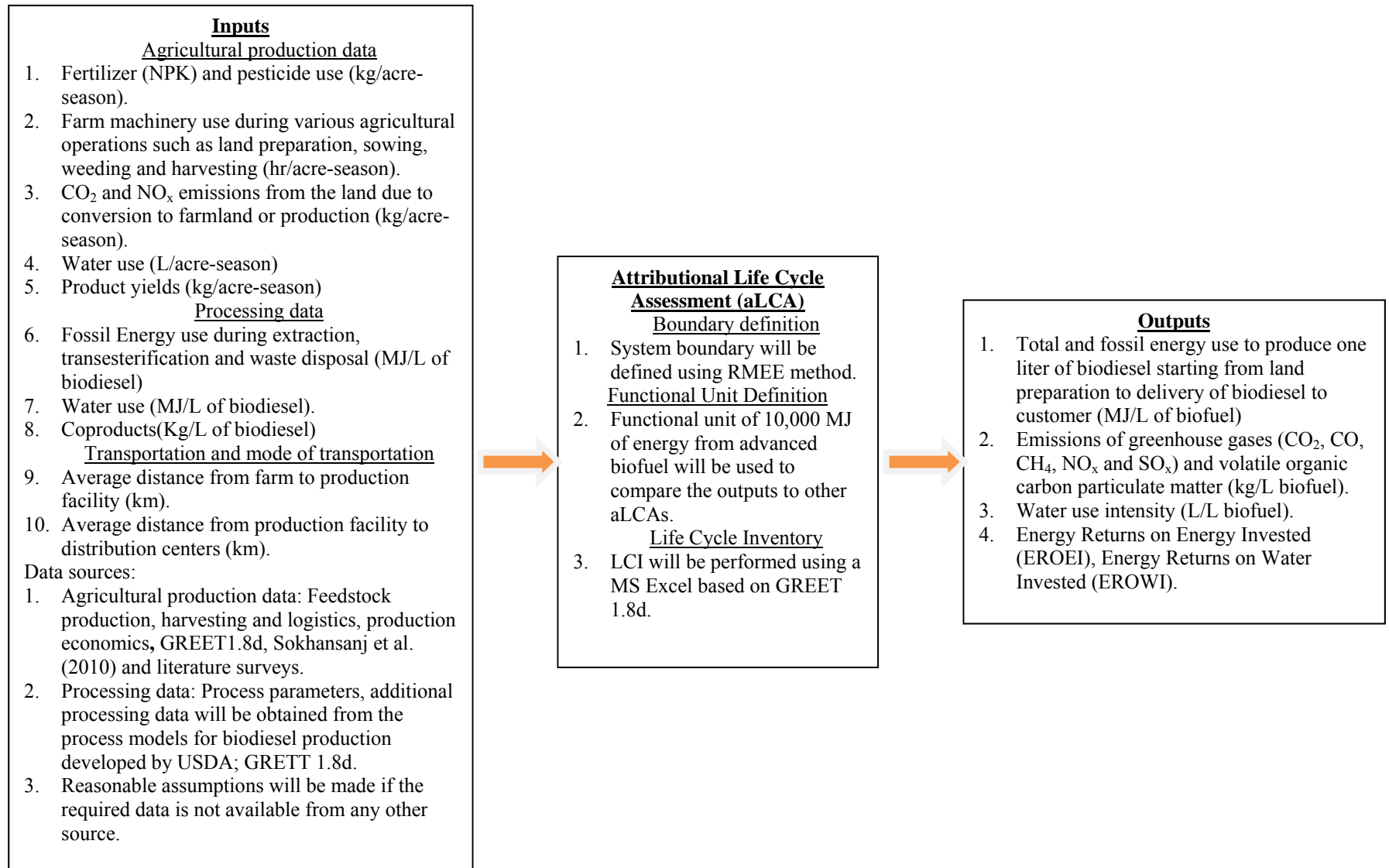


Fig. 2. Inputs and Outputs to aLCA.

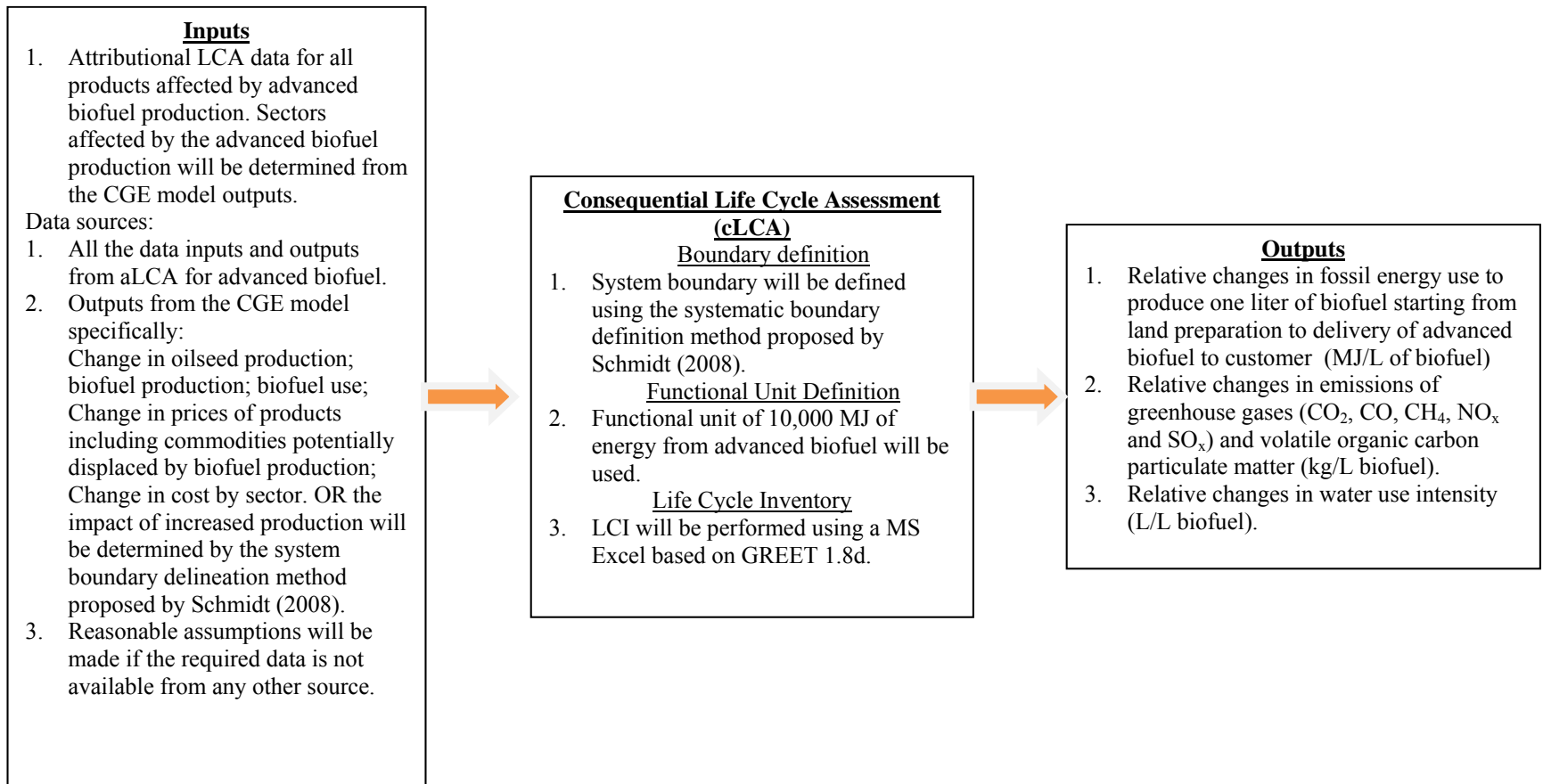


Fig. 3. Inputs and Outputs to cLCA.

Table 4. GBEP Sustainability Indicators for Bioenergy.

Environmental		Social		Economic	
Metric	Units	Metric	Units	Metric	Units
Life-cycle GHG Emissions	Grams of CO <sub>2</sub> equivalent per megajoule	Allocation and tenure of land for new bioenergy production	Percentage	Productivity	Tons/ha-year, MJ/ton, MJ/ha-year and USD/MJ
Soil quality	% change in soil organic carbon	Price and supply of a national food basket	Tons/year and USD/year	Net energy balance	Ratio
Harvest levels of wood resources	Tons/ha-year	Change in income	%	Gross value added	US\$/MJ
Emissions of non-GHG air pollutants, including air toxics	Emissions of PM <sub>2.5</sub> , PM <sub>10</sub> , NO <sub>x</sub> , SO <sub>2</sub> and other pollutants (mg/MJ bioenergy)	Jobs in bioenergy sector	Number of new jobs per MJ of bioenergy	Change in consumption of fossil fuels and traditional use of biomass	MJ/year
Water use and efficiency	m <sup>3</sup> /MJ of bioenergy	Change in unpaid time spent by women and children collecting biomass	Hours per week-household and %	Training and re-qualification of the workforce	%/year
Water quality	kg N, P and active ingredients per ha-year. BOD and COD from bioenergy processing plant.	Bioenergy used to expand access to modern energy services	MJ/year	Energy diversity	MJ bioenergy/year
Biological diversity in the landscape	Land (ha) in three priority areas as defined in GBEP methodology.	Change in mortality and burden of disease attributable to indoor smoke	%	Infrastructure and logistics for distribution of bioenergy	Number, MJ and percentage
Land use and land-use change related to bioenergy feedstock production	ha, ha/year and percentages as defined in GBEP methodology	Incidence of occupational injury, illness and fatalities	Number/MJ of bioenergy	Capacity and flexibility of use of bioenergy	Ratio

Legend:

Plain text: indicator measured in current project.

Light shading: indicator not measured/measured to a limited extent.

Dark shading: indicator not relevant for current project.

## CONCLUSIONS

A brief overview of various aspects of bioenergy sustainability assessment was presented. An introduction to various global initiatives for sustainability certification of bioenergy also was provided. A discussion elucidating the rationale for the methodological choices for our Biomass Research and Development Initiative project entitled “Conversion of High Yield Tropical Biomass into Sustainable Biofuels” was presented. Perhaps this short paper will be a stimulus for a robust discussion among S-1041 members of appropriate sustainability indicators for the US, while at the same time being linked to global sustainability indices and indicators.

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## **IMPLEMENTING SYSTEMS METHODOLOGIES FOR A SUSTAINABLE BIOBASED ECONOMY**

C. Lindsay Anderson<sup>1</sup>, Hasan K. Atiyeh<sup>2</sup>, Sergio Capareda<sup>3</sup>,  
Chengci Chen<sup>4</sup> and Deepak R. Keshwani<sup>5</sup>

<sup>1</sup>Biological and Environmental Engineering, Cornell University, Ithaca, NY 14850

<sup>2</sup>Biosystems and Agricultural Engineering, Oklahoma State University,

<sup>3</sup>Biological and Agricultural Engineering, Texas A&M University,

<sup>4</sup>Central Agricultural Research Center, Montana State University and

<sup>5</sup>Biological Systems Engineering, University of Nebraska-Lincoln  
(607-255-4533) landerson@cornell.edu

Scientific and technological basis of biobased industries are evolving rapidly, in part motivated by federally mandated targets. Even as the science continues to progress, there is doubt surrounding the optimal form of these industries, perhaps most importantly in terms of environmental and economic sustainability. There exist many sources of uncertainty including unknowns in the development of new technologies, status of government policy and evolution of markets and consumers. To develop a viable and sustainable biobased industry, early comprehensive analyses are essential to assist researchers, government personnel and other stakeholders in making informed and efficient decisions.

To assess alternatives, system level studies are required that will examine the sustainability implications of various elements of the biomass to bioproduct supply chain. This includes feedstocks supply, conversion technologies, product distribution and the myriad possible combinations among them. One of the reformulated objectives of the S-1041 multistate research plan will be to develop and apply advanced system level analyses to assess the sustainability of a comprehensive set of biobased products and industries. These assessments can provide the guidance for efficient scientific and technological efforts moving forward.

Achievement of this objective will require contribution and cooperation from a number of participating institutions. Contributions will include specific process and product knowledge, experimental data and modeling expertise through various objective based tasks.



# **BIOMASS FEEDSTOCK SUPPLY LOGISTICS**

Alvin R. Womac

Biosystems Engineering, Tennessee Agricultural Experiment Station  
2506 E. J. Chapman Drive, University of Tennessee, Knoxville TN 37996  
(865-974-7266) awomac@utk.edu  
www.biomassprocessing.org    www.biomasslogistics.org

## **INTRODUCTION**

The abundant, economical supply of biomass feedstock delivered with predictable specifications that meet conversion needs is a critical step towards developing a biobased economy. The required scale and biomass diversity exceed the capacity of current agricultural/forestry logistic supplies. This remarkable quantity redefines the scope for growing, harvesting, storing, transporting and processing feedstock. Biomass type and availability depends on climate and growth conditions by geographic location. In general, biomass from agricultural, forestry and energy crop sources is characterized by high moisture content, low bulk density and variable seasonal yields. Identification and evaluation of biomass feedstock and availability, characterization of biomass properties and development of engineered systems that harvest, store, preprocess and deliver biomass require new fundamental knowledge, processes and logistics systems. A key emphasis is the system must renewably supply, on a sustained basis, the abundant and inexpensive feedstock at an annual billion ton capacity to meet US renewable energy requirements.

## **PAST EFFORTS**

Past efforts generally have been focused on isolated aspects of the feedstock supply chain. Plant breeders improved biomass yield, drought resistance, pest tolerance or other traits desirable for production. Engineers improved databases of biomass properties for moisture content, bulk density, size reduction energy and other basic properties. Engineers evaluated existing hay, forage and forest harvest/collection equipment for compatibility with some biomass crops. Tub and horizontal feed grinders, hammer mills and kinetic energy mills were evaluated for suitable operating conditions, energy use and particle sizes. In some instances, novel devices for loading and handling bales of biomass formed with agricultural balers were conceptualized or

tested. Generally, biomass sources and harvest/processing equipment were tested under limited test conditions and evaluated as a unit operation, and were not tested on a holistic, supply chain basis. Acceptable ranges of biomass supply specifications for conversion were not available. Hence, the supply chain was based on best guess targets. Feedstock quality was monitored at harvest, storage and/or preprocessing stages.

## **PRESENT RESEARCH**

Present feedstock supply chain research has improved the evaluation of overall supply chain logistics that integrates basic unit processes. For example, five supply systems were developed for evaluation as DOE High Tonnage Grant projects that involved members of this multistate project (<http://energy.gov/articles/doe-selects-biofuels-projects-receive-21-million-funding>). Bale format, bulk format and forest product supply systems were selected for evaluation of harvest, storage, transport and supply logistics to targeted biorefineries. Logistics involved biomass physical properties coupled with the efficient use of equipment systems for moving biomass. GPS on vehicles often was used for tracking purposes. In some cases, improved unit operations were developed as a result of the holistic approach. Research needs of commercial scale feedstock supply chains were identified better than by only focusing on a unit operation. Biorefinery partners helped evaluate biomass specifications. Projects provided a platform to use the Integrated Biomass Supply and Logistics (IBSAL) model developed by Oak Ridge National Laboratory (ORNL) and applied to each project for a uniform comparison basis.

The first generation of cellulosic fuel biorefineries is now underway. Industry representatives have revealed many questions associated with acceptable biomass specifications. Based on limited data, there is a trend the biomass storage should minimize biomass exposure to excessive precipitation. Biomass that gets wet, and stays wet, first loses the potential sugars necessary for biochemical conversion processes. Some members of the multistate project have agreements with Idaho National Laboratory (INL) which is developing biomass commodity feedstock supply systems. The idea is to use existing commodity scale solids handling infrastructure for biomass processed at local depots near production fields. INL developed a deployable process demonstration unit (PDU) that includes modules for bale decomposition, drying, grinding and densification. Emphasis was placed on high density, bulk flowability and aerobic stability. The PDU includes pelleting which creates high bulk densities useful for long distance transport. Input material ultimately will consist of wheat straw, barley straw, rice straw, corn stover, switchgrass, miscanthus, wood products and biowaste.

## **FUTURE NEEDS**

Within the multistate project, there is expertise to address four critical feedstock logistics needs:

1. **Reduced costs:** Current supply systems, especially for agricultural residues or dedicated energy crops, deliver biomass at costs typically ranging from \$60 to 100 per dry ton, not including grower payment. Exact costs depend on assumptions regarding capital expenditures, other equipment applications, annual utilization and a host of other details. However, most will agree that overall costs must be reduced to entice substantial investment in biorefineries and feedstock delivery systems.
2. **Sustainable production:** In depth agronomic knowledge of the wide possible array of biomass production crops is lacking to make well informed decisions about selecting and investing in crop stands, especially perennials. Sustainability of large plantings based on expected nutrient management, pest control, climate conditions, stand suitability for harvest and impact on water and air quality, integration with other crops, grower acceptance and other indices is not well documented.
3. **New equipment and storage technologies:** Current feedstock supply logistics relies on equipment developed and improved over many years for forage crops typically used on farm. In general, biomass crops require harvesters that have improved robustness to handle increased stem lengths and sizes. Densification systems need increased throughput capacity and the ability to retain confining stresses with minimal impact on throughput. High capacity storage systems are needed to reduce the required footprint for annual harvests and to reduce biomass exposure to precipitation.
4. **Optimization:** Knowledge to optimize the feedstock logistics system is lacking. An example is the integration of feedstock logistics and biorefinery conversion. First, as biomass quality increases, and particle size decreases, costs increase. A complete curve of this benefit cost curve is lacking, but a few data points are available. On the other hand, a biorefinery is expected to increase production and decrease cost per unit as biomass quality increases and particle size decreases. Since there are few operational biorefineries, the benefit cost curve is not apparent. Optimization involves examining the combined benefit cost curves, one for feedstock supply and the other for the biorefinery conversion process.



## **EDUCATION: BIOENERGY AND SUSTAINABLE TECHNOLOGY DISTANCE EDUCATION GRADUATE CERTIFICATE**

Danielle Julie Carrier<sup>1</sup> and Charles West<sup>2</sup>

<sup>1</sup>Biological and Agricultural Engineering and <sup>2</sup>Crop and Environmental Sciences,  
University of Arkansas, Fayetteville, AR 72701  
(479-575-2351) carrier@uark.edu

The American Graduate Education System is efficient, robust and credible, and is in part responsible for giving a research and development edge to the American economy. The American Graduate Education System is a national pipeline that has trained the 20<sup>th</sup> century workforce and is in the process of preparing the 21<sup>st</sup> century workforce, which will need to develop innovative solutions to many of our sustainable development problems. Everyone wants clean water and food, shelter and ways of earning a living. The context in which to offer this quality of life is different than from the Second World War. In the 21<sup>st</sup> century, we are experiencing shrinking resources and expanding population, which restrict the confines of the design sandbox. Our nation's colleges and universities are key to developing long term sustainable solutions to these colossal growth challenges. Unfortunately, most public institutions and many private ones have been forced to reduce expenses, leaving less money to train and educate students.

It is difficult for one single university to offer graduate courses in each discipline or topic. It is in that spirit that Kansas State, Oklahoma State and South Dakota State Universities, and the University of Arkansas, all S-1041 participants, formed a partnership to design an on line graduate certificate in bioenergy and sustainable technology (BST). This certificate will be instrumental in training a new generation of professionals to be equipped to function in the interdisciplinary environment typical of sustainable biomass supply chains, biotechnologies and energy conversion technologies. The BST certificate is affiliated with Great Plains-AG IDEA and is governed by its structure. The BST certificate is for professionals who already hold an undergraduate degree in any field, not specifically in science or engineering. We will present an overview of the BST certificate.





## **BIOENERGY/BIOPRODUCT PRODUCTION AND PROCESSES: SUMMARY OF RESEARCH ACTIVITIES OF S-1041**

Bernie Tao

Agricultural and Biological Engineering, Purdue University,  
225 South University Street, West Lafayette, IN 47907  
(765-494-1183) tao@purdue.edu

Research on developing novel biobased processes for energy and materials requires a highly diverse set of scientific and technological expertise, often beyond the experience of a single researcher or group. It encompasses everything from fundamental molecular biology to biomass production to processing to energy/product conversion/delivery and environmental management. It incorporates a variety of geographical, economic and industrial settings. To address these needs requires the diversity of research and collaboration found in the S-1041 group personnel. We will provide a summary of bioenergy/bioproducts research activities of the S-1041 researchers, highlighting their achievements and accomplishments as well as collaborations.



## **THERMOCHEMICAL CONVERSION AND REVISION OF OBJECTIVE 2**

Roger Ruan and Paul Chen

Center for Biorefining and Bioproducts and Biosystems Engineering,  
University of Minnesota, St. Paul, MN 55108  
(612-625-1710) ruanx001@umn.edu

Agricultural and forest byproducts and residues, specialty energy crops, algae and municipal wastes are potential feedstocks for production of renewable energy. Thermochemical processes, such as pyrolysis, gasification, hydrothermal liquefaction and torrefaction, are efficient ways to convert solid wastes to energy and biochar. Current status of these processes will be reviewed. The needs and methods for stabilizing and upgrading of primary conversion products, eg, bio-oil or bio-crude, will be presented. The technical challenges with these processes also will be discussed. In addition, revision of S-1041 Objective 2 (pretreatment, conversion and product development of biological and thermochemical processes) with inputs from participating university representatives will be summarized.



# **HYBRID THERMOCHEMICAL-BIOCHEMICAL PROCESSING FOR BIORENEWABLE ALCOHOL PRODUCTION USING *Alkalibaculum bacchi***

Hasan K. Atiyeh<sup>1</sup>, Kan Liu<sup>1</sup>, Ralph S. Tanner<sup>2</sup>, Mark R. Wilkins<sup>1</sup> and Raymond L. Huhnke<sup>1</sup>

<sup>1</sup>Biosystems and Agricultural Engineering, Oklahoma State University,  
Stillwater, OK 74078 and

<sup>2</sup>Botany and Microbiology, University of Oklahoma, Norman, OK  
(405-744-8397) hasan.atiyeh@okstate.edu

Lignocellulosic ethanol can be produced via either the biochemical, thermochemical or hybrid thermochemical-biochemical platforms. The hybrid platform utilizes gasification-fermentation. In gasification, the biomass is gasified into producer gas (CO, H<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>). Particulates and inhibitors are cleaned from producer gas, which is fermented using acetogens to produce ethanol, butanol and other coproducts. The primary advantage of the hybrid conversion process over the biochemical or thermochemical platforms is a complete utilization of cellulose, hemicellulose and lignin components of the biomass into producer gas, leading to a greater potential for alcohol production per unit of biomass. In addition, producer gas fermentation operates near ambient pressure and temperature. The hybrid process has several challenges that our team is tackling including gas-liquid mass transfer and low productivity related to low cell density. *Alkalibaculum bacchi* strain CP15 was discovered recently in our laboratories to produce ethanol and acetic acid from producer gas. Standard yeast extract (YE), an expensive medium, was used in our previous studies. To improve the economical feasibility of producer gas fermentation, the YE medium was replaced with low cost corn steep liquor (CSL). Fermentations with YE and CSL media were compared. CSL medium produced twofold more ethanol compared to YE medium. In addition, over 94% of the medium cost was reduced using CSL, which was indicative of the potential use as a cost effective nutrient for producer gas fermentation at a large scale.



## FOULING RATES OF SYNTHETIC THIN STILLAGE

Ravi Challa<sup>1</sup>, David B. Johnston<sup>2</sup>, Vijay Singh<sup>1</sup>,  
M. E. Tumbleson<sup>1</sup>, Nicki J. Engeseth<sup>3</sup> and Kent D. Rausch<sup>1</sup>

<sup>1</sup>Agricultural and Biological Engineering,

University of Illinois at Urbana-Champaign, Urbana, IL 61801,

<sup>2</sup>Eastern Regional Research Center, Agricultural Research Service, USDA, Wyndmoor, PA and

<sup>3</sup>Food Science and Human Nutrition, University of Illinois at Urbana-Champaign  
(217-265-0697) krausch@illinois.edu

In the US, fuel ethanol is produced by two processes: dry grind (86%) and wet milling (14%) [1]. Ethanol production has become more energy efficient with innovative energy saving methods, which reduced the energy requirements per liter ethanol from 33.4 MJ in 1981 to 7.2 MJ in 2008 [1]. Thin stillage is one of the coproducts from the dry grind process. It is concentrated to form condensed distillers solubles (25 to 30% total solids, w/w) in multiple effect evaporators [2]. Undesirable deposits on heat transfer surfaces increases resistance to heat transmission and decreases energy efficiency [3]. Costs associated with fouling include: labor and equipment needed to clean fouled heat transfer surfaces, increased capital, antifoulant chemicals, production loss and environmental impact of chemical disposal from equipment cleaning. To make ethanol production more sustainable it is important to make the dry grind process economical. Proteins, carbohydrates, fats and fiber may cause evaporator fouling; studies published in corn processing have been limited [2, 4, 5, 6]. None of these researchers has determined which thin stillage components causes evaporator fouling. Our objective was to investigate fouling tendencies of individual thin stillage components. Composite fouling is difficult to understand as interactions among fluid particles and heat transfer surfaces are complex. Synthetic fluids were prepared with model components of thin stillage (eg, starch). Effects of starch and glucose composition in a synthetic thin stillage fluid on fouling resistance ( $R_f$ ) were studied. Effects of total solids content (1 to 10% db) on  $R_f$  were investigated. Fouling resistance of starch and glucose or both was investigated to understand interactions among them under various evaporator conditions. In this synthetic thin stillage system, starch had a larger effect on fouling than glucose. Glucose alone did not foul the probe but had an effect in combination with starch at 10% total solids.

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**AUTOHYDROLYSIS OF *Miscanthus x giganteus*  
FOR THE PRODUCTION OF XYLOOLIGOSACCHARIDE (XOS):  
PRODUCT CHARACTERISTICS AND RECOVERY**

Ming-Hsu Chen<sup>1</sup>, Bruce S. Dien<sup>2</sup>, Kent D. Rausch<sup>1</sup>, M. E. Tumbleson<sup>1</sup> and Vijay Singh<sup>1</sup>

<sup>1</sup>Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign,  
Urbana, IL 61801 and <sup>2</sup>NCAUR/ARS/USDA, Peoria, IL 61604  
(217-333-9510) vsingh@illinois.edu

*Miscanthus x giganteus* (MG), a perennial grass, has potential as a new bioenergy crop due to its cellulose and hemicellulose content. Currently, MG has been tested in central Illinois and has been reported to attain an average yield of 36 MT/ha/year [1]. The process for converting MG to ethanol only is not cost effective and not ready for commercialization. There is a need to make this process more economical by recovering high value coproducts in addition to ethanol. Xylooligosaccharides (XOS) are sugar oligomers made from xylose units and can be produced during the hydrolysis of xylan, one of the main hemicellulose components. The growing commercial importance of these nondigestive sugar oligomers is based on their prebiotic effect to human health. We recovered XOS through an autohydrolysis process using MG. *Miscanthus* from the University of Illinois research farm was oven dried overnight to 2.6% moisture and milled to pass through a 0.25 mm screen. The raw material consisted of 35.9% glucan, 19.5% xylan, 2.1% arabinan, 19.6% lignin, 11.3% extractives and 1.8% ash. Hot water pretreatment was performed in a 25 mL tubular reactor with solid:liquid ratio (1:9); temperatures varied from 140 to 200°C. XOS could be produced effectively at 160, 180 and 200°C at different reaction times. Depending upon reaction conditions, XOS yields up to 13.9% (w/w) of initial dry biomass and 71.4% (w/w) of initial xylan were observed. In gel permeation chromatography (GPC), molecular weight distribution migrations at different reaction times and temperatures were observed. Using water/ethanol solutions at the ratio of 50:50 and 30:70 could recover effectively XOS from carbon adsorption.

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## **MICROWAVE ASSISTED PYROLYSIS OF MICROALGAE FOR RENEWABLE BIO-OIL PRODUCTION**

Zhenyi Du, Yanling Cheng, Xiangyang Lin, Paul Chen and Roger Ruan

Center for Biorefining and Department of Bioproducts and Biosystems Engineering,  
University of Minnesota, 1390 Eckles Ave., St. Paul, MN 55108  
(612-625-1710) ruanx001@umn.edu

Microalgae recently received much attention in the field of biofuels production due to its numerous advantages, such as high biomass production, high lipids content, CO<sub>2</sub> sequestration and potential for wastewater treatment. However, most algae utilization researchers are concentrating on biodiesel production through conventional transesterification processes. There are few reports about bio-oils production from pyrolysis of microalgae. The pyrolysis of *Chlorella* sp. was carried out in a microwave oven with char as microwave reception enhancer. Liquid product from microwave assisted pyrolysis (MAP) was a mixture of an oil phase and a water phase which separated automatically. Maximum bio-oil yield of 28.6% was achieved under the microwave power of 750 W. Bio-oil properties were characterized with elemental, GC-MS, GPC, FTIR and thermogravimetric analyses. Algal bio-oil had a density of 0.98 kg/L, a viscosity of 61.2 cSt, pH of 9.5 and a higher heating value (HHV) of 30.7 MJ/kg. Using GC-MS we showed the bio-oils were composed mainly of aliphatic and aromatic hydrocarbons, phenols, long chain fatty acids and nitrogenated compounds, among which aliphatic and aromatic hydrocarbons (22.18 % of the total GC-MS spectrum area) are desirable compounds as those in crude oil, gasoline and diesel. Fast growing algae are a promising source of feedstock for advanced renewable fuels production via MAP.



# **BIO-OIL FROM SWITCHGRASS PYROLYSIS: UPGRADE TO TRANSPORTATION FUEL BY HYDROGENATION AND CATALYTIC TREATMENT**

Tahmina Imam and Sergio Capareda

Biological and Agricultural Engineering, Texas A&M University,  
College Station, TX 77840  
(979-458-3028) scapareda@tamu.edu

Bio-oil produced from biomass conversion through pyrolysis is a useful product and can be a promising alternative source of energy. This product may be upgraded to biobased gasoline, diesel and jet fuels. The chemical composition of bio-oil is complex, and is composed of water, organics and small amounts of ash. Stabilizing these bio-oil products includes lowering the oxygen content, reducing acidity, removing char and reducing moisture. Without the upgrade process, bio-oil is unstable and difficult to flow for ease of transport. The objective of this research was to upgrade pyrolyzed bio-oil into transportation fuel, such as gasoline, by fractionation and hydrogenation using catalysts, such as palladium and nickel, at controlled temperature and pressure. A plug flow reactor in a continuous system was used for maximal oxygen removal and high catalytic activity. Detailed hydrocarbon analysis (DHA) of bio-oil and products at each upgrading step was performed. Finally, products were compared to gasoline through ASTM gasoline standard tests: thermal stability, diene number and gum. If bio-oil can be upgraded to transportation fuel that would have a favorable environmental impact, gasoline from our research could be used as a replacement for petroleum fuel.



## COMPARISON OF MONOSACCHARIDE PRODUCTION FROM PRETREATED *MISCANTHUS* OF VARYING PARTICLE SIZE

Esha Khullar<sup>1</sup>, Bruce S. Dien<sup>2</sup>, Kent D. Rausch<sup>1</sup>, M. E. Tumbleson<sup>1</sup> and Vijay Singh<sup>1</sup>

<sup>1</sup>University of Illinois at Urbana-Champaign, Urbana, IL 61801  
and <sup>2</sup>NCAUR/ARS/USDA, Peoria, IL 61604  
(217-333-9510) vsingh@illinois.edu

The effect of particle size on enzymatic hydrolysis of pretreated *Miscanthus x giganteus* was determined. *Miscanthus* was ground using a hammer mill equipped with screens having 0.08, 2.0 or 6.0 mm openings. Particle size distribution and geometric mean diameters were determined. Ground samples were subjected to hot water, dilute acid or dilute ammonium hydroxide pretreatment. Enzyme hydrolysis was conducted on washed pretreated solids; sugar generation was used as a measure for pretreatment efficiency. Glucose and xylose concentrations were monitored using HPLC. Glucose and xylose profiles were generated and hydrolysis rates estimated. Glucan, xylan and total conversion yields were determined by comparing final sugar concentrations obtained to theoretical amounts present in raw biomass.

Geometric mean diameters were the smallest from 0.08 mm sieve screen (56  $\mu\text{m}$ ) followed by 2.0 mm (301  $\mu\text{m}$ ) and 6.0 mm (695  $\mu\text{m}$ ) screens. Across all pretreatments, an increase in total polysaccharide conversion (12 to 26%) was observed when particle size was decreased from 6.0 to 0.08 mm. Enzyme hydrolysis of unpretreated biomass samples also resulted in increased total conversions as particle size decreased, although mean conversions (10 to 20%) were lower than for pretreated biomass samples (40 to 70%), indicating the need for chemical pretreatments in biomass conversion.





# **TECHNOECONOMIC ANALYSIS AND ENVIRONMENTAL IMPACT OF ETHANOL PRODUCTION FROM PERENNIAL RYEGRASS STRAW**

Deepak Kumar and Ganti S. Murthy

Biological and Ecological Engineering, Oregon State University, Corvallis, OR 97331  
(541-737-6291) murthyg@onid.orst.edu

Bioethanol, an important renewable transportation fuel, can be produced in large quantities from fermentation of sugars derived from hydrolysis of lignocellulosic feedstocks. Technoeconomic feasibility and environmental sustainability play a vital role in determining the overall suitability of a feedstock and conversion process for producing cellulosic ethanol. Our aim was to evaluate economic viability and environmental impact of ethanol production from perennial ryegrass (*Lolium perenne* L.) straw. Perennial ryegrass straw, a coproduct of grass seed production, contains 26% cellulose, 13% hemicellulose and 14% lignin. A comprehensive well to pump life cycle assessment was performed to investigate the overall net energy balance and greenhouse gas emissions during ethanol production from straw. A process model for an ethanol plant with a processing capacity of 250,000 metric ton biomass/ year, incorporating feedstock handling, dilute acid pretreatment, simultaneous saccharification and cofermentation, ethanol recovery, coproduct utilization and waste water treatment was developed using SuperPro Designer (Intelligen, Inc.). Ethanol yield and production capacity were estimated to be 250.7 L/dry metric ton of biomass and 58.2 million L/year, respectively. Initial capital investment, annual operating cost and production cost of ethanol were estimated as \$114.9 MM, \$48.5 MM and \$0.83/L of ethanol, respectively. Energy from lignin residue (26.8 MJ/L ethanol) was more than that of steam energy (19.1 MJ/L ethanol) used in the plant. Grass straw (21.45 ¢/L ethanol) and cellulase enzymes (11.2 ¢/L ethanol) were the main contributors in the total material cost. Fossil energy required and GHG emissions during life cycle of ethanol production were estimated as 4283 MJ and -228 kg CO<sub>2</sub> equivalent per 10,000 MJ of ethanol, respectively.



## **CHEMICAL COMPOSITION OF LIGNOCELLULOSIC FEEDSTOCKS FROM PACIFIC NORTHWEST CONSERVATION BUFFERS**

Deepak Kumar<sup>1</sup>, Ankita Juneja<sup>1</sup>, William Hohenschuh<sup>1</sup>, John D. Williams<sup>2</sup> and Ganti S. Murthy<sup>1</sup>

<sup>1</sup>Biological and Ecological Engineering, Oregon State University, Corvallis, OR 97331 and

<sup>2</sup>Columbia Plateau Conservation Research Center, ARS/USDA, Pendleton, OR 97801  
(541-737-6291) murthyg@onid.orst.edu

Bioethanol is an important alternative to liquid transportation fuels due to advantages such as compatibility with current infrastructure, comparable energy values and lower net life cycle greenhouse gas emissions. Development of sustainable feedstocks that can be used for bioethanol production and contribute to renewable energy is a critical need. Conservation reserve program (CRP) was initiated for controlling soil erosion and providing other ecological benefits. Currently, 2.5 to 3.0 million acres in the Pacific Northwest region are under this program. Biomass harvested from these lands could contribute to total available biomass for bioethanol industry. Our aim was to determine the chemical composition of common plant species found in Pacific Northwest Conservation buffers. Nine feedstocks (two grass and seven forb species) commonly found in these buffers were examined to determine their chemical composition and potential bioethanol yields. Samples were collected from areas planted to simulate conservation buffers alongside stream channels within three common resource areas in the interior Pacific Northwest. Composition was determined as per laboratory analysis protocols from the National Renewable Energy Laboratory. Composition differences for total glucan (19.39 to 33%), xylan (7.03 to 20.31%) and lignin content (10 to 18%) were found among the nine feedstocks. Potential maximum ethanol yields ranged from 182 to 316 L/dry ton of biomass for different plant species.



# **UNDERSTANDING AND ENHANCING ALKALINE AND OXIDATIVE CHEMICAL PRETREATMENTS FOR THE PRODUCTION OF CELLULOSIC BIOFUELS THROUGH IMPROVED CHARACTERIZATION**

Muyang Li<sup>1,2</sup>, Daniel Williams<sup>2,3</sup>, Charles Chen<sup>3</sup>, Zhenglun Li<sup>2,3</sup>,  
Trey Sato<sup>2</sup>, Tongjun Liu<sup>2</sup> and David Hodge<sup>1,2,3,4</sup>

<sup>1</sup>Biosystems and Agricultural Engineering,

<sup>2</sup>Great Lakes Bioenergy Research Center,

<sup>3</sup>Chemical Engineering and Materials Science,

Michigan State University, East Lansing, MI 48824 and

<sup>4</sup>Chemical Engineering, Luleå University of Technology, Luleå, Sweden  
(517-353-4508) hodgeda@egr.msu.edu

We will present recent research on improving technologies for oxidative chemical pretreatments and alkaline fractionation of plant biomass. One theme underlying this research is how improved characterization of the chemical, structural and physical changes to the plant cell wall and the spectrum of compounds solubilized from the cell wall can better inform technologies for plant cell wall deconstruction and conversion to renewable fuels and chemicals. Our work will span four areas: 1) characterizing how lignin properties (S/G ratio, *p*-hydroxycinnamic acid content and total lignin content) and their alteration during alkaline hydrogen peroxide (AHP) pretreatment impacts enzymatic digestibility for grasses with diverse lignin phenotypes, 2) identifying the spectrum of fermentation inhibitors generated by AHP pretreatment of grasses for high sugar concentration fermentation by xylose fermenting *Saccharomyces cerevisiae* strains and demonstration of improved xylose fermentation and hydrolyzate tolerance through evolutionary engineering and 3) quantifying the impact of AHP pretreatment on plant cell wall water swelling capacity and how the water-cell wall environment influences its susceptibility to enzymatic hydrolysis.



# **PRODUCTION OF BIOPOLYOLS AND POLYURETHANES FROM LIGNOCELLULOSIC BIOMASS AND CRUDE GLYCERIN**

Yebo Li

Ohio State University, 1680 Madison Ave, Wooster, OH 44691  
(330-263-3855) li.851@osu.edu

Flexible and rigid petroleum based polyurethane foams are their most common applications; they can be found in automotive, construction and insulation industries, among others. To combat concerns over the depletion of global petroleum reserves and rising petroleum prices, extensive research has been conducted to produce biobased polyols (biopolyols) from renewable sources to replace conventional petroleum based polyols. Biopolyols from soy and vegetable oil have been an attractive alternative but will continue to compete with demand for foodstuffs. A compelling substitute to natural oil and petroleum based feedstock is crude glycerin. Crude glycerin is a byproduct of the biodiesel production process and differs from pure glycerin in composition due to the presence of various impurities. Because crude glycerin is an inexpensive feedstock, it has the potential to produce biopolyol products at a cost competitive with petroleum based polyol products. Since 2008, researchers at Ohio State University / Ohio Agricultural Research and Development Center have developed a one pot catalytic process for the production of biopolyols from crude glycerin and biomass.





## **BIOBASED ENERGY EDUCATIONAL MATERIAL EXCHANGE SYSTEM (BEEMS)**

Yebo Li<sup>1</sup>, Scott Pryor<sup>2</sup>, Wei Liao<sup>3</sup>, Brian He<sup>4</sup>, Abolghasem Shahbazi<sup>5</sup>,  
Lijun Wang<sup>5</sup>, Ann Christy<sup>1</sup>, Fred Michel<sup>1</sup> and Thaddeus Ezeji<sup>1</sup>

<sup>1</sup>Ohio State University, Wooster, OH 44691; <sup>2</sup>North Dakota State University,  
<sup>3</sup>Michigan State University, <sup>4</sup>University of Idaho and <sup>5</sup>NC A&T State University  
(330-263-3855) li.851@osu.edu

Project members have noted that new courses related to biobased energy are introduced regularly around the country. There are few resources adequately synthesizing information in this diverse and changing field. Compiling expertise and course materials from existing courses would help those instructors currently teaching courses and those who will offer a new course at their institution. Team members are developing a biobased energy education material exchange system for faculty members to share course materials and encourage student interaction among institutions. Course materials such as PowerPoint slides, homework exercises and examination problems also will be developed by team members. Thus far, we have developed PowerPoint modules for eight (8) topics: biomass pretreatment; enzymatic conversion; biodiesel; sugar based and starch based ethanol; biobutanol; anaerobic digestion; biomass gasification and biomass pyrolysis. More than 30 faculty members currently teaching biobased energy related courses are reviewing and using these modules in their classes. The following six (6) modules are under development: algae; liquefaction; physical, chemical and structural properties; fermentation; microbial fuel cells and feedstock logistics. We expect to have up to 50 faculty members using BEEMS for their bioenergy teaching. Hopefully, this program will reduce teaching preparation time by 50% via sharing of course materials, improve the quality of the biobased energy courses among member universities and increase student enrollment in such courses (up to 1,000 students are enrolled annually in courses utilizing BEEMS).



## VINASSE CONVERSION INTO AQUATIC FOODS VIA FUNGAL FERMENTATION

Saoharit Nitayavardhana and Samir K. Khanal

Molecular Biosciences and Bioengineering (MBBE), University of Hawai'i at Mānoa  
1955 East-West Road, Agricultural Science Building 218, Honolulu, HI 96822  
(808-956-3812) [khanal@hawaii.edu](mailto:khanal@hawaii.edu)

We examined the potential for large scale production of an edible fungus, *Rhizopus oligosporus*, on vinasse, a liquid waste stream generated during sugar to ethanol production. An airlift bioreactor (2.5 L working volume) was used for cultivating the fungus on 75% (v/v) vinasse with nutrient supplementation (nitrogen and phosphorus) at 37°C and pH 5.0 (an optimal fungal growth condition on vinasse). Aeration rates were varied from 0.5 to 2.0  $\text{volume}_{\text{air}}/\text{volume}_{\text{liquid}}/\text{min}$  (vvm). Fungal biomass yield depended on aeration rate; an aeration rate of 1.5 vvm resulted in the highest fungal biomass yield of  $8.0 \pm 0.8 \text{ g}_{\text{biomass increase}}/\text{g}_{\text{initial biomass}}$ . Influent organic matter, measured as soluble chemical oxygen demand (SCOD), was reduced by 80% (26 g/L). Reduction in organic content was suggestive of a potential for recycling treated effluent as process water for in plant use or land application as fertirrigation. Fungal biomass can be processed into ingredients for aquatic feed applications as it contains 50% crude protein and comparable amounts of essential amino acids to commercial protein sources for aquatic feeds (fishmeal and soybean meal). Cofeeding fungal biomass with commercial protein could address the problem of low methionine and phenylalanine in fungal biomass. Further, utilizing the low value vinasse would provide an unique sustainable option for a sugar to ethanol biorefinery by providing an additional source of revenue from its residue with concomitant waste treatment.



## **EFFECT OF FERTILIZATION AND GROWING SEASON ON CONSERVATION RESERVE PROGRAM (CRP) PASTURELAND AS A BIOFUEL FEEDSTOCK**

Tucker Porter, Chengci Chen, Rick Lawrence and Bok Sowell

Montana State University, P.O. Box 172900, Bozeman, MT 59717  
(406-570-1387) tucker.f.porter@gmail.com

US Secretaries of Agriculture and Energy established a national goal that by 2030 biomass will supply 5% of the nation's power, 20% of its transportation fuels and 25% of its chemicals. Perennial forage crop species are considered to be the future ideal bioenergy feedstock. Achieving the goal will require more than one billion dry tons of biomass feedstock annually, a fivefold increase over the current consumption. Researchers suggest agricultural land can provide nearly one billion dry tons of sustainably collectable biomass while continuing to meet food, feed and export demands. We present an investigation using forage from Conservation Reserve Program (CRP) land as potential biofuel feedstock source. We investigated nitrogen fertilizer, harvest timing affecting the biomass yield, species composition and biomass characteristics of plant materials on CRP land in central Montana with grass and alfalfa mixture. In addition, remote sensing techniques were used to predict biomass yields at different growing stages. Through more efficient methods of determining above ground plant biomass production will allow land managers to make more informed ecological and economic decisions, and allow bioenergy industry to predict feedstock availability for biorefineries.



## **IMPACT OF TREATED EFFLUENT WATER USE IN CELLULOSIC ETHANOL PRODUCTION**

Divya Ramachandran, Kishore Rajagopalan, Timothy J. Strathmann and Vijay Singh

University of Illinois at Urbana-Champaign, Urbana, IL 61801  
(217-333-9510) vsingh@illinois.edu

The bioethanol industry exerts a significant demand on water supplies. Current water consumption rates in corn dry grind ethanol plants is 3 to 4 gallons of water per gallon of ethanol produced (gal/gal) and 6 to 10 gal/gal for cellulosic ethanol plants. The main goal of this study was to examine the use of treated wastewater effluent in place of potable freshwater for cellulosic ethanol production. The effects of using two types of filtered treated effluent, Bloomington-Normal, IL (residential type) and Decatur, IL (industrial/residential mix type), on fermentation rates and final ethanol yields from a pure cellulosic substrate were evaluated. Final ethanol concentrations with Bloomington-Normal and Decatur effluents and our control study using deionized water were similar, resulting in  $4.57 \pm 0.22$  % v/v (0.36 g/g, db),  $4.74 \pm 0.13$  % v/v (0.37 g/g, db) and  $4.55 \pm 0.28$  % v/v (0.36 g/g, db), respectively. Residual glucose concentrations were  $<0.04\%$  w/v at 48 hr in all cases, suggesting complete fermentation.

Further study with Decatur effluent using 0.08 mm finely ground *Miscanthus* as the substrate resulted in a final ethanol concentration of  $0.46 \pm 0.008$  % v/v (0.14 g/g db) which was similar to an ethanol concentration of  $0.52 \pm 0.07$  % v/v (0.17 g/g db) obtained with a control treatment using deionized water. With proper characterization studies and under appropriate conditions, the use of treated effluent water in cellulosic ethanol production is feasible.





## **PRODUCING FURFURAL FROM BIOMASS IN AN INTEGRATED BIOREFINERY**

Troy Runge and Anurag Mandalika

Biological Systems Engineering, University of Wisconsin-Madison,  
460 Henry Mall, Madison, WI 53706  
(608-890-3143) mandalika@wisc.edu

The pentose fraction of biomass is an ideal candidate for utilization in biorefineries to produce fuels, energy and materials. The 5 carbon sugars are difficult to ferment in ethanol plants and are hydrolyzed easily, making them susceptible to loss in processes such as pulp production. Additionally, pentosans are reactive, enabling their extraction from biomass and conversion into furans and organic acids. We evaluated a novel process of creating furfural, a useful platform chemical, from biomass and compared its viability to other methods. Our process fractionates biomass into a hexosan rich stream for producing paper and a pentosan rich liquid stream. The latter is converted into furfural, catalyzed by sulfuric acid, followed by vapor phase separation of furfural. Conventional batch furfural production process is characterized by high losses due to formation of resinous substances called humins leading to theoretical yields of 50%. Our new process, in which both biomass separation and furfural separation strategies are used, creates both higher yield of furfural, in excess of 80%, and also creates a hexosan rich stream that can be used to create high value products such as ethanol or pulp. Condensation of furfural/water vapors produces a fairly pure but dilute furfural product, providing the possibility of converting it into other products, such as furfuryl alcohol, by biological conversion. Therefore, there exists potential for conversion of pulp mills into integrated biorefineries that produce one or more value added coproducts.



## **EFFECT OF STEAM INJECTION LOCATION ON BIOMASS GENERATED PRODUCER GAS IN A FLUIDIZED BED GASIFIER**

Ashokkumar M. Sharma, Ajay Kumar and Raymond L. Huhnke

Biosystems and Agricultural Engineering, Oklahoma State University, Stillwater, OK 74078  
228 Agricultural Hall, Stillwater, OK 74078  
(405-744-8396) [ajay.kumar@okstate.edu](mailto:ajay.kumar@okstate.edu)

Synthesis of liquid fuels and chemicals requires a producer gas with different concentrations of H<sub>2</sub>, CO and CO<sub>2</sub>. For a fluidized bed gasifier, reaction conditions vary along the height of the reactor. In addition, steam injection location can have an effect on the quality of biomass generated gas. Our objective was to determine the effects of steam injection location on producer gas composition, tar and particulates content, and gasifier efficiency. Air-steam gasification of switchgrass was performed in a laboratory scale fluidized bed reactor with internal diameter of 102 mm. Experimental design included three steam injection locations and three steam to biomass ratios. Steam injection locations were at the heights of 51, 152 and 254 mm above the air distributor plate. Steam to biomass ratios were 0.1, 0.2 and 0.3. There was a significant ( $p < 0.05$ ) effect of steam injection location on producer gas CO content, as well as cold and hot gas efficiencies. However, producer gas H<sub>2</sub> content, carbon conversion efficiency, and tar and particulates contents were not dependent on steam injection location. The best gas quality (9.8% H<sub>2</sub> and 17.9% CO) and gasifier performance (75% cold gas efficiency and 80% hot gas efficiency) were observed when steam was injected at 254 mm and using a steam to biomass ratio of 0.1. Maximum carbon conversion efficiency of 98% was observed at a steam injection location of 254 mm and using a steam to biomass ratio of 0.3.



## **GREEN PROCESSING OF TROPICAL GRASSES FOR BIOFUEL AND BIOPRODUCTS**

Devin Takara, Andrew G. Hashimoto and Samir K. Khanal

Molecular Biosciences and Bioengineering,  
University of Hawaii, Honolulu, HI 96822  
(808-956-3812) [khanal@hawaii.edu](mailto:khanal@hawaii.edu)

*Pennisetum purpureum*, banagrass, is a perennial species that has been naturalized in Hawaii and resembles the former state staple crop, sugarcane. Because of its high moisture content, banagrass presents a unique opportunity for fractionation into valuable solid and liquid components via green processing. The resulting clean, solid fibers serve as a substrate for advanced biofuel production, while the green, nutrient rich liquids (juice) serve as a supplemental additive for microbial coproduct generation. As banagrass matures, changes may occur in its biochemical composition, subsequently affecting biofuel and bioproduct production. Current conversion practices of lignocellulosic feedstocks (to biofuel) use dilute acid pretreatments to weaken plant fibers and facilitate deconstruction to fermentable monomeric sugars (precursors of biofuel) via cellulolytic enzymes. In this study, banagrass was hand harvested from Waimanalo, HI, at ages of 2, 4, 6 and 8 mo and passed through a commercial cutting mill for initial size reduction. Banagrass was passed through a screw press, under 40 psi of pneumatic backpressure, for fractionation into solid and liquid components. Solid fibers were pretreated under optimal conditions (5% w/w sulfuric acid, 120°C, 45 min) and saccharified enzymatically. Banagrass juice, for nutrient supplementation in microbial bioproduct formation, was collected and analyzed on the basis of chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN) and pH. The results of this study have implications in the technoeconomic feasibility of biorefineries in Hawaii and other subtropical regions of the world.



## **BIOBASED CONCRETE SEALANT**

Bernard Tao<sup>1</sup>, Jason Weiss<sup>2</sup>, Michael Golias<sup>2</sup>, Javier Castro<sup>2</sup>,  
Alva Peled<sup>2</sup>, Tommy Nantung<sup>3</sup> and Paul Imbrock<sup>2</sup>

<sup>1</sup>Agricultural and Biological Engineering, Purdue University,  
<sup>2</sup>Civil Engineering, Purdue University, West Lafayette, IN 47907 and  
<sup>3</sup>Indiana Department of Transportation  
(765-494-1183) tao@purdue.edu

Concrete is used globally for buildings, roads, bridges and consumer housing. With 30 billion tons of concrete produced annually, the industry is one of the major energy consumers/carbon dioxide producers in the world. While concrete is one of the most durable construction materials available, its durability suffers from corrosion/degradation, often caused by moisture ingress which can result in decreased performance life. This is particularly relevant in cold climates, due to freeze-thaw expansion. Additionally, salts used on roadways to melt ice can accelerate corrosion of both concrete and reinforced concrete.

We will present results from our work in developing an effective biobased concrete sealant using soy methyl esters and polystyrene. In exposure to over 300 freeze-thaw cycles, these biobased sealants have demonstrated performance benefits vs current reactive silane-based sealants. The biobased sealant also demonstrated superior protection from salt ingress and preliminary results were indicative it may retard/prevent concrete spalling. The cost of this sealant is lower than current reactive silane sealants and may extend the performance life of concrete by up to 30%. Industrial/commercial testing of this biobased sealant is underway by the Indiana Department of Transportation and private concrete companies.





## **BIOMATERIALS AND BIOPROCESSING RESEARCH AT KANSAS STATE UNIVERSITY**

Praveen V. Vadlani<sup>1</sup>, Xiuzhi Susan Sun<sup>1</sup> and Donghai Wang<sup>2</sup>

<sup>1</sup>Grain Science and Industry and <sup>2</sup>Biological and Agricultural Engineering  
Kansas State University, Manhattan, KS 66506  
(785-532-5012) vadlani@ksu.edu

Biomaterials and bioprocessing research is being conducted in two research laboratories (Bioprocessing and Renewable Energy Laboratory (BPRL), Biomaterials and Technology Laboratory (BTL)) at Kansas State University. BPRL, directed by Praveen Vadlani, Grain Science and Industry, is focused on efficient utilization of agricultural resources available in the state of Kansas and conversion of those resources into value added biofuels and biochemicals. The laboratory is equipped with a state of the art facility to perform enzymatic and microbial bioprocessing and analyses of raw materials and products. BTL, directed by Susan Sun, Grain Science and Industry, and Donghai Wang, Biological and Agricultural Engineering, is a multifunctional laboratory focused on basic and applied research in biobased materials and bioenergy, training graduate students with interdisciplinary skills in this field and developing enabling technologies for environmentally friendly biobased products. BTL has advanced facilities and professional staff, allowing for performing design, formulation, processing, analyzing and testing of various biobased monomers, polymers, materials and fuels, as well as converting low cost biorenewable materials to value added products.

We will highlight research projects directed by the three principal investigators. Dr. Vadlani's research includes: 1) D(-)lactic acid production from paper residues, 2) yeast oil biosynthesis from biomass derived sugars, 3) effect of biomass pelleting on ethanol production and 4) soy meal bioprocessing to premium animal food products. Dr. Sun's research includes: 1) morphology and structure of hydrophobic protein polymers, 2) protein nanomaterials, 3) soy protein adhesives, 4) biocomposites and bionanocomposites and 5) resins from plant oils. Dr. Wang's research includes: 1) acid functionalized nanoparticles for cellulose hydrolysis, 2) processing photoperiod sensitive sorghum for ethanol, 3) synchrotron X-ray scattering study of biomass structure and 4) development of biobased adhesives from canola protein.



## **CLEMSON SUSTAINABLE BIOREFINERY**

Terry Walker

Biosystems Engineering, Clemson University, Clemson, SC 29634  
(864-656-0351) walker4@clemson.edu

The Clemson University Sustainable Bioenergy Initiative has created a biorefinery concept that ranges from laboratory to pilot and full scale facilities. The facility now converts all used cooking oils on campus to biodiesel which has displaced 30% of diesel used by the campus fleet. The facility has production of up to 5,000 gallons per year while using both solar and biodiesel power generation to power the facility off grid. The sustainable bioenergy complex also includes close collaboration with the Clemson Student Organic Farm where a black soldier fly digester has been implemented to produce biofuels and food for aquaculture. The aquaculture ponds currently are under renovation to produce algal based biofuels and foods with a coupled photobioreactor/greenhouse partitioned aquaculture/hydroponic pond system to be powered by a combination of solar, gasification and biodiesel generator. A full scale 10 MW biomass gasification plant feasibility study currently is taking place that will tie into the proposed Clemson University Sustainable Bioenergy Center to link many of the projects on campus as a means to meet the goals of a net zero carbon emissions campus as part of the Clemson President's Climate Commitment.



## **BIOWINOL: CAPTURING RENEWABLE ELECTRICITY AND CARBON DIOXIDE FOR TRANSPORTATION FUEL**

Mark Wilkins<sup>1</sup>, Dimple Kundiyana<sup>2</sup>, Karthikeyan Ramachandriya<sup>1</sup>, Jennine Terrill<sup>3</sup>,  
Xiaoguang Zhu<sup>1</sup>, Kan Liu<sup>1</sup>, Hasan Atiyeh<sup>1</sup> and Raymond Huhnke<sup>1</sup>

<sup>1</sup>Biosystems and Agricultural Engineering, Oklahoma State University, Stillwater, OK 74078

<sup>2</sup>E & J Gallo Winery, Modesto, CA, and

<sup>3</sup>Coskata, Inc., Warrenville, IL

(405-744-8416) mark.wilkins@okstate.edu

Many renewable electricity sources (eg, wind and solar energy) are available only at certain times, which may not coincide with the times of highest demand. As a result, efforts to develop storage methods to store electricity produced during times of low demand are being pursued. The BioWinol concept is a microbial process utilizing hydrogen produced from renewable electricity and carbon dioxide from industrial gas emissions to produce ethanol. In the initial development of BioWinol, laboratory scale experiments were conducted using two microorganisms (*Clostridium carboxidivorans* and *Clostridium ragsdalei*) which previously have been shown to produce ethanol from H<sub>2</sub>/CO<sub>2</sub> mixtures. Various feed-gas compositions and culture media components also were tested. *C. carboxidivorans* produced more ethanol than *C. ragsdalei*. After 15 days, a maximum of 2.66 gL<sup>-1</sup> of ethanol was produced by *C. carboxidivorans* vs 2.00 gL<sup>-1</sup> by *C. ragsdalei*. Another valuable product, n-butanol, was produced at a concentration of 0.7 gL<sup>-1</sup> by *C. carboxidivorans*. It was observed the expensive medium used in previous laboratory experiments with *C. carboxidivorans* can be replaced with a simple medium of 0.5 gL<sup>-1</sup> of cotton seed extract without a loss of ethanol or butanol production. The laboratory scale experiments were conducted in serum bottles with limited volumes of gas, which resulted in low productivity.



## **PRODUCTION OF FERMENTABLE SUGARS FROM EASTERN RED CEDAR**

Mark R. Wilkins, Karthikeyan D. Ramachandriya,  
S. Hiziroglu, N.T. Dunford and Hasan K. Atiyeh

Biosystems and Agricultural Engineering, Oklahoma State University, Stillwater, OK 74078  
(405-744-8416) mark.wilkins@okstate.edu

Eastern red cedar is the most widely distributed indigenous conifer in the Central Plains; its invasiveness has brought many ecological concerns to farmers, ranchers and wildlife species. Conversion of red cedar polysaccharides into fermentable sugars is a viable option to provide value to red cedar and produce biofuel and/or chemicals. Acid bisulfite pretreatment was used to pretreat red cedar. Use of 3.75 g sulfuric acid/100 g dry wood and 20 g sodium bisulfite/100 g dry wood, a dry wood to liquid ratio of 1:5, 200°C and a reaction time of 20 min was found to achieve the highest conversion of glucan to glucose in pretreated wood by cellulase (0.5 g enzyme/g glucan, Accelerase 1500). However, 45% of glucan in untreated wood was lost during pretreatment. To prevent glucan loss during pretreatment, reaction time during pretreatments was reduced. Reaction times of 5 and 10 min were compared to a control of 20 min. Wood glucan to glucose yield from enzymatic hydrolysis (0.5 g enzyme/g glucan, Accelerase 1500) was the response variable used for comparison. Highly digestible biomass (90% digestibility) and low glucan loss (6%) was achieved when a pretreatment time of 10 min was used. This condition resulted in the highest wood glucan to glucose yield of 85%. Highly digestible material was achieved due to removal of lignin and hemicellulose from the biomass. In the future, we will focus on the statistical optimization of the pretreatment process with focus on reducing chemical loading to reduce the cost of the process.





## **ESTABLISHMENT OF A THREE STAGE SOLID SUBSTRATE CULTIVATION FOR SOLVENT PRODUCTION USING CORN STOVER**

Julia Yao<sup>1</sup>, Sue E. Nokes<sup>1</sup>, Michael Flythe<sup>2</sup>, Bert Lynn<sup>3</sup>, Dawn Kato<sup>3</sup>, Mike Montross<sup>1</sup>

<sup>1</sup>Biosystems and Agricultural Engineering, <sup>2</sup>ARS/USDA and <sup>3</sup>Department of Chemistry, 215 C.E. Barnhart Building, University of Kentucky, Lexington, KY 40546 (859-257-3000) sue.nokes@uky.edu

Production of biochemicals from lignocellulose is of interest to replace chemicals produced from petroleum. To improve biochemical marketability, research is focused on efforts to improve production efficiency and yield from lignocellulosic feedstocks. We adopted microbial pretreatment of corn stover by solid substrate cultivation (SSC) using *Phanerochaete chrysosporium* to degrade lignin in the pretreatment stage. Thereafter, we directly inoculated *Clostridium thermocellum* into the pretreated biomass to accomplish hydrolysis, followed by acetone/butanol/ethanol production initiated by introducing *Clostridium beijerinckii*. Our hypothesis is that microbial fermentation by SSC is a low cost, environmentally friendly process which can be used as a model and extended to other types of biomass, demonstrating a potential to be an on farm alternative for biochemical production.

Process parameters, ie, the effects of substrate moisture content and culture temperature on lignin degradation, culture time for each of the three phases, availability of carbohydrates and solvents production were monitored and examined to determine the optimal process for profitability. The yield of reducing sugar produced by *Clostridium thermocellum* on biomass pretreated with *Phanerochaete chrysosporium* was increased two fold as compared with biomass which was not pretreated. A comprehensive comparison among pretreated biomass and nonpretreated biomass (corn stover, *Miscanthus*, switch grass and wheat straw) using the three stage SSC for solvent production will be explored to evaluate the applicability of the established model to other biomass.



# **BIOMASS TO LIQUID HYDROCARBON PROCESS VIA CATALYTIC CONVERSION ON CARBON ENCAPSULATED IRON NANOPARTICLES**

Fei Yu and Eugene Columbus

Agricultural and Biological Engineering, Mississippi State University,  
Mississippi State, MS 39762  
(662-325-0206) fyu@abe.msstate.edu

There are several strategies to convert syngas to fuels and chemicals. Fischer-Tropsch (FT) synthesis is the major part of gas to liquids (GTL) technology, which converts syngas into liquid fuels with a wide range of liquid hydrocarbons and high value added chemicals. However, FT products are controlled by the Anderson-Schulz-Flory (ASF) polymerization kinetics, resulting in a nonselective formation of hydrocarbons. Another approach is to convert syngas to methanol over a hydrogenation catalyst and subsequently polymerize methanol to hydrocarbons over ZSM-5. Currently, many investigators have demonstrated the advantages of one stage processes by using bifunctional catalysts compared with two stage and three stage processes of synthesis gas conversion to gasoline.

The use of a bifunctional catalyst allows for simultaneously carrying out the synthesis of methanol from syngas over the metallic function and the transformation of methanol into hydrocarbons over the acidic function. Fulfillment of both steps in the same reaction medium promotes displacement of the thermodynamic equilibrium of methanol synthesis. Also, the shape selectivity of the acidic function provides a high selectivity that cannot be reached in the Fischer-Tropsch synthesis. Moreover, previous syngas to gasoline technologies are based on using pure syngas or low nitrogen syngas, which are derived from natural gas or coal. There are a limited number of publications using nitrogen rich producer gas to produce hydrocarbons. In this research, the existing downdraft gasifier at Mississippi State University is generating producer gas from lignocellulosic biomass feedstocks. Currently, biomass derived producer gas contains about 20% hydrogen, 19% CO, 12% CO<sub>2</sub>, 2% CH<sub>4</sub> and 49% N<sub>2</sub>. The N<sub>2</sub> and CO<sub>2</sub> contents are too high for the hydrocarbon synthesis if we use existing technologies. Developing high activity and high stability catalysts is the key for a better overall performance when using the biomass derived producer gas. A series of new catalysts with high activity and high stability are being developed for a single stage hydrocarbon mixture production process from biomass derived nitrogen rich producer gas. We demonstrated the process of biomass to aviation biofuels via gasification and catalytic conversion.



## Author and Affiliation Index

<b>Author</b>	<b>Affiliation</b>	<b>Page</b>
Anderson, C. Lindsay	Cornell University	19
Arbuckle, Peter W.	NIFA/USDA	1
Atiyeh, Hasan K.	Oklahoma State University	19, 31, 71, 73
Capareda, Sergio	Texas A&M University	19, 39
Carrier, Danielle Julie	University of Arkansas	25
Castro, Javier	Purdue University	65
Challa, Ravi	University of Illinois	33
Chen, Charles	Michigan State University	47
Chen, Chengci	Montana State University	19, 55
Chen, Ming-Hsu	University of Illinois	35
Chen, Paul	University of Minnesota	29, 37
Cheng, Yanling	University of Minnesota	37
Christy, Ann	Ohio State University	51
Columbus, Eugene	Mississippi State University	77
Dien, Bruce S.	NCUAR/ARS/USDA	35, 41
Du, Zhenyi	University of Minnesota	37
Dunford, N.T.	Oklahoma State University	73
Engeseth, Nicki J.	University of Illinois	33
Ezeji, Thaddeus	Ohio State University	51
Flythe, Michael	ARS/USDA, Lexington, KY	75
Golias, Michael	Purdue University	65
Hashimoto, Andrew G.	University of Hawaii	3, 63
He, Brian	University of Idaho	51
Hiziroglu, S.	Oklahoma State University	73
Hodge, David	Michigan State University	47
Hohenschuh, William	Oregon State University	45
Huhnke, Raymond L.	Oklahoma State University	31, 61, 71
Imam, Tahmina	Texas A&M University	39
Imbrock, Paul	Purdue University	65
Johnston, David B.	ERRC/ARS/USDA	33
Juneja, Ankita	Oregon State University	45
Kato, Dawn	University of Kentucky	75
Keshwani, Deepak R.	University of Nebraska	19

<b>Author</b>	<b>Affiliation</b>	<b>Page</b>
Khanal, Samir K.	University of Hawaii	53, 63
Khullar, Esha	University of Illinois	41
Kumar, Ajay	Oklahoma State University	61
Kumar, Deepak	Oregon State University	43, 45
Kundiyanana, Dimple	E & J Gallo Winery	71
Lawrence, Rick	Montana State University	55
Li, Muiyang	Michigan State University	47
Li, Yebo	Ohio State University	49, 51
Li, Zhenglun	Michigan State University	47
Liao, Wei	Michigan State University	51
Lin, Xiangyang	University of Minnesota	37
Liu, Kan	Oklahoma State University	31, 71
Liu, Tongjun	Great Lakes Bioenergy Research	47
Lynn, Bert	University of Kentucky	75
Mandalika, Anurag	University of Wisconsin-Madison	59
Michel, Fred	Ohio State University	51
Montross, Mike	University of Kentucky	75
Murthy, Ganti S.	Oregon State University	3, 42, 45
Nantung, Tommy	Indiana Department of Transportation	65
Nitayavardhana, Saoharit	University of Hawaii	53
Nokes, Sue E.	University of Kentucky	75
Peled, Alva	Purdue University	65
Porter, Tucker	Montana State University	55
Pryor, Scott	North Dakota State University	51
Rajagopalan, Kishore	University of Illinois	57
Ramachandran, Divya	University of Illinois	57
Ramachandriya, Karthikeyan	Oklahoma State University	71, 73
Rausch, Kent D.	University of Illinois	33, 35, 41
Ruan, Roger	University of Minnesota	29, 37
Runge, Troy	University of Wisconsin-Madison	59
Sato, Trey	Great Lakes Bioenergy Research	47
Shahbazi, Abolghasem	North Carolina A&T State University	51
Sharma, Ashokkumar M.	Oklahoma State University	61
Singh, Vijay	University of Illinois	33, 35, 41, 57
Sowell, Bok	Montana State University	55
Strathmann, Timothy J.	University of Illinois	57
Sun, Xiuzhi Susan	Kansas State University	67

<b>Author</b>	<b>Affiliation</b>	<b>Page</b>
Takara, Devin	University of Hawaii	63
Tanner, Ralph S.	Oklahoma State University	31
Tao, Bernard	Purdue University	27, 65
Terrill, Jennine	Coskata	71
Tumbleson, M. E.	University of Illinois	33, 35, 41
Vadlani, Praveen V.	Kansas State University	67
Walker, Terry	Clemson University	69
Wang, Donghai	Kansas State University	67
Wang, Lijun	North Carolina A&T University	51
Weiss, Jason	Purdue University	65
West, Charles	University of Arkansas	25
Wilkins, Mark R.	Oklahoma State University	31, 71, 73
Williams, Daniel	Michigan State University	47
Williams, John D.	CPCRC/ARS/USDA	45
Womac, Alvin R.	University of Tennessee	21
Yao, Julia	University of Kentucky	75
Yu, Fei	Mississippi State University	77
Zhu, Xiaoguang	Oklahoma State University	71