Biomass Program

2007 Accomplishments Report

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Biomass Program Accomplishments

Introduction

The Office of Energy Efficiency and Renewable Energy's (EERE's) Biomass Program works with industry, academia and its national laboratory partners on a balanced portfolio of research in biomass feedstocks and conversion technologies. Through research, development, and demonstration efforts geared toward the development of integrated biorefineries, the Biomass Program is helping transform the nation's renewable and abundant biomass resources into cost-competitive high-performance biofuels, bioproducts, and biopower.

The Biomass Program conducts R&D in cooperation with a Project Management Center hosted at the Department of Energy's Golden Field Office in Colorado. Project work is conducted at national laboratories across the country, including the National Renewable Energy Laboratory, Argonne National Laboratory, Oak Ridge National Laboratory, and Pacific Northwest National Laboratory. In addition, across technology areas, the Program seeks to collaborate with industry and academia to conduct R&D and integrate their programmatic feedback. Recent partners have included ADM, DuPont, Abengoa and multiple large university groups including the Sun Grant Universities. R&D projects are also conducted by groups from across the spectrum of organizations at local, state, regional and interagency levels. International activities (i.e., Memoranda of Understanding with Brazil and China) round out the Program's approach to efficient and timely fulfillment of its goals.

Program Goal

To develop cost-competitive biomass technologies to enable the production of biofuels nationwide and reduce dependence on oil through the creation of a new domestic bioindustry supporting the President's goal of reducing gasoline use 20 percent by 2017.

The U.S. Department of Energy (DOE) recognizes the importance of a diverse energy portfolio in meeting the nation's energy security challenges. DOE has, therefore, set a goal in its Strategic Plan to promote energy security through a diverse energy supply that is reliable, clean, and affordable. As a key strategy for attaining both Presidential and Department goals, the EERE's Biomass Program is focused on developing biofuel, bioproduct and biopower technologies in partnership with other government agencies, industry and academia.

The Biomass Program supports four key priorities of the EERE Strategic Plan:

- Dramatically reduce dependence on foreign oil;
- Promote the use of diverse, domestic and sustainable energy resources;
- Reduce carbon emissions from energy production and consumption; and
- Establish a domestic bioindustry,

Biomass is the single renewable resource that has the potential to supplant our use of liquid transportation fuels, providing the opportunity to fuel our cars using indigenously grown feedstocks and thus helping to create a more stable energy future.

Program Progress & Accomplishments

Analysis

- Developed the "Biomass Scenario Model" tool to understand the transition dynamics associated with the development of a cellulosic ethanol industry. Specifically the model allows for investigating potential market penetration scenarios for cellulosic ethanol and identifies high-impact drivers as well as bottlenecks to system evolution.
- Extensively tested an ethanol-optimized Saab vehicle, including exhaust specification, acceleration and fuel mileage evaluations. These tests determined that the vehicle's fuel economy is very good

compared to the US FFV fleet and that the performance advantage is not at the expense of emissions or fuel economy.
- Continue to develop a spatially referenced decision support system that will map current and potential feedstock availability and environmental and infrastructure constraints to collection of that feedstock. The tool will be utilized to assess relevant resources and infrastructure both regionally and nationally.

Feedstock Platform

- Established the Regional Feedstock Partnership in all five regions of the U.S. through a series of workshops.
- Established separate teams within the Regional Feedstock Partnership to: a) create, implement, and maintain a GIS-based resource assessment tool; b) conduct sustainable corn residue removal trials; and c) to conduct energy crop trials.
- Completed regional feedstock supply curves, as well as an inventory of existing feedstock work in each region.

Biochemical Conversion Platform

- Achieved a modeled cost target of $0.125 (2007$ estimated) per pound of sugars (equivalent to $2.43 per gallon of cellulosic ethanol) through the formulation of improved enzyme mixtures and pretreatments.
- Made awards to applicants selected for improving saccharifying enzymes to meet the target of reducing the cost of enzyme systems to $0.10 per gallon of ethanol produced by 2012.
- Conducted two Funding Opportunity Announcements to address key areas within the biochemical platform that can assist in meeting the $1.33/gallon ethanol target.

Thermochemical Conversion Platform

- Developed the public Thermochemical Conversion Design Case that was industry validated under a current ethanol cost goal of $1.33 per gallon.
- Developed correlations for tar yields from components of various types of biomass feedstocks for gasification.
- Identified catalyst deactivation mechanism and metal-substrate interactions in gas clean-up/conditioning process. Additionally, the platform improved tar-cracking catalyst activity by 2.5 times, meeting the 2010 target.

Integrated Biorefinery Platform

- Three of the 932(d) selected projects were awarded but may not cost until one or two conditions are met, primarily the production of a risk mitigation plan satisfactory to DOE. The three awards are Abengoa Bioenergy of Kansas, Poet Project Liberty, and BlueFire Cellulose to Ethanol plant.
- Fermentation organism work at DuPont and NREL was concluded in FY 2007. A strain was demonstrated to meet the milestone levels for the rate of ethanol production, final ethanol titer, extent of glucose and xylose conversion. This task was thus completed and a milestone report will be submitted next quarter. This strain is not yet adequate for a production strain.

Infrastructure Platform

- The Infrastructure Platform is in it’s infancy as a new platform. In FY 2007, activities were centered on evaluating next steps for future information exchange and joint efforts.
- Co-developed and co-funded with EERE’s Vehicle Technologies Program an ethanol intermediate blend testing program on light-duty vehicles and small non-road engines.

Market Transformation & International

- Initiation of a Bilateral Working Group to manage collaborative efforts between the U.S. and Sweden on topics including: a) research and development for new and improved sources of biomass production for energy use, (b) research and development of conversion technologies for different

types of liquid biofuels and other kinds of renewables, and (c) research and development for more efficient engines and lightweight vehicles.
- On April 25, 2007, Assistant Secretary Andy Karsner met with Ambassador Antonio Simões, Director of the Department of Energy, Ministry of External Relations (MRE) of Brazil. The Principals agreed to cooperate on a study to quantify use of biofuels and greenhouse gas reduction. Ethanol was selected as the first biofuel to be evaluated. The National Renewable Energy and Argonne National Laboratories are involved in the study.

New Projects Selected

In FY 2007, the Biomass Program competitively selected many new projects to address key barriers in the development of cellulosic ethanol technologies. These included the following:
- Six biorefinery projects ($385 million over five years) for the commercial demonstration of advanced biorefineries that use cellulosic feedstocks to co-produce ethanol, bioproducts, heat and power. The proposed plants are expected to produce over 130 million gallons of cellulosic ethanol annually.
- Five ethanologen projects ($23 million over three years) that focus on developing highly efficient fermentative organisms to convert biomass material to ethanol. Commercialization of fermentative organisms, capable of fermenting both hexose and pentose sugars, is crucial to the success of biochemical-based integrated biorefineries.

External Coordination, Input and Assessment

- The Biomass Program collaborates with 11 Federal agencies and administrations via the Biomass R&D Board, co-chaired by EERE Assistant Secretary Alexander A. Karsner and U.S. Department of Agriculture Under Secretary for Rural Development Thomas C. Dorr. Ongoing Board activities include compilation of a National Biofuels Action Plan drafted by working groups for the following areas:
  - Sustainability Working Group
  - Feedstock Production Working Group
  - Feedstock Logistics Working Group
  - Conversion Science and Technology Working Group
  - Distribution Infrastructure Working Group
  - Environment, Health and Safety Working Group
  - Blending

- The Program supports EERE's effort to facilitate international discussion, agreements and cooperation on energy-related issues. 2007 actions included Memoranda of Understanding with China and Brazil and an Implementing Agreement with Sweden (including organization of a Bilateral Working Group).

- The Biomass R&D Technical Advisory Committee is an external group providing input to the Departments of Agriculture and Energy under the auspices of the Federal Advisory Committee Act (FACA). The group's annual recommendations to the Secretaries are provided to the public and Congress on their website (www.biomass.govtools.us), and include discussion of key issues in Biomass R&D: cellulosic recalcitrance, feedstocks logistics and handling, bioproducts development, and strategic analysis. The Program collaborates with USDA to provide comprehensive responses to each recommendation, and incorporate the annual feedback into ongoing Program activities.

- During 2007, Program Technology Managers and staff met with projects' Principal Investigators, conducted a comprehensive peer review of its Technology Platform R&D projects, and invited peer review of the Program as a whole. Independent reviews were provided by 31 technological, finance, and policy experts. The Program is providing direct responses to the feedback from these reviews in the final Program Peer Review Report.

In Closing

We are pleased to present the first edition of the U.S. Department of Energy's 2007 Biomass Program Annual Accomplishments Report. The report is divided into sections and organized by platforms (e.g., Feedstock, Biochemical Conversion, etc.). Each section is introduced with an overview written by the DOE Technology Manager and includes project descriptions submitted for the Peer Review by the principal investigators (PIs) of the projects supported by the platform. The format of these project descriptions differ slightly, as the template was revised during the Program Review process.

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Analysis

Introduction

The Biomass Program conducts a broad spectrum of analyses to support decision-making, demonstrate progress toward goals, and direct research activities. The analysis group, a combination of Headquarters Biomass Program and National Laboratory staff, performs both programmatic (strategic) and platform-level analysis. Platform analysis activities help to monitor and check the program accomplishments in each platform and results from these activities integrate into cross-cutting strategic analysis tasks. Current strategic analysis activities are focused on ethanol, but as the Program expands its interest into other biofuels, the analysis group is evaluating other alternative biofuels that may have the potential to make significant contributions in the U.S. transportation sector.

Platform Performance Goal

To support the Program in realizing a competitive processing cost for sustainable conversion of cellulosic feedstocks to ethanol and other biofuels. Additionally, the Analysis Group will be performing resource and market assessments.

Objectives

- Develop standards and a process for development of state of technology (SoT) reports and updates. These SoTs will be completed for priority biorefinery pathway/fuel combinations.
- By 2012, model an nth plant production cost of $1.33/gallon ethanol from a cellulosic resource.
- By 2012, evaluate the potential and risk of investing in R&D on alternative biofuels.

FY 2007 Accomplishments

- Funded a study with the DOE Policy and International Affairs Office on the *World Biofuel Assessment: Potential for US Imports.*
- Commissioned a supply chain analysis to analyze constraints to rapid biofuels expansion and support DOE initiative planning. The effort focused on the development of Infrastructure requirements (for sustainable production of cellulosic ethanol at 5, 10 and 20 billion gallons per year) and identification of the technology targets and policy factors that would be necessary to achieve 2017 cellulosic ethanol production scenarios.
- Developed the "Biomass Scenario Model" tool to understand the transition dynamics associated with the development of a cellulosic ethanol industry. Specifically the model allows for investigating potential market penetration scenarios for cellulosic ethanol and identifies high-impact drivers as well as bottlenecks to system evolution.
- Extensively tested an ethanol-optimized Saab vehicle, including exhaust specification, acceleration and fuel mileage evaluations. These tests proved the vehicle's fuel economy to be very good compared to the US FFV fleet and determined that the performance advantage does not come at expense of emissions or fuel economy.
- Partially funded the 2007 Northwest Biomass Business Study. This study assessed potential opportunities for use of biomass and biofuels in the future for the Pacific Northwest.

Budget

The President's FY 2008 budget allows for the acceleration of research into cellulosic ethanol conversion from a wide range of feedstocks in order to meet the near- and longer-term goals of the Initiative. The Analysis budget is a cross-cut activity that amounts to approximately $7.5 million.

2008 Plans

- Develop an analytical tool to address the issue of direct and indirect land use changes associated with enhanced biofuels production.
- Develop a spatially referenced decision support system (using GIS) that will map current and potential feedstock availability and environmental and infrastructure constraints to collection of that feedstock. The tool will be utilized to assess relevant resources and infrastructure both regionally and nationally.
- Enhancing and using the GREET model to run new scenarios for energy and GHG emissions of biofuels.
- Conduct a “Water Use for Ethanol Production” study that will provide a baseline of current consumptive water use in the biofuel and petroleum industry.
- Develop a biorefinery siting model in partnership with ORNL, University of California Davis, Western Governors Association and USDA. This model will take into account feedstock availability and infrastructure issues in determining optimal sites for future biorefineries.
- Develop several reports in joint activity:
  - Integrated biochemical and thermochemical pathway analysis and biorefinery design report; this will be an update of the 2002 and 2006 Aden design report and will look at the impact of refinery sizes and issues for the integration of biochemical and thermochemical processing technologies.
  - An industry/lab joint alternative fuels assessment that will be developing ASPEN based model of biochemical and thermochemical processes to produce alternative biofuels (i.e., green gasoline, green diesel, biobutanol) and other value-added products.
  - A woody feedstock supply system design report; the report is being coordinated with the US Forest Service.
  - An herbaceous feedstock design report. This report will cover issues with sustainable biomass resource assessment and removal analysis.

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Feedstock Platform

Introduction

The size of the U.S. bioindustry will, to a large degree, be determined by the quantity and quality of biomass available. As the starting material in the biomass-to-biofuels supply chain, a sufficient and secure supply of affordable feedstocks is a critical step in accomplishing the Program goals. The Feedstock platform therefore relates strongly to all other facets of the program portfolio; it is, however, specifically linked to the Conversion platform as feedstock is the substrate for conversion technologies.

The Feedstock platform core R&D supports the first two elements of the biomass supply chain: feedstock production and feedstock logistics. Feedstock production includes all the steps required to sustainably produce biomass feedstocks to the point they are ready to be collected or harvested from the field or forest. The Program's feedstock production R&D is focused on selecting the best-suited feedstocks and solving specific feedstock production issues on a regional basis. The Program also partners with DOE Office of Science and USDA on advanced feedstock production R&D.

Feedstock logistics encompasses all the unit operations necessary to prepare and deliver biomass feedstocks to the biorefinery and to ensure that the delivered feedstock meets the specifications of the biorefinery conversion process. The Program's feedstock logistics R&D is focused on developing and optimizing cost-effective integrated systems for collecting, storing, preprocessing, and transporting a range of potential lignocellulosic feedstocks, including agricultural residues, forest resources and dedicated energy crops.

Platform Performance Goal

To develop technologies to sustainably provide a secure, reliable, and affordable cellulosic biomass supply for the U.S. bioindustry.

Objectives

- The feedstock production goal is to validate that a sustainable high-quality accessible feedstock supply of 130 million dry tons per year can be available by 2012, growing to 250 million dry tons per year by 2017. This goal is necessary to spatially quantify the accessible resource and validate the percentage of the resource that could be recovered cost effectively.
- The feedstock logistics goal is to reduce the feedstock logistics cost to $0.37 per gallon of ethanol (equivalent to approximately $33/dry ton in 2007$) by 2012, with further reduction to $0.33 per gallon of ethanol by 2017. Cost-saving and process-improving technologies will be developed within each stage of the feedstock supply chain. The logistics goal applies to the dry herbaceous, wet herbaceous and woody feedstock types.

FY 2007 Accomplishments

- Established the Regional Feedstock Partnership in all five regions of the U.S. through a series of workshops.
- Established separate teams within the Regional Feedstock Partnership to create, implement, and maintain a GIS-based resource assessment tool; conduct sustainable corn residue removal trials; and conduct energy crop trials.
- Completed regional feedstock supply curves, as well as an inventory of existing feedstock work in each region.
- Established a sustainability element to all feedstock production efforts.
- Completed a supply system design useful as a starting point for developing feedstock supply systems for pioneer biorefining facilities.
- Compared quantitative benefits of single pass harvesting with mow and rake harvesting.
- Completed preliminary rheological property data & analysis on archived samples for handling and transportation systems.

- Identified how preprocessing contributes to the uniform format necessary to hit 2012 targets.
- Identified three wet storage system designs that can potentially achieve cost targets: Wet-Dry Hybrid, Biological Preprocessing & Storage/Queuing, and Green Harvest/Wet.

Budget

The President's FY 2008 budget request includes increased funding for biomass feedstock R&D from $9,967,000 in 2007 to $10,000,000.

2008 Plans

- Establish industrial partnerships to address feedstock logistics.
- Continue to work with the Regional Feedstock Partnership teams to identify and develop available, cost-effective, and sustainable biomass feedstocks that can make a significant impact to the nation's biofuels production.
- Leverage Program deployment projects and/or state-funded efforts to conduct large crop demonstration projects that will accomplish the following:
  - Allow for equipment validation trials with manufacturers;
  - Address sustainability issues at a variety of scales;
  - Educate growers on viability of energy crops at a demonstration scale;
  - Help educate the grower community at a near-commercial scale; and
  - Allow for a real life test of providing feedstocks on a year-round basis to a conversion facility.
- Complete the first phase of the GIS-based resource assessment tool.

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Project Summaries

Feedstock Platform Support

Feedstock Regional Partnerships

Idaho National Laboratory

Principal Investigator:	Richard Hess	Funding Partners:	N/A
HQ Technology Manager:	John Ferrell	Sub-contractors:	N/A
PMC Project Officer:	Kevin Craig		

Goals and Objectives: Regional partnerships will enable development of more accurate cost supply information and improved communication with all elements and partners in the feedstock supply chain.

- Assist in the organization of the final three regional partnerships (Western, South
- Central, Northeastern) and work scope planning of all five regional partnerships
- Biomass Resource Tonnages and Cost quantified for 1, 5 and 60 B gal. ethanol (Supply demand and technology interactions validated and peer reviewed)

Project Description: The joint DOE/USDA billion ton study establishes the resource base and future potential for a large-scale biorefinery industry. The ethanol price target of $1.07/gallon by 2012 is based on a total biomass feedstock cost of $35/dry ton. This 2012 feedstock cost target can be subdivided into at $10/dry ton grower payment (stumpage fee for forest resources) to cover the biomass value and $25/dry ton for the feedstock supply system costs, which include harvest and collection, storage, preprocessing, and transportation and handling. It is estimated that from the 1.3 billion ton potential, as much as 130 million tons could be accessed for a grower payment at or near $10/dry ton. The expanding utilization of lignocellulosic biomass resources will create a demand for feedstocks, which will result in biorefineries paying more to access larger tonnages of more expensive resources (i.e., resources requiring >$10/dry ton grower payment). As the industry expands from grain ethanol to include cellulosic ethanol, it is expected that agriculture crop residues and forest logging residue resources will be the first to develop for biorefining purposes. Energy crops will develop and become integrated into the agricultural cropping systems as the biorefining industry matures and creates a demand for those resources. The increase in energy crop production will likely occur as land managers (i.e., farmers, plantation foresters, etc.) use these additional cropping options provided by a biomass energy market to maximize the productive capacity and economic returns of the land they manage. Collaborations with USDA and regional partners will become critical in developing sustainable biomass production and crop rotation strategies for both existing and new biomass resources.

Summary of Work to Date - Accomplishments (FY05-current): Organization of the regional partnerships and development of the collaborative scope of work between the DOE laboratories and regional partnership universities has been accomplished. The Southeastern and North Central regional partnership workshops were completed in May 10-12, 2006 and August 15-17, 2006 respectively. Of the three remaining regional meetings, the Western meeting will be held August 27-29, 2007, and the other two are targeting workshop dates for later this year. In addition, the Sun Grant regional partners completed a biomass related solicitation, and INL participated in the review of submitted proposals. As a matter of course, this review process identified numerous project opportunities for greater leveraging of DOE and other regional funding in the areas of resource assessment and resource development. This leveraging more effectively assists in accomplishing regional and national bioenergy goals.

Three additional key meetings between the Sun Grant Initiative leaders and DOE-OBP/Labs were held, one in October in St. Louis, MO, a second in December in Washington, DC and a third in February at ORNL for the initiation of the GIS resource assessment task with the regional partnerships. The outcome of these meetings was the ultimate agreement on the major scope of work tasks for the regional partnership. Work scope tasks included: 1) Resource Assessment; 2) Resource Development; and 3) Educations and Extension. The resource assessment task included development of GIS-base regional biomass supply curves, and completion of the regional road mapping workshops necessary to identify and develop regional biomass resources. The resource development task included inventorying existing and establishing new field trials for the development of sustainable agronomic cropping systems for crop residues and new energy crops, as well as, new biomass crop development. Finally, the education and extension task focused on enhancements to the bio-web as a mean to disseminate original research results, technical memos and resource assessment information development through the regional partnerships. INL and ORNL will continue working with each of the partnership groups in planning the workshops, as well as helping formulated the objectives and scope of each region's efforts that support DOE program objectives, specifically the FY08 milestones.

INL's accomplishments connecting supply systems to resource assessments, in conjunction with regional partners, have been two fold. First, efforts were initiated with Steve Fales (Iowa State University) and Wally Wilhelm (USDA-ARS, Lincoln, NE) to develop a white paper that assesses the status of cellulosic ethanol from the perspective of feedstock supply and critical issues associated with transitioning from the present day state to the future state of supply system envisioned in the billion ton study. This effort identifies critical issues with developing feedstock supplies that are cost-effective and sufficiently plentiful for the biofuel markets and at the same time sustainable. Feedstock value refers to the price that must be paid for biomass, standing or laying on the land, in order to purchase it from the producer (farmer or forester). While different feedstocks (i.e., corn stover, cereal grain straw, sorghum stover, switchgrass, prairie grass, logging residues, forest thinnings, etc.) have different median or average values, the price range for these different feedstocks can vary from less than $10/dry ton to $40/dry ton (or more in some cases). The specific reasons for this variability are as wide and diverse as the geographic regions and growers producing the biomass. However, the single largest variable affecting the feedstock value is tied to the tonnage demanded with respect to competing demands (competing demands include competing markets as well as soil/agronomic sustainability). ORNL (using POLYSYS) estimated that about 10% of the total 1.3 billion ton potential domestic biomass resource could be purchased at or below $10/dry ton. The analysis, as well as subsequent reviews from various parts of the U.S., demonstrated that the 10% resource availability was not uniform on a per acre basis nor across resource types; rather the 10% resource availability comes from the sum of all acres and biomass resources totaling the estimated 130 M dry tons (or 10% of 1.3 billion tons) that is accessible at or near the $10/dry ton price. This analysis is important in establishing the 2012 feedstock R&D and cost target goals for two reasons. First, based on the ethanol market demand estimates for cellulosic ethanol, the cellulosic biomass resource demand will not exceed 130 M dry tons until sometime after 2015. Thus, the $10/dry ton feedstock threshold value for an estimated 130 M dry tons is a practical feedstock cost estimate for the 2012 cost target. Second, the 130 M dry ton estimate includes all major feedstock types, so feedstock supply system technologies must be developed and validate for each of the major feedstock types. Additionally, by setting the biomass feedstock cost target at the entry point of the conversion process, all feedstock supply system unit operations are included in the Feedstock R&D scope. This also allows R&D technology development to be optimized across all feedstock supply business elements and unit operations. A draft paper discussing these issues is currently in review for publication as a Council for Agriculture Science and Technology assessment paper.

Schedule:

Project Initiation Date:	Sunday, October 01, 2006
Planned Completion Date:	Sunday, September 30, 2012

Feedstock Supply Chain Analysis

Idaho National Laboratory

Principal Investigator:	Richard Hess	Funding Partners:	ORNL
HQ Technology Manager:	Zia Haq	Sub-contractors:	N/A
PMC Project Officer:	Kevin Craig		

Goals and Objectives: The feedstock platform analysis effort will focus on studies to assess feedstock availability, cost (feedstock value or purchase price), and price (delivered to conversion process) for the 1 – 5 billion gallons of ethanol per year goal by 2017 and the 60 billion gallons of ethanol per year goal by 2030. The primary objective of analyses addressing the 2017 goal will be to concentrate on feedstock issues that ensure the near-term competitiveness of cellulosic ethanol. Analyses focusing on the 2030 goal will address the feedstock volumetric issues for longer-term cellulosic ethanol goals. These INL feedstock platform analysis studies will provide answers to the fundamental question for both the near-term and longer-term feedstock goals of, "What are the feedstock supply options and costs?" Other critical questions including, 1) What are the feedstocks? 2) What are the available feedstock tonnages and costs? and 3) What are the feedstock locations' opportunities / constraints? are questions that will be addressed through the regional partnerships tasks and by the ORNL analysis effort. Considering that this INL analysis task is part of a larger inter-laboratory and regional partnership effort, the collective intermediate target for answers to all four of these questions can succinctly be described as "demonstration of cellulosic biomass feedstock for all major feedstock types at pilot scale by 2012," with the analysis needs targeted to develop and validated the $35 feedstock supply system designs.

Project Description: As the deployment of cellulosic ethanol biorefineries approaches, one of the biggest unanswered set of questions is centered on feedstocks. The joint U.S. Department of Energy and U.S. Department of Agriculture billion ton study (Biomass as Feedstock, 2005) identified a domestic cellulosic feedstock resource potential sufficient to displace more than 30% of the 2004 U.S. finished motor gasoline demand. However, the questions of "How to cost effectively and sustainably get the biomass to the biorefinery?" and "How much biomass is available at what cost?" are significant looming challenges for the 2012 ethanol cost target of $1.07/gallon and the 2030 ethanol fuel target of 30% fuel displacement.

The 2030 goal to produce 60 billion gallons of ethanol will require the production of 40-45 billion gallons from cellulosic feedstocks (estimated 500 M dry tons of biomass), with the initial 15-20 billion gallons being produced from starch feedstock resources. While this ultimate goal of producing, supplying and converting 500 M dry tons of cellulosic biomass is important, it is useful to have an intermediate goal that 1) represents a realistic near-future biomass tonnage demand, 2) includes every major type of cellulosic feedstock, 3) provides feedstock at a price that the resulting ethanol product could be competitive in the near-future transportation fuels market, and 4) can be described and achieved with technology currently under development. Collectively, these four goals direct the path forward for the feedstock analysis.

Summary of Work to Date - Accomplishments (FY05-current): Biomass feedstock analyses have focused on support of the 2009 technology options milestone and tonnage targets for dry biomass systems, as well as defining supply system options for high moisture and woody biomass resources in support of the FY11 (woody) and FY12 (high moisture) technology options and tonnage targets. In addition to supply system options and cost analyses, GIS based feedstock location analyses conducted by ORNL are identifying feedstock production practices, availability constraints, local feedstock price ranges, and regional infrastructure options/constrains.

<u>1.6.1.2. A Feedstock Supply System Design</u> In FY06 a draft feedstock supply design for wheat and barley straw in a Pacific Northwest setting was completed. The model analyzed equipment, personnel, materials and facilities necessary to gather 800,000 tons of wheat and barley straw and deliver it in a preprocessed bulk format to a bioreactor. This model involved detailed investigations of: Costing Methodologies for Bulk Supply Systems, Straw Contracts and Supplies, Harvest and Collection of Harvest Data, Scheduling and

Dispatching, Bailing Operations, Roadsiding Bales, Quality Assurance, Inventory Mgt. and Field Storage, Grinding Operations, Transportation of Ground Feedstock, Weighing, Accounting and Unloading of Ground Feedstock, Plant Feedstock Storage, and In-Plant Transportation of Feedstock.

The FY06 design report content and requirements were evaluated for relevance to OBP programmatic interests as well as industry interest. Due to increasing interest in feedstock supply system issues, the scope of the design report was expanded to include a wet feedstock supply system design, and consider advanced designs beyond pioneer feedstock supply systems (i.e., uniform format commodity scale supply system). Prior to this, the scope of the feedstock design report was limited to the dry feedstock system. This decision has increased the scope of this report as well as the scope of the analysis efforts that support the development of this report.

As part of this expanded design scope, focused on the pioneer design case and understanding current practices, supply system options and processes that will affect feedstock costs and logistics as the cellulosic ethanol industry emerges has been conducted. An analysis of transportation cost factors was developed to show the significance of the fixed costs associated with transportation and to address the prevailing misunderstanding of transportation that overemphasizes the impact of transportation distance. The objective of this analysis was to quantify the relationship between the fixed costs associated with loading and unloading and variable costs, or mileage costs, which vary linearly with distance traveled. For example the fixed costs associated with loading and unloading the truck, totaling nearly $70 per load, exceed mileage costs out to about a 40 mile haul. In addition, the analysis compared the costs of various transportation methods including a self-propelled bale transporter, semi transport and rail transport. A self-propelled bale transporter is machine the can pick up bales in the field, transport them to the storage location and place them in a stack. This analysis shows the relative impact of the fixed and variable transportation costs on the economics of each of these transportation methods. The self-propelled transporter had the lowest fixed cost followed by semi hauling bulk feedstock and then semi hauling bales, with rail having the highest fixed cost. In comparison, the variable costs in this comparison is affected by the capacity of the transporter, so rail has the lowest variable cost and the Stinger has the highest variable cost, with semi variable costs in between. Accordingly, the self-propelled transporter is the most economical method of feedstock transportation for roadsiding up to five miles from the field. Semi transport then becomes most economical beyond five miles, with rail transport only being viable option for hauling bulk feedstock beyond about 180 miles.

Based on this transportation analysis, equations for self-propelled bale transport, semi transport of bale and bulk feedstock, as well as rail transport that include both the fixed cost and variable cost components were developed, and these equations were supplied to Steve Peterson to support the feedstock module of the Biomass Scenario Model. Additional analyses are ongoing to develop similar cost equations for the harvest and collection operations for feedstock in square bale, round bale and bulk format.

Work continues to develop an IBSAL interface for coupling to the INL spreadsheet model and performing sensitivity analyses of the INL designs. The IBSAL modules for each of the supply system unit operations have been developed, but additional work is necessary to directly couple IBSAL to the INL designs.

Out of these efforts a new draft Feedstock Design Report: the “Uniform Format Feedstock Supply System Design” report was completed. The purpose and objectives of this uniform format feedstock design document is threefold:

1) Provide (a) a supply system design basis that will be useful as a starting point for developing feedstock supply systems for pioneer biorefining facilities and (b) sufficient supply system attribute and modeling data to evaluate the efficacy of those designs.
2) Set forth the supply system design concepts for the “uniform format feedstock supply system,” which will allow for simplified and highly replicable supply system infrastructure and biorefinery conversion facility designs that can be rapidly and universally deployed to achieve the 20 in 10 Plan (Bush, 2007) and 30 x 30 Scenario (Foust et al., 2007) fuel displacement goals.
3) Present a uniform feedstock supply system design that can achieve the feedstock cost and quantity targets set forth in the biochemical (Aden et al., 2002) and thermochemical (Aden et al. 2007) conversion platform design documents.

1.6.1.2.B Corn Stover Removal Analysis In FY06, field research was performed to determine the impact of corn stover removal for a specific set of harvesting scenarios. Data collected from the research was analyzed and presented in a peer-reviewed publication that has been accepted for print. The conclusions from the research provide an initial look at the limiting factors that affect the environmental and economical impact of removing stover (referenced to the amounts identified in the "Billion Ton Study") for use in a biorefinery.

Methods for establishing sustainable biomass production solutions in response to the limiting agronomic factors were discussed with USDA. A method of establishing thresholds for each of the agronomic factors was considered as the basis for sustainable production solutions. This method has been used by other researchers to identify residue removal restrictions. However, it was determined that the interaction between these agronomic factors must be better understood in order to develop robust production solutions capable of addressing these issues. Therefore, it was decided to pursue additional limiting factor multivariant analysis as the basis for the production solutions developed by this task.

A draft corn stover analysis plan was developed that identifies the agronomic and soil management models and a proposed method of managing and structuring the flow of information for performing a multivariant analysis of the limiting agronomic factors (loss of soil organic carbon, increased soil erosion, increased nutrient leaching or run-off, loss of soil quality, reduced productivity, and environmental degradation) that were previously identified as potential constraints to crop residue removal. This analysis plan is currently submitted to the USDA for review and consensus on the methods.

1.6.1.2.C Woody Feedstock State of Technology The forest resources account for approximately one quarter of the estimated future biomass resources in the US in the Billion Ton Study, but a better understanding of the current technology is needed in preparation for future core R&D on woody feedstock supply. The United States contains large amounts of unused woody biomass with significant potential of becoming an important feedstock for the production of bioenergy, biofuels, and bio-based products. The potential to use these residues as a renewable source of energy, fuels, and chemicals and the recognized need to thin forests for wildfire mitigation, as prescribed by the Healthy Forest Restoration Act (2003), has established a national interest in recovering and utilizing these resources. This State of Technology will provide foundation knowledge in support of woody feedstock cost estimates needed for future logistical planning for forest residues and dedicated feedstock supply.

Woody supply systems in the U.S. are extremely variable. They are as hi-tech as helicopter logging and as low-tech as skidding with a horse. The approaches to obtaining forest biomass vary depending on: size and volume of area to be logged, topography, road availability, and types of wood to be harvested. Also local regulations pertaining to water shed protection and soil compaction may influence the approach.

Some of these unit operations are flexible and can feed into a variety of handling configurations, others necessitate specific machinery. Several forest harvest models have been developed and are available at various websites including the USDA site and sites maintained by individual universities. A list of these models include: The Auburn Harvesting Analyzer, the Sloan Logging Cost Calculator, and SIMYAR. In addition, the Forest Inventory and Analysis Data Center (FIA), operated by the USDA, has a tremendous quantity of data on timber inventories, harvests and technology.

The two largest end-users of forest products are the pulp and paper industry and lumber mills. These industries produce low value lignocellulosic waste streams. In the case of lumber production, this waste is primarily in the form of sawdust. The most prevalent process for paper production is the Kraft process which produces a waste stream called black liquor. Most Kraft pulp and paper mills burn the black liquor to produce steam and power for the process. Sawdust may be pelletized, burned, or composted. Both black liquor and sawdust could potentially be used in a thermochemical or biochemical plant.

Typical timber harvesting operations leave behind 20% to 30% of the harvestable biomass. This biomass is in the form of woody under story, limbs, leaves, and tree tops. Costs associated with gathering and transporting these materials often is higher than what an end user will pay. Sometimes the land owner will stipulate that the materials be removed for aesthetic reasons and to facilitate replanting. Spot markets for hog fuel (ground residues) exist in some areas of the country where direct-fired or co-fired power plants are present.

Forest products waste streams are often utilized for heat and power. In fact, a modern Kraft mill produces more energy than it consumes and sells electricity to the grid. Over 10% of logging residues are currently collected and burned in direct-fire or co-fire power plants. Any biofuels technology that seeks to utilize these feedstocks will compete for these materials.

Schedule:

Project Initiation Date:	Saturday, October 01, 2005
Planned Completion Date:	Sunday, September 30, 2012

Feedstock Platform Portfolio – Feedstock Supply & Sustainability

Feedstock Analysis

Bob Perlack, Oak Ridge National Laboratory

Principal Investigator:	Richard Hess	Funding Partners:	ORNL
HQ Technology Manager:	Zia Haq	Sub-contractors:	N/A
PMC Project Officer:	Kevin Craig		

Goals and Objectives: Expand BTV results to determine regional and local feedstock availability, cost and price, based on production goals of 1 BGY by 2015 and 60 BGY by 2030 (also consider production goals of 1, 5, 10, and 20 BGY of cellulosic ethanol by 2017). Develop a more comprehensive GIS-based data framework that addresses the prime question where feedstocks are located (current and potential) and at what cost.

Project Description: The results from the “Billion-Ton” biomass availability report will be expanded to determine regional and local feedstock availability, cost and price, based on production goals of 1 BGY by 2015 and 60 BGY by 2030. Included with this analysis will be a curve with crude oil price range, ethanol production, and delivered price range over time. This task will require cost modeling including updating existing cost of production models to answer some basic questions such as how much biomass is available, when, and with what level of development. These models will also require the development of new data, such as that on crop productivity (separate task) and feedstock values. This task will focus on the primary feedstocks – agricultural crop residues, forest residues, and perennial energy crops. Recommendations from the stage gate review will be addressed in this follow-up study.

To support the expansion and updating of the “Billion-Ton” report more comprehensive GIS-based methods are needed to identify and predict changes in the spatial and temporal distribution of biomass resources. To be comprehensive, these methods must rely on environmental sustainability data (e.g., temperature, humidity, rainfall, soil, nutrient values, etc.) and be capable of incorporating feedstock cost data and results of feedstock spatial analysis tools. Research outcomes include the identification of resource potential and availability at a fine-spatial scale and the examination and evaluation of environmental sustainability issues and how these issues affect feedstock availability and costs.

Summary of Work to Date - Accomplishments (FY05-current): Biomass has great potential to provide renewable energy for America’s future. Biomass recently surpassed hydropower as the largest domestic source of renewable energy and currently provides over 3% of the total energy consumption in the United States. In addition to the many benefits common to any renewable energy use, biomass is particularly attractive, because it is the only current renewable source of liquid transportation fuel. This, of course, makes it an invaluable way to reduce oil imports — one of our most pressing energy needs. The U.S. Department of Energy and the U.S. Department of Agriculture are both strongly committed to expanding the role of biomass as an energy source. In particular, they support biomass fuels and products as a way to reduce need for oil and gas imports; to support the growth of agriculture, forestry, and rural economies; and to foster major new domestic industries — biorefineries — making a variety of fuels, chemicals, and other products.

A key question, however, is how large a role biomass could play. Assuming policy and conversion technology make biomass fuels and products economically viable, could the biorefinery industry be large enough to have a major impact on energy supply and oil imports? Any and all contributions are certainly needed, but would the biomass role be big enough to justify any needed infrastructure changes? Petroleum refineries, for example, are very large, capital-equipment-intensive operations. Would there be enough biomass feedstock available to warrant retooling some of those refineries to process biomass instead of or in addition to petroleum?

ORNL was asked to determine whether the land resources of the United States are capable of producing a sustainable supply of biomass sufficient to displace 30% or more of the country’s present petroleum consumption. This 30% goal was set by a joint advisory committee to the two departments as a vision for making a major contribution to energy needs. It would require approximately 1 billion dry tons of biomass feedstock per year.

The short answer to the question of whether that much biomass feedstock can be produced is yes. Looking at just forestland and agricultural land, the two largest potential biomass sources, ORNL found the potential exceeding 1.3 billion dry tons per year — enough to produce biofuels to meet more than one-third of the current demand for transportation fuels. This annual potential is based on a more than seven-fold increase in production from the amount of biomass currently consumed for bioenergy and biobased products. About 368 million dry tons of sustainably removable biomass could be produced on forestlands, and about 998 million dry tons could come from agricultural lands. In the context of the time required to scale-up to a large-scale biorefinery industry, the annual biomass potential of more than 1.3 billion dry tons can be produced with relatively modest changes in land use and agricultural and forestry practices.

Since publication of the Billion-Ton Vision report, efforts have focused on extending the results by disaggregating the resource potential to counties and pixels (1 km or 30 m), examining environmental sustainability (e.g., soil erosion and removal of crop residues) concerns and how these affect resource availability, and answering questions involving what feedstocks will be used, when will they be used, and what will be the costs.

Schedule:
Project Initiation Date: Saturday, October 01, 2005
Planned Completion Date: Friday, September 30, 2011

Regional Biomass Energy Feedstock Partnership

Terry Nipp, Sun Grant Association

Principal Investigator:	James Doolittle	Funding Partners:	Cornell University, Oklahoma State University, University of Tennessee, Oregon State University
HQ Technology Manager:	John Ferrell	Sub-contractors:	N/A
PMC Project Officer:	Kevin Craig		

Goals and Objectives: Regional partnerships will enable development of more accurate cost supply information and improved communication with all elements and partners in the feedstock supply chain.

- Assist in the organization of the final three regional partnerships (Western, South Central, Northeastern) and work scope planning of all five regional partnerships.
- Biomass Resource Tonnages and Cost quantified for 1, 5 and 60 B gal. ethanol (Supply demand and technology interactions validated and peer reviewed).

Project Description: The joint DOE/USDA billion ton study establishes the resource base and future potential for a large-scale biorefinery industry. The ethanol price target of $1.07/gallon by 2012 is based on a total biomass feedstock cost of $35/dry ton. This 2012 feedstock cost target can be subdivided into at $10/dry ton grower payment (stumpage fee for forest resources) to cover the biomass value and $25/dry ton for the feedstock supply system costs, which include harvest and collection, storage, preprocessing, and transportation and handling. It is estimated that from the 1.3 billion ton potential, as much as 130 million tons could be accessed for a grower payment at or near $10/dry ton. The expanding utilization of lignocellulosic biomass resources will create a demand for feedstocks, which will result in biorefineries paying more to access larger tonnages of more expensive resources (i.e., resources requiring >$10/dry ton grower payment). As the industry expands from grain ethanol to include cellulosic ethanol, it is expected that agricultural crop residues and forest logging residue resources will be the first to develop for biorefining purposes. Energy crops will develop and become integrated into the agricultural cropping systems as the biorefining industry matures and creates a demand for those resources. The increase in energy crop production will likely occur as land managers (i.e., farmers, plantation foresters, etc.) use these additional cropping options provided by a biomass energy market to maximize the productive capacity and economic returns of the land they manage. Collaborations with USDA and regional partners will become critical in developing sustainable biomass production and crop rotation strategies for both existing and new biomass resources. The Sun Grant Initiative, authorized under Section 9011 of the Farm Bill, encompasses all of the land grant universities in each State and U.S. territory into five bio-geographical regions, with its overall purpose to coordinate and support research and education programs on bioenergy and bio-product development. The Regional Biomass Energy Feedstock Partnership will utilize this unique regional land grant university network to develop a consortium that focuses on feedstock issues on a regional basis.

Summary of Work to Date - Accomplishments (FY07-current): Two of the regional meetings have been held and the architecture for the GIS database has been established.

Schedule:

Project Initiation Date:	Monday, July 01, 2007
Planned Completion Date:	Sunday, September 30, 2012

Mississippi State University Sustainable Energy Center

Michael Collins, Mississippi State University

Principal Investigator:	William D. Batchelor	Funding Partners:	N/A
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	N/A
PMC Project Officer:	John Scahill		

Goals and Objectives:

- Characterize candidate bioenergy crops for Mississippi.
- Understand and reduce physiological and cell wall limitations to biomass production and conversion.
- Develop appropriate harvesting and processing technologies that increase biofuel production efficiency.

Project Description: The main goal of this project is to define which bioenergy crops may be useful in Mississippi by carrying out multiple field experiments around the state representing distinct physiographic regions, and to determine their yield potential using existing and project-developed best management practices. The same data will be useful in developing economical cropping systems for these species. Varietal studies are underway to determine which lignocellulosic and oilseed crops grow best in the different environments in Mississippi. The lignocellulosic varieties being studied include varieties of switchgrass (*Panicum virgatum*), such as 'Alamo', 'Cave-in-rock' and 'Kanlow' as well as several new switchgrass genotypes. The study also includes giant miscanthus (*Miscanthus floridulus*) and johnsongrass (*Sorghum halepense*). The oilseed species being tested are castor (*Ricinus communis*) varieties, such as 'Lynn' and 'Hale,' canola/ rapeseed (*Brassica napus*), flax (*Linum usitatissimum* L.), crambe (*Crambe abyssinica* Hochst.), indian mustard (*Brassica juncea*), hesperis (*Hesperis matronalis*), camelina (*Camelina sativa* L.), and sunflower (*Helianthus annus* L.). Cropping systems for several biomass crops are being studied to develop production systems that maximize yield while minimizing production costs and providing sustainability. Another key research goal is to discover growth and production limits of bioenergy crops under environmental and nutritional stresses. Also, the growth and development limitations of the crops under stressful conditions are being analyzed. In addition to the lignocellulosic and oilseed crop research, work has begun to define how much existing woody biomass inventories are available in Mississippi through the use of remote sensing technologies and other data acquisition tools. This information will then be used to complete an economic analysis of the use of woody biomass as a biofuel feedstock.

Researchers are also attempting to genetically modify plants to make conversion to biofuels easier and more efficient. For example, rice is being modified to lower the energy needed to breakdown the cell wall which makes sugars needed for biofuel production easier to obtain. Once this procedure is well understood for rice, it can be duplicated in a variety of other crops. Biological enzymes have also been identified that aid in the degeneration of the cell wall. Microorganisms have also been sought that are able to degrade plant cell walls which will lead to lower cost and more efficient conversion processes.

The processing technology being studied is pelletization which densifies biomass to decrease the cost of transportation to biofuel plants. Feedstocks such as switchgrass, giant miscanthus, elephantgrass, and wheat straw are being collected and pelletized to discover the best methods to densify different types of biomass. Analysis of the feedstocks and pellets will be completed to determine the chemical composition and physical characteristics.

Summary of Work to Date - Accomplishments (FY05-current): Multiple field experiments were established during 2005 using several candidate bioenergy species. Management variables evaluated in one or more of the locations include fertilizer and weed management, as well as seed production and germination as related to establishment. Effects of multiple harvests per season are also being evaluated. Alternating winter and summer crops for annual species is another research topic. For several of the studies involving switchgrass and other perennial grass, this first year was mainly used to establish productive stands of the perennial species. Switchgrass and other native warm season perennials are characterized by slow establishment so this represents typical responses. Thus, the yield data cannot yet be used to develop yield expectations for established stands of these crops. The study involving multiple harvest dates for switchgrass showed that biomass harvested in December was suitable for bioenergy use but not for livestock feeding. Dual-use stands may be possible for switchgrass since forage quality of multiple-harvested switchgrass was sufficient to support certain classes of beef cattle. The option for dual use of switchgrass could enhance the likelihood that farmers will establish this crop by spreading the risk associated with either market option alone. However, total biomass yield during the establishment year was greater in the plots harvested only in December, compared with the June and December regime. Seed yield was much greater for full-season switchgrass.

Preliminary (establishment year) results suggest that several of the new switchgrass breeding lines and 'Alamo' produced higher dry matter yields than other named cultivars. A study was underway to reduce seed dormancy in native grasses. Switchgrass was the most successful in dormancy reduction followed by indiangrass. The results from the weed management study were not conclusive because of the poor establishment due to the drought throughout the state. For oilseed crops, first-year data suggest that winter canola and winter mustard may be viable options for winter biodiesel crops for Mississippi.

Switchgrass and castor where subjected to multiple environmental stresses to determine effects on productivity. Various assessments were conducted to determine the effects of nitrogen deficiency. All growth and developmental rates declined with leaf N. The photosynthetic rate was more sensitive to leaf N followed by leaf and stem growth rates and leaf addition rates. Nitrogen deficiency decreased the absolute amounts of all plant component dry weights. Remote sensing algorithms were also compiled to aid in the observation of the plant growth and productivity.

In the forestry study, researchers collected data from forest inventories to develop a database that can be used to identify the amount of woody biomass available in the state by region. The types of biomass considered were logging residues, mill waste, thinned trees, and urban waste. Other capabilities are also being added to the database to allow the user to be able to identify locations that provide enough biomass for fuel production plants with a minimal amount of biomass transportation. The project's first results indicate that Mississippi can yield up to 110 million gallons of ethanol per year, based on an estimated 4 million dry tons per year of biomass from logging residues, small diameter trees, urban waste, and mill residues.

Another objective of our work is to identify genes involved in modification of plant cell wall composition or susceptibility to degradation. Transformation of rice with WAX genes has progressed well. Transgenic calli have been obtained and moved to the plant regeneration stage. Transgenic seedlings for both genes were obtained. The WAX1 transgenic plants set seeds. Mass spectrometry of proteins from protoplasts and suspension cells are in progress. To study rice cell walls using a proteomic approach, we established the cell wall enzymatic removal system in both suspension cells and young seedlings of this species. We developed a vacuum infiltration method to improve enzyme access to the cell walls for large scale cell wall removal from seedlings of cereal crops. The two-dimension gel proteome map of the rice protoplasts was obtained. A large number of differentially regulated proteins after removal of cell wall were identified. Several microorganisms were isolated from fresh rice straw samples. Results suggest that a greater variety of microorganisms can be isolated using an incubation of cultures associated directly with the soil environment rather than utilizing traditional plating techniques.

Pelletization was studied as a method of feedstocks densification. Various feedstocks were collected and processed to produce pellets. The chemical and mechanical properties of the feedstocks before and after pelletization were compared to determine the effect of pelletization. During pellet making process it was found that steam conditioning the feedstocks prior to pelletization would aid in producing more uniform pellets. For this reason, researchers are engineering a mixing system to treat the biomass before pelletization. Results from the composition tests showed that the ash content and heat value of switchgrass pellets were similar to the ash content and heat value of raw switchgrass.

Schedule:
Project Initiation Date: June 1, 2006
Planned Completion Date: November 30, 2007

Switchgrass Demonstration Project

Burton English, University of Tennessee

Principal Investigator:	Burton C English	Funding Partners:	N/A
HQ Technology Manager:	Sam Tagore	Sub-contractors:	Lexington Logistics, Iowa State University - BECON Lab, Tennessee Agricultural Statistical Service, Southern Co
PMC Project Officer:	Kevin Craig		

Goals and Objectives: This year, the project will continue the experiments as designed at the Milan research and Education Center and the farmer production trials located in Henry and Benton Counties. Production for the 4th year at Milan and 3rd year on farm fields will be evaluated. Samples taken the last three years will be evaluated as to sugar and other nutrient content. Farmers will be interviewed as to potential problems that they experienced this past year. This past year has seen different climate then the other years. First, a freeze occurred in April resulting in new growth being knocked back. Then in May, June, and July rainfall has not been plentiful and the area has been declared a extreme drought area.

Four hundred bales of switchgrass were transported to Alabama Power and emissions tests were conducted with 240 of these bales used in the experiment. Four runs examining the emissions that occur from co-firing switchgrass with coal had the following characteristics:

1) First year harvest after frost - harvested in 2004,
2) First year harvest after frost - harvested in 2005,
3) Second year harvest before frost, and
4) Second year harvest after frost.

The emissions that occur under co-firing conditions were compared to 100% coal emissions. Samples of switchgrass harvested after frost had lower nitrogen content then the samples taken from bales before frost. Grass nitrogen content; however, did not appear to affect overall NOx emissions. CO emissions from grass harvested before frost were about the same as those resulting from grass harvested after frost. Unburned carbon was about the same when co-firing as compared to firing with coal alone. Proximate and ultimate analyses were conducted on the material prior to combustion.

Approximately one bale of switchgrass will be converted to bio oil at Iowa State University's BECON facility. The experimental design will be a complete block design considering 3 variables at 3 different sizes. The variables under examination include temperature, moisture content, and particle size. Samples will be sent back to UT for further analysis to be conducted next year. Information from the survey taken and summarized last year will be analyzed this year.

Project Description: This project is designed to evaluate the potential of producing switchgrass on commercial agricultural land and to utilize that switchgrass as an energy feedstock. The proposed project addresses three primary questions:

1) What incentives are required to induce producers to convert commercial cropland to switchgrass?
2) What impact would a mature switchgrass feedstock industry have on Tennessee's economy and the Nation's agricultural sector?
3) What is the potential of converting switchgrass to bio-oil for use as light-off fuel in a coal fired burner?

Schedule:

Project Initiation Date:	September 01, 2004
Planned Completion Date:	December 31, 2008

Alternate Fuel Source Study – An Energy Efficient and Environmentally-Friendly Approach

Ralph Zee, Auburn University

Principal Investigator:	Dr. Ralph H. Zee	Funding Partners:	N/A
HQ Technology Manager:	Neil Rossmeissl	Sub-contractors:	Lafarge North America
PMC Project Officer:	John Scahill		

Goals and Objectives: The overall objective of this project is for Auburn University and Lafarge North America to form a logical and synergistic partnership to develop a better fundamental understanding and to improve technologies with higher efficiency for the use of alternate fuel. This project has seven tasks as follows:

- Task A, the preliminary survey will determine the amount of alternate waste fuels available, their value as currently used, location, cost as a fuel, ease and cost of shipping, and the year-round availability, using a cement plant as a model.
- In Task B, two alternate fuel sources will be identified for evaluation and then tested to determine their effect on emissions, how they may affect the production operations of a cement production plant, and how they may affect the quality of the Portland cement.
- Task C involves coordinating with a cement industrial partner to use their cement kiln in the state of Alabama to conduct two cycles of test burn using two alternate fuel sources as identified in Task B. Results of the two test burns will be compared with standard operation to determine the feasibility of these alternate materials in terms of (1) energy, (2) cost, (3) emissions, and (4) product quality.
- Task D is devoted to the analyses of the results from the kiln operation and the quality of the cement and concrete produced.
- Task E is the development and testing of a cement burn simulator to enhance the confidence of the selection of alternate fuel based on scientifically obtained data.
- Task F involves the test burn of two additional alternate fuels and a synergistic burn in collaboration with Lafarge.
- Task G is a feasibility analysis of commercially available gasification technologies specifically applied to the cement kiln based on thermodynamic analysis.

Project Description: There are numerous industries that are energy intensive and can benefit from using alternate fuel sources. Cement is the most widely used manufactured material in the construction industry. Auburn University will focus their effort on the following five fundamental areas of research for use of alternate fuel sources in energy intensive operations:

1) a preliminary survey of available energy sources in a global manner, and the characteristics that each of these sources has in terms of burn efficiency and impact on the environment;
2) selection of two alternate sources of fuel for laboratory and field testing; and
3) testing of the burn characteristics in a cement production environment.
4) The development of a burn simulator to better understand the thermal process involved.
5) A feasibility study of the application of gasification technologies to the process.

Summary of Work to Date - Accomplishments (FY05-current): Task 1 was completed and it will be beneficial to other commercial processes that are highly energy intensive. Literature searches focused on the types of alternative fuels currently used in the cement industry around the world. Information was obtained on the effects of particular alternative fuels on the clinker/cement product and on cement plant emissions. Federal regulations involving use of waste fuels were examined. Information was also obtained about the trace elements likely to be found in alternative fuels, coal, and raw feeds, as well as the effects of various trace elements introduced into system at the feed or fuel stage on the kiln process, the clinker/cement product, and concrete made from the cement.

An emission monitoring system was installed and certified at the cement plant. An alternate fuel feed system was designed, constructed and is being installed. The delivery and installation of this extensive system was delayed. This system is essential for both alternate fuel test burns (coal+tire+plastics and coal+tire+broiler litter).

The sampling and analysis plans were developed to ensure that relevant and pertinent information about the effects of using alternative fuels in the cement manufacturing process will be obtained. Data were collected for the following two baseline burn conditions: (1) coal only as fuel, (2) coal+tires as fuel. The sample collection and testing was successfully executed in accordance with the test plan. In addition, the pre-burn sampling for all the alternative fuels was completed in December 2006.

Four test burns were completed, samples collected and analyzed. The four burns involved (1) coal only, (2) coal plus tire, (3) coal plus tire plus plastic, and (4) coal plus tire plus broiler litter.

Schedule:
Project Initiation Date: August 01, 2005
Planned Completion Date: December 31, 2007

Jefferson County Bio-Energy Initiative

Wade Yates, Jefferson County

Principal Investigator:	Wade Yates	Funding Partners:	N/A
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	CVL Consultants of Colorado Inc
PMC Project Officer:	John Scahill		

Goals and Objectives: The development of economically viable market outlets for biomass, encouraging the creation of new business and public-private sector partnerships, while simultaneously reducing the risk of catastrophic fires. Project focus is on the creation of a large centrally located biomass-processing site which will help reducing the supply uncertainty barrier to biomass utilization along the Front Range. Tasks: (A) Site selection and pre-application for development. (B) Property Survey. (C) Initiate formal re-zoning application (from Agricultural to Industrial). (D) Site development plan application and associated permits (County Planning and Zoning) (E) Site engineering, grading and drainage plan (F) Site Construction.

Project Description: The Jefferson County Bio-energy Initiative (JCBI) seeks to develop economically viable market outlets for forest thinning biomass through the creation of new businesses and public-private sector partnerships, while simultaneously reducing the risk of catastrophic fires and associated costs and damages. We have a strong interest in cooperating with the United States Forest Service (USFS) and private industry to help create the infrastructure that will reduce the barriers to new bio-energy markets due to logistical concerns over long-term forest biomass supply availability. We believe that the creation of a large central biomass-processing site will help reduce the costs and risks associated with supply uncertainty. The JCBI will operate as a cooperative between public and private sector entities, with Jefferson County acting as facilitator and not a competitor.

Summary of Work to Date - Accomplishments (FY05-current):

1) Site selection and pre-application for development. Three sites were selected based on their availability, ownership and current zoning. Ingress and egress eliminated two of the sites due to the fact truck traffic would be crossing HWY 285 and reconfiguring the roadway would cost more than the project funding would allow. The third site is simply too far from the source of material and would require a lease at a significant annual expense. The pre- application review process for the site has been completed with the Planning and Zoning Division of the County. The review response recommend re-zoning the project from a mixed status of light industrial and agricultural to one designation - Light Industrial.
2) Property Survey. A boundary survey of the site has been completed and ownership rights identified. Ownerships consist of Jefferson County, Jefferson County Open Space, Hayden Investment LLC, CDOT and Public Service Company of Colorado. The Board of County Commissioners visited the site location in order to familiarize themselves with any potential view-shed issues that may arise in the future since the project sits in what is considered the “Gateway to the Rockies”. Open Space has approved a land swap with like property in the General Fund. This removes and restrictions and allow the property to be rezoned to support log storage.
3) Contract for Design Analysis and Engineering work necessary to prepare the site prior to actual construction. The County has successfully selected a contractor to through a competitive bid process to perform a phased site feasibility study.

Schedule:

Project Initiation Date:	June 1, 2006
Planned Completion Date:	December 31, 2008

Feedstock Platform Portfolio – Feedstock Logistics Core R&D

Feedstock Infrastructure Project

Corey Radtke, Idaho National Laboratory

Principal Investigator:	Corey Radtke; Chris Wright; Kevin Kenney	Funding Partners:	N/A
HQ Technology Manager:	Sam Tagore	Sub-contractors:	Antares, University of TN, Diamond Z, Diamondback Technology, Iowa State University, Vermeer
PMC Project Officer:	Kevin Craig		

Goals and Objectives: 1.3.1.1.A Sustainable Harvest and Collection The overall objective of this task is to develop cost effective and sustainable harvest technologies and practices through the development of advanced harvesting equipment and through the development of predictive models capable of identifying the impacts of agronomic and agribusiness practices on feedstock sustainability. As such, this task focuses on advanced engineering systems, sustainable practices and the relationship between the two. Biomass harvest systems must not be designed solely on cost and performance targets. Rather, the contracting interface and sustainability boundaries are also key parameters that must be included in the design of equipment and the development of harvesting practices. The contracting interface is important because it determines whether biomass is the primary crop or the secondary crop, and the harvesting system performance must reflect this hierarchy. Sustainability boundaries are important because it dictates the ultimate viability of equipment and the long-term success of harvesting practices. The specific objectives of this task are as follows:

- Identify the performance requirements and design specifications for advanced harvesting equipment capable of achieving the performance and cost targets that have been established based on feedstock supply analyses
- Develop analytical techniques and modeling tools needed to engineer advanced harvesting systems
- Identify the agronomic, environmental, social and political factors (i.e., sustainability factors) that impact sustainability
- Develop tools and models for predicting the potential consequences associated with resource shifts resulting from food and fuel demands within the United States, as well as mitigating actions to minimize these potential impacts.

1.3.1.1.B Biomass Preprocessing The main objective of this task is to reduce the cost of preprocessing within the dry feedstock supply system to $2.75/dry ton by increasing the efficiency and capacity of preprocessing equipment. With this said, specific objectives have been identified that will guide logical, and often fundamental research, that targets the necessary performance parameters underpinning efficiency and capacity improvements. These specific objectives include the following:

- Determine current hardware performance parameters for various biomass feedstocks as demonstrated by barley straw in FY05
- Define critical hardware parameters, design specifications, and instrumentation needed to develop a prototype research grinder capable of testing multiple feedstock types and varieties based on FY06 performance parameters
- Quantify preprocessing losses and if necessary mitigation strategies to minimize feedstock cost impacts and air quality issues
- Identify the performance parameters of a separation system that can be coupled to a preprocessing operation and take advantage of value-add fractions identified in FY06
- Understand preprocessing tissue deconstruction and its relationship to grinder configuration, tissue fractions, tissue moisture, and grinder capacity, in order to optimize grinder configurations for capacity, efficiency, and quality
- Apply the fundamental rheological properties of preprocessed feedstocks, including uniformity, compactability, and flowability, to the design, performance, and cost of the preprocessing operation

- Identify strategies to increase bulk densities of preprocessed feedstocks by coupling the understanding of biomass deconstruction and rheological properties with innovative bulk compaction methods
- Identify the drying capacity of full-scale grinding operations to determine its impact on biomass moisture content with respect to applied feedstock assembly system technologies and cost

<u>1.3.1.1.C Biomass Storage and Queuing</u> The objectives of this task are two-fold. First, the soluble sugars in wet stored biomass will be investigated. Because soluble sugars are largely lost in wet harvested biomass during transportation and storage, and because of the tremendous value of these sugars, recovering the value of soluble sugars is paramount for wet harvested biomass to become an economically viable feedstock. Second, there will likely be advantages in treating biomass with xylanase at key entry points in feedstock supply chains, is the objective of the secondary investigation.

The specific objectives for this task include the following:
- Test advanced wet storage scenarios, focusing on the dynamics of soluble sugars in biomass
- Determine soluble sugar conversion efficiencies
- Measure impacts on residual solid biomass
- Estimate impacts on the feedstock supply infrastructure
- Test the effects of using xylanase throughout the feedstock supply chain

1.3.1.1.D Biomass Transportation and Handling As evidenced by the focused efforts in the harvest and collection, preprocessing, and storage elements of the feedstock platform core R&D, a bulk feedstock supply system is both necessary and inevitable. Compared to the existing or “pioneer’ supply systems where feedstock is packaged into bales for transport and handling operations, a bulk feedstock supply system presents many challenges. The first of these challenges occurs at the instant the biomass is harvested. Rather than baling the residues, harvest and collection equipment is needed to collect, handle and transport the bulk biomass to a processing or storage location. Next, preprocessing equipment is needed that both grinds the bulk biomass to accomplish some level of size reduction, and fractionates the biomass into discrete product streams of bulk biomass that are sent to storage. While current methods of bulk storage included pile or bunker storage, bin or silo storage, and some form of packaged storage, such as silage tubes, the handling operations, methods and equipment vary widely. Finally, the bulk biomass is transported to the biorefinery, where again some form of short-term storage (referred to as queuing) is utilized prior to moving into the conversion process. All of these operations mentioned, involve different aspects of bulk biomass transportation and handling. Many of the issues affecting bulk feedstock supply system design are common among the different unit operations with regards to equipment function and design. Consequently, all of these bulk transportation and handling issues are collectively embodied in this task of feedstock platform core R&D. The specific objectives for this task include the following:
- Determine how biomass physical properties (particle size, moisture content, etc.), feedstock type, and environmental conditions (such as temperature and humidity) influence rheological properties.
- Investigate various compaction methods to control and improve biomass bulk densities that will lead to the design and construction of viable bench scale systems to optimize and guide the implementation of full-scale equipment into the feedstock assembly system. Perform an assessment of large scale systems in other industrial operations to determine potential alternate handling and transportation methods.
- Determine the relationship between rheological parameters and transportation and handling systems in order to optimize their capacities and efficiencies, thus decreasing the net cost of this unit operation.
- Quantify biomass losses with current transport and handling methods based on material balance calculations or initial/final weight measurements.

<u>1.3.1.1.E Woody Harvest, Handling, Preprocessing, and Storage</u> The objective of this task is to assess current woody feedstock supply systems and determine points of adoption and improvement for the emerging biorefinery industry for transportation fuels. This objective will rely on the fundamental assembly system features of the current pulp and paper industry and on other fundamental science and engineering R&D being performed within the Feedstock Infrastructure Project. The specific objectives for this task include the following:

- Assess the current woody biomass infrastructure and assembly system structure based on existing woody biomass industries
- Identify key unit operations and potential improvements within current woody biomass infrastructure that can be applied to a biorefinery industry
- Complete an initial assessment and measurement of currently available woody biomass rheological properties
- Apply woody biomass rheological data to harvesting, collecting, preprocessing, transporting, and handing requirements for a biorefinery supply system

Project Description: 1.3.1.1.A Sustainable Harvest and Collection INL analysis of agricultural residue feedstock supply system costs from various parts of the U.S., has shown that current feedstock costs for corn stover (dry) and milo stover (dry) exceed the $35 cost target by about $18 per ton and $17 per ton, respectively. A breakdown of these costs shows the harvest and collection element to be the most expensive of all the feedstock supply system elements, totaling 50% of the allowable $35 feedstock cost. Accordingly, this is a critical area of focus for feedstock research and development. The problem with current farming practices is that they are not designed for the large scale removal of crop residues, and consequently, current practices are too inefficient to achieve the cost goals of the biomass program. This is revealed by looking at the current technology which includes five separate unit operations for getting the crop residues from the field to storage. Incremental improvements (e.g., increased equipment capacities and efficiencies) to the harvest and collection processes will not achieve the level of cost reductions needed. Rather, significant technological advancements must occur that enable the elimination of entire unit operations within the harvest and collection processes. This task will focus on this issue through the design of single-pass harvester that enables the grain and residues to be collected together in a single-product stream in a single pass across the field. Accomplishing this could reduce the harvest and collection costs by as much as $14 per dry ton, thus achieving nearly 75% of the necessary feedstock cost reductions.

The prudent allocation of valuable and limited resources is fundamental to achieving a sustainable biomass harvest that supports both food and fuel goals. Resource allocation is a critical component of the sustainable harvest question. In agriculture, essential resources include: land, water, nutrients, seed crops, energy, labor, technology, residue, etc. These resources vary spatially and temporally as a result of natural processes, market shifts, and technological innovation. Properly balancing these resources to meet future demands requires that appropriate government policies integrate agricultural and forestry systems with both food and fuel production processes, consumer markets, and demands for other petro-chemical substitutions.

“Sustainability” describes an interdisciplinary process that integrates economic development, social values, and environmental health considerations. Sustainability strives to meet the needs of the present without compromising the ability of future generations to meet their own needs. Key to the sustainability concept is acknowledging that human beings, and their associated influences, are intimately linked to the natural environment.

This subtask will apply the principles of sustainability to define a framework of the projected impacts associated with the harvest of biomass for food and fuel. It will also define a set of sustainable harvest indicators with which to monitor the potential consequences of competing agricultural resource allocation scenarios.

Sustainable harvest indicators are metrics that delineate the potential consequences of resource allocation decisions. These proposed sustainable harvest indicators will incorporate into a dynamic framework the following factors:

- Economic – supply, demand, prices, employment, energy balance, capital and opportunity costs, tax supports and credits, etc.
- Environmental - land-use patterns, water resources, waste, pollution, climatic changes, etc.
- Social - political, community development, technological advancements, infrastructure demands, distribution systems, consumer values, patterns of consumption, etc.

These indicators will be useful gauges for monitoring the biomass strategy with regard to resource allocations, agricultural/forestry profitability, environmental quality, food and fuel sufficiency, and community viability.

Given that some implementation actions could result in negative performance it will be important for DOE/USDA to have the ability to identify these actions as soon as possible. This subtask will also use these indicators to identify mitigating actions that can be applied to minimize negative consequences associated with “less-than-sustainable” agricultural resource allocations. This systems-level interdisciplinary framework (resource allocations, sustainability indicators, consequences, mitigating actions) will be integrated with pertinent resource data and ongoing modeling efforts such as POLYSYS, GREET, Biomass Scenario Model, etc.

1.3.1.1.B Biomass Preprocessing Biomass preprocessing is a critical operation in the feedstock assembly system and the front-end of a biorefinery. Its purpose is to chop, grind, or otherwise format the biomass into a suitable feedstock for conversion to ethanol and other bioproducts. Without this operation, the natural size, bulk density, and flowability characteristics of harvested biomass would decrease the capacities and efficiencies of feedstock assembly unit operations and biorefinery conversion processes to the degree that programmatic cost targets could not be met. Thus, the preprocessing unit operation produces a bulk flowable material that 1) improves handling and conveying efficiencies throughout the feedstock assembly system and biorefinery 2) increases biomass surface areas for improved pretreatment efficiencies, 3) reduces particle sizes for improved feedstock uniformity and density, and 4) fractionates structural components for improved compositional quality. In addition, the preprocessing operation has the potential to change traditional methodologies for handling biomass that can lead to revolutionary improvements in the feedstock assembly system. For example, non-bale harvesting systems can be achieved by moving the preprocessing operation from the biorefinery to earlier stages in the feedstock assembly system where traditional bale handling equipment can be eliminated and conventional bulk solids handling and transport equipment can be utilized.

1.3.1.1.C Biomass Storage and Queuing A large portion of the agricultural residues in the US will be harvested while in a relatively wet state. For example when corn grain is harvested, corn stover is typically over 40% moisture. This moisture presents two major problems, one from the weight of the water and one from the microbial destabilization that the water provides. The weight of water increases the unit costs of the feedstock supply chain that scale with tonnage more than volume. For example, once trucks are grossed out in weight carrying biomass, additional water directly offsets the dry tonnage of biomass transported (i.e.: 50% moisture feedstock would require twice as many trucks as 0% moisture biomass). Further, water provides a microbial medium that can lead to biomass damage. This microbial susceptibility can be diminished by converting some of the available sugars in the biomass to organic acids, which in turn lower the pH and help stabilize the biomass (ensiling). However, to a biorefinery, these available sugars can be effectively lost in such a process, either by being metabolized (consumed) by the microbes, or contaminated with a stream of ethanol-fermentation inhibitors such as acetic acid and lactic acid. Further, for anaerobic storage of the biomass, air exclusion is necessary, which requires higher priced storage systems. And finally, wet biomass requires faster handling systems because of the microbial instability, which impacts the unit operations upstream and downstream of the stored biomass.

The problem is that the wet feedstock supply chain costs are likely too high to support a biorefinery, yet are necessary to access enough tonnage to significantly impact the petroleum displacement goals. The solutions for this problem are equally simple, but need to be linked together as part of an integrated feedstock supply chain coupled to a specific biorefinery operation to be valid. These solutions may include the careful manipulation of the soluble sugars and sugar-oligomers in biomass, to make a wet/dry hybrid feedstock assembly system.

1.3.1.1.D Biomass Transportation and Handling Handling and transportation systems represent a significant assembly system cost with little added value to the feedstock creating a barrier to utilizing certain feedstock resources and reaching the respective cost and tonnage targets. This task is focused on quantifying the physical and rheological properties (including bulk density) of low and high moisture herbaceous biomass as they relate to handling systems for optimizing handling and transportation capacities, efficiencies, and feedstock quality. Determining the feedstock rheological properties is important since it significantly impacts the design, function, and cost of preprocessing and other feedstock assembly system unit operations. The properties to be tested include: 1) uniformity, 2) compactability, and 3) flowability. These properties are a function of feedstock type, particle size, moisture content, consolidation pressures, time at rest and atmospheric conditions (e.g., temperature and humidity).

Advanced feedstock supply systems that will handle large tonnages of biomass over wide geographical areas will also rely heavily on the development of new handling methods and technologies that implement value-added preprocessing and merchandising of the raw feedstock material. Traditional biomass transportation systems, such as trucks, may not be economically possible because of the large transport distances, traffic congestion, or community opposition. Rail transport of biomass reduces the frequency of loads, but is often more expensive than truck because of infrastructure constraints and handling costs. Advanced transportation systems will likely incorporate technologies that not only provide infrastructure and operational cost savings but also incorporate in-transit value-add processes.

<u>1.3.1.1.E Woody Harvest, Handling, Preprocessing, and Storage</u> The United States contains large amounts of unused woody biomass with significant potential of becoming an important feedstock for the production of bioenergy. The potential to use these residues as a renewable source of energy, fuels, and chemicals and the recognized need to thin forests for wildfire mitigation, as prescribed by the Healthy Forest Restoration Act (2003), has established a national interest in recovering and utilizing these resources. Transportation costs and low conversion efficiencies are two factors that increase the costs of products produced from these materials. The infrastructure for woody biomass is well developed to support a number of existing markets (e.g., timber, pulp and paper, fuel wood and urban residues), and the supply systems vary widely with respect to equipment, products, land use, markets, and resource environment (policy, accessibility, slope, compaction, etc.) Therefore, the focus of this task is to assess the importance of material properties and their interactions with the current woody infrastructure and identify improvements that are needed in each of the fundamental components of the feedstock supply infrastructure (harvest and collection, storage, preprocessing, and transportation and handling) to meet the cost and supply targets of the DOE biomass program. It is anticipated the infrastructure requirements for woody biomass will be significantly different from typical agriculture-based feedstocks. Perhaps feedstock location provides the most complex and critical set of inputs into the analysis of woody feedstock supply analyses. There is also a pressing need to understand the natural variations in the chemical composition of woody biomass, and how harvesting methods may impact the quality of woody feedstocks.

Summary of Work to Date - Accomplishments (FY05-current):
<u>1.3.1.1.A Sustainable Harvest and Collection</u> A multi-year Sustainable Harvest and Collection Task (1.3.1.1. A) Plan was completed and submitted on December 15, 2007 The task is divided into two sub-tasks: (1) Integrated Conceptual Design of a Single-Pass Harvesting System (1.1.3.1.A.1) and (2) Sustainable Harvest for Food and Fuel (1.1.3.A.2). The plan describes the research objectives, technical approach, budget and schedule for producing a virtual prototype of a single pass harvesting system, including an integrated combine platform and a biomass separator. The plan also details the technical approach, budget, and schedule for developing a sustainable harvest indicators model, including economic, environmental and social aspects of biomass use, for application in making better-informed management and policy decisions.

The focus of FY-07 activities is to develop the performance requirements and design specifications that will serve as the basis of the single-pass harvester concept. Identifying performance requirements has involved the following activities:

- Evaluating the performance of existing multi-pass harvesting systems
- Evaluating the performance of other research or commercial whole-crop harvesting systems
- Evaluating integrated supply system processes to identify the impacts of harvester design parameters (such as feedstock format) on downstream operations
- Developing analytical methods for designing handling, separation and densification systems required in the harvester design.

A solid understanding of existing multi-pass harvesting systems is important to identify the deficiencies that necessitate change as well as the performance and logistical attributes that should not change with the advent of advanced harvesting systems. The performance of existing multi-pass harvesting systems is difficult to assess due the variability in equipment configuration, operator skill, field conditions, and a host of other factors. Consequently, the INL, in collaboration with an industrial partner, initiated a first-of-a-kind large scale field test program to quantify harvest, collection and transportation costs of herbaceous crop residues, related to the monitoring and evaluation of equipment performance over a range of field conditions, biomass yields, machine configurations, etc. This project will provide the baseline data necessary to evaluate machine performance parameters and associated feedstock harvest and collection costs that serve two main purposes. First, data collected from this project will serve as a baseline to which advanced harvesting systems will be compared. Second, this project will identify key performance parameters that will be used to evaluate the performance of advanced harvester systems.

A review of whole crop harvesting technologies and applications was conducted to help formulate the current concept based on successes and deficiencies of other design concepts. This review of past and current research and commercial whole crop harvesting systems helped to identify key design issues, approaches to address these issues and common barriers to achieving a successful design. Data compiled from this review will be used to benchmark parameters and to establish specifications in the conceptual design of the Single Pass Harvester System.

Residue handling, separation, densification and collection represent the main requirements of single-pass harvest. Many single-pass designs have basically side-stepped the engineering challenges associated with these processes. We are attempting to address these issues by understanding the role of fundamental material properties in the design of these systems. Accordingly, a study of biomass bulk flow properties was conducted to develop the analytical methods for designing harvester handling, separating and densification systems based on fundamental material properties. This is a unique approach to harvester design that may provide the breakthroughs that have eluded single-pass harvest designs to date. This study focused on identifying the bulk flow properties that relate to the performance and design of two key components of the harvester design: conveying and densification.

Test methods to quantitatively measure the bulk flow properties related to conveying and densification options are currently being developed. The challenge in developing these test methods is to evaluate the applicability of current test methods, which were designed for evaluating homogeneous powders and granulated materials, to heterogeneous materials of much large particle size and morphology. Successfully developing these test methods will provide the means to select among the process options and to design the process equipment based on the properties and behavior of the biomass.

Subtask 1.1.3.1.A.2. A literature review was conducted to identify and evaluate prevailing sustainability issues as well as existing resource data and component-level models that are considered relevant to the sustainable food and fuel harvest questions related to this subtask. Based on the literature review and expertise of INL researchers, a set of “Feedstock Supply System Sustainability Indicators” (see table below) was developed for potential use in measuring economic, environmental and social outcomes associated with grower’s allocation of resources. A preliminary regional sustainable harvest model was constructed using the agricultural sustainability indicators listed in the table below to evaluate the sustainability of regional and farm-level agronomic practices and cropping systems.

Feedstock Supply System Sustainability Indicators		
Category	**Indicators**	**Measures**
Agricultural	Food production	Grain yield Grain N content
	Raw materials production	Stover yield Stover N content
	Nutrient cycling	Post–harvest soil NO_3 Soil pH
	Greenhouse gas regulation	Soil organic C Pre–plant soil NO_3
	Water use efficiency	Agricultural units produced / water consumed
	Erosion	Off-site transport of soil Nutrient and soluble chemical loss
Waste Streams	Residues	Tons per acre Value per ton
	By-products	Cost of disposal for by-products per ton; Value per ton
Environmental Impacts	Occurrence of Invasive Species	Observed presence or absence of exotic species (plant, animal, microbial)
	Loss of wildlife habitat	Land Allocation of farm acreage {% cropland, % pasture, % CRP, % domestic (homes, roads), % water bodies, % undisturbed}
Socioeconomic	Producer health	Farmers with/without health insurance
	Producer preparation	Educational achievement of farm workers
	Farm Income	Farm Income (Farm Income + Supplemental Non-Farm Income)
	Producer persistence	Farmers with/without successor(s)
	Producer investment	Farm acreage owned by farmer
	Consumer prices	Food and beverage prices indexed against other CPI major groups

1.3.1.1.B Biomass Preprocessing The preprocessing unit operation has focused on grinding dry feedstocks of one type and variety. This focus provided an initial assessment of the grinding operation to be performed and has lead to the establishment of specific performance targets based on operational efficiency, machine capacity, and resulting feedstock quality. The data collected during FY04 full-scale preprocessing tests, encompassing machine cost and feedstock characteristic metrics (capacity, efficiency, bulk density, flowability, and fractional quality), have been implemented into integrated feedstock assembly system models and have been shown through cost and sensitivity analysis to be critical parameters in the techno-economics of the preprocessing unit operation. Current preprocessing tests are furthering the full-scale preprocessing work to include a wider variety of grinding parameters, biomass feedstocks and moistures. The scope of these new tests is incorporating more aggressive capacity, efficiency, and bulk density targets based on previous preprocessing results. These targets are guiding the work scope for the INL and their industrial partners. The preprocessing section of the draft feedstock assembly system design report for dry biomass feedstocks is based on the performance targets for efficiency, capacity, and feedstock quality as determined by the core R&D efforts of this preprocessing task. The final feedstock assembly system design will identify a clear path to demonstrate and validate the preprocessing unit operation by FY09.

1.3.1.1.C Biomass Storage and Queuing The key attributes of storage systems are the overall cost of the system and changes in biomass quality over the storage period. In FY 2006 we tested the quality changes of biomass in wet storage as well as dry storage.

The milestone targets and the accomplishments of this year for mechanical preprocessing are as follows:

FY06 dry storage loss target = **<5%** → FY06 accomplishment = **0.85%**
FY06 cost target = **<$1.75/dry ton** → FY06 accomplishment = **$1.18/dry ton**

Meeting these goals was largely done by selecting a geographic region which is optimal for dry storage. Southeast Idaho was used as the location to evaluate the effects of storage types and conditions on the final cost of lignocellulosic biomass at the throat of a reactor. The input data and set of assumptions come from the FY 2005 full-scale harvest and collection effort where bales, loafs, and a chopped pile were established for storage evaluation. The effects of the bale storage were evaluated using the INL feedstock assembly design spreadsheet (Dry_Bulk_Bale_Processing v7-05-06) developed in 6.2.3.5 HQ Analysis Coordination and Studies Support – INL. It should be noted that this version of the static spreadsheet model does not take into account losses outside of the storage unit operation such as preprocessing, transportation, and handling losses. The scenario was for; cereal straws, windrowed, made into 4x4x8ft bales, stored roadside without tarps, and ground with a mobile grinder, and transported by truck to a 3-day interim bin storage system before loading the biomass into a reactor. The other two storage methods (loafs and chopped piles) were also analyzed as a stand alone unit operation, as opposed to being integrated with the rest of the assembly system.

The effects of dry matter losses in wet storage were estimated in terms of the impact on the compositional quality of the biomass. A large portion of the dry matter losses come directly from the microbial utilization of soluble and structural sugars during wet storage, and this effect was found to be potentially large. For example, losing 5% of the dry matter, if coming directly at the expense of sugars, would lower the feedstock allowable purchase price by about $8/ton. In our optimized system, where corn stover was stored 12 months in an ensiled system, there was no dry matter loss found. However, bunker losses appear large in the Harlan Iowa (B/MAP) project, while bag-type systems (bale wrap, silo tube) reportedly have around 5% dry matter losses.

Feedstock Infrastructure Subtask (1.3.1.1.C.1)

Target Milestone: Complete a core R&D engineering design and techno-economic assessment of an integrated wet storage - biomass field pre-processing assembly system with a pretreatment process that could potentially be scaled up to produce feedstocks to achieve a reduction to $35 per ton by 2012 from $53 per ton as of 2003.

Lignocellulosic biomass which is harvested relatively dry and supports a fully dry feedstock supply chain is slated to support the pioneer biorefineries. However, wet harvested biomass is projected to become a major portion of the available tonnage in order to meet ethanol production goals in 2012 and beyond. In order to understand the storage of wet harvested biomass, an iterative approach was taken, between engineered systems (modeling) and potential responses (field and lab work) of the feedstock during storage.

We analyzed potential pathways for the feedstock supply chain, binned these into three major supply chain operations (dry, wet/dry hybrids, and wet), and performed cost analyses for the respective storage operations. Dry assembly pathways are appropriate for relatively dry harvested crops. Wet/dry hybrid assembly pathways begin with wet harvested biomass and include drying within the supply chain. Wet assembly pathways include long term wet storage and retaining biomass moisture throughout the feedstock supply chain.

To analyze the feedstock assembly pathways mentioned above, the following key parameters were needed: A) the value of soluble sugars in the feedstock, B) potential storage options and their respective costs for wet-stored biomass, C) costs for drying of biomass and potential capture of a value-added product (ethanol) to support wet/dry hybrid assembly pathways, D) the composition of wet-stored biomass and the quality (in terms of structural sugars) of the biomass in relation to biological dry matter loss (DML), D) the stability of ethanol produced in solid-state fermentation, and E) the potential cost-offset for biomass containing ethanol.

The soluble sugars in biomass feedstocks represent significant fractions of the overall chemical composition. For example, corn stover is composed of about 6 to 12% (w/w) soluble sugars, while in switchgrass soluble sugars reportedly range from about 4 to 16%. These soluble sugars constitute a significant component of the overall feedstock value. Given that high quality corn stover contains 65% structural sugars, the soluble sugar fraction ranges from 8.4 to 15.6% of the total sugar content. These soluble sugars make up 14.6 to 25.5% of the C-6 sugars in corn stover. The values of the soluble sugars may be estimated to range from $4.01 to $13.20/dry ton for switchgrass and $5.48 to $10.20/dry ton for corn stover, assuming that the soluble sugars in biomass are at least as valuable as structural sugars in biomass. However, this resource value is often not recovered because the soluble sugars in the feedstocks are typically degraded by microbial activities promoted by prolonged contact with moisture during storage.

One way to capture the value of soluble sugars is to simply ferment them to a product, ethanol for example, within the biomass in storage or in a queuing system. However, capture of ethanol (or any chemical that may be captured by volatilization) would involve drying the biomass, which could be a synergistic cost impact because of the lower transportation and handling costs of dry biomass. To obtain relevant biomass drying costs, a subcontract was placed with a commercial food and chemical process equipment manufacturing firm, with specific details to model the complete greenfield cost of supplying commercial drying systems to support 0.3, 0.8, and 5M dry tons/year biomass supply over moisture ranges from 40 to 60% w.b. This was necessary to support the wet/dry hybrid pathways where drying is needed at the commercial scale.

The costs of wet stored systems (bunker, bale wrap, drive-over pile, vertical storage structure) ranged from 13 to 31$/DMT, assuming no dry matter losses. Using published mechanical dry matter losses, the final costs ranged from 16 to 34$/DMT.

The amount of dry matter loss in storage from microbial and metabolic activity is a function of storage method and environmental factors that determine water activity in the stored material. Part of storage strategy in wet feedstocks is preservation; due to high water activity, some dry matter will be consumed. Traditional preservation for wet livestock feed is a mixed acid fermentation which stops plant metabolism and eliminates most microbial activity. Although investment cost would be greater for storage systems engineered to produce ethanol fermentation, such a system could accomplish the same reduction in activity as traditional ensiling and offer the added advantage of producing recoverable ethanol. Our model suggests such systems could result in storage costs competitive with dry storage, and they would produce a dried and compacted product that would reduce transportation costs. Depending on feedstock type and condition, an ethanol capture wet storage system could even result in a net profit out of storage.

Laboratory studies were conducted to investigate A) the stability of ethanol produced in solid state fermentation of corn stover, and B) the compositional impacts on the residual solid biomass. Although ethanol production was used as a model fermentation product, the data generated allows inference into other in-storage pathways which would use soluble sugars for conversion into value-added chemicals. In two cuts of corn stover, ethanol could be produced in storage ranging from zero to about 4% (wt/dry-wt biomass). Furthermore, these results show that the ethanol is relatively stable out to 90 days of storage, which may support several supply chain options.

<u>Feedstock Supply Chain Preprocessing Using Endoxylanases Subtask (1.3.1.1.C.3)</u> The purpose of this task is to examine the effects of using endo-1,4-beta xylanases at various stages within the feedstock supply chain on the preprocessing and downstream processing of corn stover and other lignocellulosic agricultural residues. Examples of such effects include potential improvements in the energy usage during preprocessing steps such as grinding and densification, and the reduction of required pretreatment severity without producing significant soluble oligomers.

An experimental plan was developed to assess the enzymatic activity of commercial endoxylanases on pre-purified arabinoxylan and selected cellulosic biomass samples at low water activities. Results obtained using wheat arabinoxylan will be used to determine enzyme activity/water activity relationships, which will then be combined with water activity/water content relationships for various lignocellulosic substrates to define the water content ranges that support enzymatic activity in the field. Rates of reaction will be measured over time at various fixed water activities. Methods developed for the pre-purified arabinoxylan will be applied to lignocellulosic biomass sources including corn stover, wheat straw, and switchgrass.

Initial method validation tests using wheat arabinoxylan indicate that enzyme activity is observed in under one week at an aw of 1.0 when water is transferred through the vapor phase to freeze-dried samples. Tests underway at aw ranging from 0.19 - 0.80 (4 - 21% moisture on a dry basis) will determine the minimum water activity necessary to support enzyme activity for selected commercial endoxylanases for use in dry storage systems.

1.3.1.1.D Biomass Transportation and Handling The barriers associated with transportation and handling costs in the feedstock assembly system have primarily been addressed by increasing feedstock bulk densities through a reduction of particle sizes during the preprocessing operation. Established particle size versus bulk density relationships in previous preprocessing R&D has shown that there is a point of diminishing returns where the cost of grinding to smaller particle sizes exceeds the bulk density gains achieved in transportation and handling. The purpose of this dedicated transportation and handling task is to investigate the effects of biomass rheological properties on advanced bulk systems as they are directly implemented into transportation and handling equipment, and not necessarily tied to the preprocessing operation.

A detailed multi-year task plan has been developed. The work expands upon previous work conducted by the INL Harvesting and Preprocessing Feedstock Tasks and is directed at developing techniques, and ultimately engineered systems, that will increase the bulk density of biomass materials transported in various feedstock conveying operations. The techniques will exploit fundamental rheological properties of the feed-stocks and range from mechanical compaction to two-phase flow systems. The initial step in this development effort is to design and conduct testing that will allow a detailed characterization of materials properties of various feedstocks under conditions that are representative of field, process, and storage environments. Properties of interest include particle size distribution, bulk density, compressibility, unconfined yield strength, permeability, internal and surface friction, elastic spring back, shear strength, and viscosity. Combinations of these properties allow the flow of materials to be defined and predicted when bulk feedstocks are fed, mixed, compacted, stored, or conveyed. Consequently, they are also critical for the design and optimization of transportation and handling systems for diverse feedstock unit operations.

Laboratory testing protocols for producing biomass flow property databases have been developed, and components and instrumentation for conducting the benchscale testing have been identified and procured. Since commercial rheological testers are typically designed for use with fine powders; and consequently, do not accommodate particulate that is greater than ¼ inch in diameter, the project has designed versions of these measurement systems for characterizing larger feedstock particles. Systems include compaction and shear cells that can be scaled for various material sizes, integrated with commercial load frames, and operated over a range of consolidation pressures. These cells will be used to determine compressibility, unconfined yield strength, permeability, and spring back for various feedstocks as a function of grind size and uniformity, moisture content, and degree of compaction. These properties can, in turn, be related to flowability of the material within storage bins, hoppers, augers, and other conveying systems.

A one cubic meter volume test hopper has been designed and fabricated that will allow feedstock flow to be observed as a function of various surface liner materials over hopper wall angles that can be varied from 0 to 60 degrees and outlet diameters that can be varied from a few entimeters to one meter. The test hopper will allow the visualization of flow properties, determine a material's tendency to arch or rat-hole, and measure frictional properties. Hopper tests will also be used to validate observations from testing conducted at smaller scales.

Bench scale testing of selected feedstock materials, including samples of wheat straw, corn stover, and switchgrass, has been conducted at the smaller particulate sizes (E Milestone). These initial tests serve as a baseline and allow the measurement protocols to be validated using commercial systems. The feedstocks were first ground into 1/4 inch minus (6.25 mm) fractions. The 1/4 inch minus fractions were then further processed to a size of approximately 1/12 inch minus (2 mm). The two size fractions were then adjusted in moisture content from the dry (<8%) condition to 45%. The parameters measured included bin density, feed density, permeability, spring back, compressibility, relaxation, unconfined yield strength, and frictional properties. The data collection procedures were based upon techniques developed for the flow classification system developed by J. R. Johanson. The classification scheme allows the fundamental rheological parameters listed above to be translated into index values that are predictors of material flow through systems of a particular geometry. The rheological testing is being expanded to larger size fraction feedstocks currently being collected in conjunction with the INL's harvesting and preprocessing activities.

A literature and vendor survey of high density bulk and slurry pipeline technologies has been completed. The survey examined the parameters needed to design, develop, and evaluate the cost-benefits of the use of these systems for the delivery of feedstocks to ethanol production plants. The availability of existing data on the flow properties of various feedstock materials that could be used in the development of advanced conveying systems was also assessed.

Based upon the experiences in mining industry, the survey indicated that pipeline transportation of materials may be cost-effective when there are: (a) high annual volumes of materials to be shipped; (b) long distances to be traversed; (c) travel through difficult terrain; (d) high anticipated rates of inflation; (d) low real interest rates; (e) large, closely-spaced material resources to feed into the system; (e) availability of sufficient water at low delivered costs; (f) limited, or circuitous, rail routes or inefficient rail operations; and (g) low cost of electric power relative to that of diesel fuel for railroad locomotives. Throughputs of at least one million tons per year are generally required to make transport using a new slurry line competitive with other modes of transportation. In addition, for pipelines that require slurry preparation and separation facilities, a distance of 50-100 miles is often necessary to spread the costs.

The search also found little data on the rheological properties of herbaceous feedstocks that could be used in the design and optimization of long distance slurry pipelines or shorter pneumatic conveying systems that could serve as feeder lines to ethanol production plants. The transport of biomass in water-based slurries presents a number of challenges not found in the minerals industries. In particular, the material is more susceptible to physical; and potentially, chemical/biological damage than minerals. The design of laboratory scale testing and evaluation systems are being investigated to address these data gaps and allow a more detailed assessment of these technologies.

<u>1.3.1.1.E Woody Harvest, Handling, Preprocessing, and Storage</u> Completion of E Level Milestone 1.3.1.1.E.ML.1 "Initial assessment of woody biomass industrial linkages to lignocellulosic fuel production and verification of near infrared (NIR) and other analytical tools for rapid characterization" was completed June 29, 2007. INL traveled to North Carolina State University (NCSU) and met with Steve Kelley to finalize project details and tour the university facilities. Meetings were held with local loggers and timber contractors to discuss current logging practices and availability of forest residues. Sample gathering and NIR scanning is continuing at various sites in North Carolina. Idaho loggers have been contacted and sampling in northern Utah is planned. Meetings with representatives from the Idaho Department of Lands and the Caribou National Forest are also scheduled to take place.

NIR: Preliminary data show a high degree of correlation between NIR spectra and wood chemical constituents that are important to biofuels platforms. This suggests that there is a high probability of successfully creating predictive models utilizing NIR data, however, this data also suggests that separate NIR calibrations for hardwood and softwood will be necessary.

Woody Biomass Industrial Linkages: The two largest endusers of forest products are the pulp and paper industry and lumber mills. These industries produce low value lignocellulosic by-products. In the case of lumber production, this material is primarily in the form of sawdust. The most prevalent process for paper production is the Kraft process which produces a by-product called black liquor which is high in lignin and about 60% organic matter. Residues from timber harvest make up 20% to 30% of the total biomass available. These three sources represent the majority of under-utilized lignocellulosic material.

Pulp and Paper: The U.S. pulp and paper industry consumes approximately 12% of all energy used in the manufacturing sector of the economy. Most Kraft pulp and paper mills burn black liquor to produce steam and power for the plant and to regenerate the chemicals used in the pulping process. Black liquor is the single largest source of bioenergy in the U. S. Older plants use relatively inefficient boilers and must augment this power with energy from outside sources. Newer plants can produce enough energy to sustain operations and may even produce surplus electricity. Utilizing black liquor from these plants to produce a liquid biofuel will directly compete with the energy needs of the plant. In order to compete with the existing technologies utilizing this energy source, a new process would need to be efficient enough to provide power to the mill and have a marketable surplus. Additionally, recovery of the pulping chemicals must be part of the over all design. A gasification system that produces steam and syngas to run a turbine to produce electricity for the plant with enough excess to produce fuels via Fischer-Troph may be feasible, however, it maybe difficult to economically compete with electricity production given that electrical power must be part of the design.

Sawmill: Modern sawmills utilize waste wood scraps and sawdust to generate electricity for there own needs similar to the pulp and paper industry. These mills produce a 10 % to 30% excess of electricity. Other uses for sawdust and woody scrap material are pelletization, composting, and incorporation into composite materials. As with black liquor, a biofuels process would have to compete with the current uses of these materials.

Forest residues: Typical timber harvesting operations leave behind 20% to 30% of the harvestable biomass (woody residue) which represents from 71 to 100 million metric tons. This biomass is in the form of woody under story, limbs, leaves, and tree tops. Costs associated with gathering and transporting these materials is often higher than what an end user will pay. Sometimes the land owner will stipulate that the materials be removed for aesthetic reasons and to facilitate replanting. Spot markets for hog fuel exist in some areas of the country where direct-fired or co-fired power plants are present. Forest residues represent a large lignocellulosic energy source that is largely under utilized due to difficulties in obtaining, handling and delivering these materials cost effectively. Current estimates put delivery costs at between $30 and $80 dollars a dry ton with this cost largely impacted by transportation costs. However, optimization of the unit processes associated with forest residues may lower the delivered cost substantially and these materials may represent the best opportunity to provide lignocellulosic feedstock at the scale necessary to be of national significance.

Schedule:

Project Initiation Date: September 01, 2000
Planned Completion Date: September 30, 2012

Feedstock Platform Portfolio – Feedstock Systems Integration

Supply System Logistics

Shahab Sokhansanj, Oak Ridge National Laboratory

Principal Investigator:	Shahab Sokhansanj Anthony Turhollow; Robert Perlack; Mark Downing	Funding Partners:	Natural Sciences and Engineering Research Council of Canada, USDA
HQ Technology Manager:	Sam Tagore	Sub-contractors:	University of British Columbia
PMC Project Officer:	Kevin Craig		

Goals and Objectives:
The Project Goal: The goal of Supply Systems Logistics is to accelerate the development and validation of optimum biomass delivery options that would reduce the cost of producing biofuels from cellulosic biomass to levels competitive with competing fuels.

Objectives and scope: This task develops validated models of integrated collection, preprocessing, storage, and transport systems with capabilities to:

- develop an accurate account of regional biomass availability based on harvest time-moisture content (wet and dry) of biomass;
- develop reliable cost estimates for producing and delivering biomass feedstock to biorefineries – from farm to the throat of biorefineries;
- conduct optimizations to search for minimum supply options with respect to regional biomass availability, biomass quality, and timeliness of deliveries;
- conduct risk and sensitivity analysis on costs, energy inputs, and environmental implications of innovative biomass supply options;
- integrate biomass supply with conversion and biofuel distribution operations for life cycle costing; and
- develop strategies for siting pre processing depots and organizing regional and national supply networks to ensure year round availability of feedstock supply to bio refineries.

Project Description: Two underlining goals drive this task: (1) provide an accurate account of engineering requirements and infrastructure for on-time delivery of biomass to a biorefinery, and (2) conduct risk analysis on cost variations due to inherent biomass availability and quality. The goals of this task are realized by simulating and validating individual unit operations and integrating these operations across the entire supply chain. The simulation model employed is continuously verified using experimental and commercial field data as these become available. When executed, the model optimizes every operation along the biomass supply chain with respect to cost, quality and quantity. The verified model results are used for strategic analysis in support of the pretreatment and sugar platform, the thermochemical platform, and in support of program analysis and management.

The efforts in this task uses field data from integrated biorefinery partners– the Chariton Valley Switchgrass project, the Imperial Nebraska wet storage project, and the Iowa State Integrated Corn Stover Harvest project. The data also comes from core R&D research supported by OBP and USDA as well as university based research. The model also integrates the supply chain with the conversion processes to search for minimum cost biofuel and/or bioproduct.

Other industries have developed some very sophisticated engineering tools to make their industries competitive. The DOE biomass supply logistics model is equally robust in simulating supply operations subject to regional crops and bio-ecological constraints. The model reduces potential risks associated with on-time biomass availability, cost, and quality

Summary of Work to Date - Accomplishments (FY05-current): Activities in Biomass Supply Logistics is divided into two broad spectrum: (1) modeling and simulation, (2) field and laboratory experiments in support of the modeling effort. The followings are samples of modeling and experimental efforts since 2005.

Modeling: Development of the IBSAL: The IBSAL model is a simulation of a biomass supply chain. It consists of a network of operational modules and connectors threading the modules into a complete supply chain. Each module is a mathematical simulation of a process. The process modules are drying, wetting, and biochemical reactions that may lead to dry matter changes in biomass during harvest and subsequent handlings. The model is written in an object oriented high-level simulation language EXTEND[T] (www.imaginethatinc.com). The supply chain is divided in two activities: (1) Collecting and storing the biomass at the collection sites and (2) preprocessing and transporting biomass from collection sites to a biorefinery. The collection processes start immediately following the grain harvest or wilting of the grass (switchgrass) in the field. The model execution is fast and usually does not take more than 30 seconds to complete a run. The model is highly interactive allowing changes in input and output as the program executes.

The peer review and publication of the IBSAL model constituted a major milestone for the feedstock platform to meet the stage gate review of the platform.

Reference: Sokhansanj, S., A. Kumar, and A.F. Turhollow. 2006. Development and implementation of integrated biomass supply analysis and logistics (IBSAL) model, *Biomass and Bioenergy*, 30(2006):838-847.

Large scale wet stover storage and supply: Based on experience with successfully storing water-saturated large piles of bagasse for the pulping industry, Atchison and Hettenhaus (2003) proposed that such a system can also be applied to corn stover. Regardless of the technical feasibility of this system, in this article we estimate the cost of harvesting corn stover in a single pass with corn grain, delivering the chopped biomass to a storage pile, storing the stover in a wet form in a large pile at 75% moisture in a 211,700-dry Mg facility within a radius of 24 km from the field, and transporting the stover 64 km to a biorefinery. Field-ground corn stover can be delivered to a biorefinery by rail for \$55 to \$61/dry Mg. Truck transport is more expensive, \$71 to \$77/dry Mg. To achieve a minimum cost in the system proposed by Atchison and Hettenhaus, it is necessary to field densify stover to 74 dry kg/m^3, without losing combine field efficiency, have a large storage pile to spread fixed costs of storage over enough biomass, and use rail transportation. Compared to storage in an on-farm bunker silo at \$60/dry Mg, there are limited circumstances in which large pile storage has a cost advantage.

Reference: Turhollow, A.F. S. Sokhansanj. 2007. Costs of harvesting, storing in a large pile, and transporting corn stover in a wet form. Manuscript number pm 5511; Approved for publication in Applied Engineering in Agriculture.

Ranking of biomass collection and feedstock supply chains: A recent published journal article ranks various biomass collection and feedstock supply options for the biofuels. The study details multi-criteria assessment methodology (PROMETHEE) that integrates economic, social, environmental and technical factors in order to rank alternatives for biomass collection and transportations systems. ORNL's IBSAL (Integrated Biomass Supply Analysis & Logistics) is used to calculate costs, energy input and emissions. Ranking of biomass collection systems is based on cost of delivered biomass, quality of biomass supplied, emissions during collection, energy input to the chain operations and maturity of supply system technologies. The assessment methodology is used to evaluate alternatives for collecting 1.8 million dry tonne per year - based on assumptions made on performance of various assemblies of biomass collection systems. A proposed collection option using loafer/stacker was shown to be the best option followed by ensiling and baling. Ranking of biomass transport systems is based on cost of biomass transport, emissions during transport, traffic congestion and maturity of different technologies. At a capacity of 4 million dry tonne per year, rail transport was shown to be the best option, followed by truck transport and pipeline transport, respectively. These rankings depend highly on assumed maturity of technologies and scale of utilization. These may change if technology such as loafing or ensiling (wet storage) methods are proved to be infeasible for large scale collection systems.

Reference: Kumar, A. S. Sokhansanj, and P.C. Flynn. 2006. Development of a Multi-Criteria Assessment Model for Ranking Biomass Feedstock Collection and Transportation Systems. Applied Biochemistry and Biotechnology 129-132:71-87.

Collaborative Project: The University of Tennessee, Oak Ridge National Laboratory, First American Scientific Company, University of British Columbia: The project funded through the USDA/DOE - 2004 solicitation is targeted to address biomass size reduction (chopping, grinding) and dry separation of biomass components. First year objectives investigated biomass ultimate failure stress/ energy/ physical properties to understand current equipment to identify grinder and separating actions for in-depth evaluation. Assessment tools were developed and include rapid imaging for sizing large, non-uniform particles, FT-NIR for rapid chemical analyses and wet chemical protocols to evaluate targets and separated biomass. Biomass "models" were selected as follows: corn stover, switchgrass, rice straw, hickory wood, and bagasse. Project original goal was 15% grinding savings, and is now projected to reduce typical grinding cost $3 to $4 per dry ton (about 1/4 of current costs) based current understanding of pre- and post-grinding literature data. Multiple stage grinding may be most appropriate to maximize efficiency. Size reduction technologies for further research were identified for 2nd year instrumented testing as follows: hammer mill, knife mill, disk mill, and variable-spacing linear knife grid. The project team had two recent meetings to evaluate the mid-term progress. In May, the University of Tennessee team and a USDA peer review team conducted a joint review of the project milestones. In late June, Dr. Womac (PI- University of Tennessee) traveled to Vancouver, BC where he reviewed the progress with the industrial research partner Dr. Narayan (First American Scientific Corporation), and the University of British Columbia research team. The project is progressing towards its third and final year when a pilot scale size reduction equipment will be demonstrated and a complete business plan around biomass pre processing (size reduction and fractionation) will be developed.

Reference: Womac, A.R. C. Igathinathane, P. Miu, S. Sokhansanj, S. Narayan. 2007. Biomass Pre-Processing Size Reduction with Instrumented Mills. ASABE paper 076046. Presented at the International Meeting of the ASABE, Minneapolis, MN July 17-20, 2007.

Large Scale Switchgrass supply for biofuels: Switchgrass (Panicum virgatum L.) is a promising cellulosic biomass feedstock for biorefineries and biofuel production. This paper reviews current and future potential technologies for production, harvest, storage, and transportation of switchgrass. Our analysis indicates that for a yield of 10 Mg ha^{-1}, the current cost of producing switchgrass (after establishment) is about $41.50 Mg^{-1}. The costs may be reduced to about half this if the yield is increased to 30 Mg ha^{-1} through genetic improvement, intensive crop management, and/or optimized inputs. At a yield of 10 Mg ha^{-1}, we estimate that harvesting costs range from $23.72 Mg^{-1} for current baling technology to less than $16 Mg^{-1} when using a loafing collection system. At yields of 20 and 30 Mg ha^{-1} with an improved loafing system, harvesting costs are even lower at $12.75 Mg^{-1} and $9.59 Mg^{-1}, respectively. Transport costs vary depending upon yield and fraction of land under switchgrass, bulk density of biomass, and total annual demand of a biorefinery. For a 2000 Mg d^{-1} plant and an annual yield of 10 Mg ha^{-1}, the transport cost is an estimated $15.42 Mg^{-1}, assuming 25% of the land is under switchgrass production. Total delivered cost of switchgrass using current baling technology is $80.64 Mg^{-1}, requiring an energy input of 8.5% of the feedstock higher heating value (HHV).

With mature technology, e.g. a large loaf collection system, the total delivered cost is reduced to about $71.16 Mg^{-1} with 7.8% of the feedstock HHV required as input. Further cost reduction can be achieved by combining mature technology with increased crop productivity. Delivered cost and energy input do not vary significantly as biorefinery capacity increases from 2000 Mg d^{-1} to 5000 Mg d^{-1} because the cost of increased distance to access a larger volume feedstock offsets the gains in increased biorefinery capacity. The paper outlines possible scenarios for the expansion of switchgrass handling to 30 Tg (million Mg) in 2015 and 100 Tg in 2030 based on predicted growth of the biorefinery industry in the U.S. The value of switchgrass collection operations is estimated at more than $0.6 billion in 2015 and more than $2.1 billion in 2030. The estimated value of post-harvest operations is $0.6 - $2.0 billion in 2015, and $2.0 - $6.5 billion in 2030, depending on the degree of preprocessing. The need for power equipment (tractors) will increase from 100 MW in 2015 to 666 MW in 2030, with corresponding annual values of $150 and $520 million, respectively.

Reference: Sokhansanj, S. S. Mani, A.F. Turhollow, A. Kumar, D. Bransby, L. Lynd, M. Laser. 2007. Large scale production, harvest and transport of switchgrass (Panicum virgatum L.) - current technology and visioning a mature technology. Submitted to Biomass & Bioenergy Journal.

Research progress on biomass densification: Bulkiness of crop residues and grasses is a major technical barrier against the biomass as a convenient feedstock for fuels and chemicals. Processing biomass into dense granules increases the bulk density of a group of loose biomass particles pressed into a small volume (granule). Dense granules have low moisture content (about 8% wet basis) for safe storage, a high bulk density (more than 600 kg m-3 almost 10 times when loose) for efficient transport and flowability for easy handling. The objective of this research is to determine the optimum size of particles from biomass grasses and residues and the best combination of densification parameters that would produce durable granules. Ground biomass (wheat straw, barley straw, corn stover, switchgrass) passed through three screen sizes (3.2, 1.6 and 0.8 mm) were compressed under five levels of compressive forces (1000 to 4500 N) and at two levels of moisture contents (12% and 15%) to establish compression and relaxation data. In general, smaller particle size, low moisture content, and higher pressures significantly increased the density of biomass granules. Corn stover required the least pressure while barley straw needed the most for the same granule density. Barley straw granules showed the most rigidity among the four biomass species tested. Wheat straw and switchgrass were similar in their response to particle size, moisture content, and compressive forces.

Reference: Mani, S., L.G. Tabil, and S. Sokhansanj. 2006. Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets. Biomass & Bioenergy 30(2006):648-654.

Schedule:
Project Initiation Date: September 01, 2000
Planned Completion Date: September 30, 2011

Biochemical Platform

Introduction

The Biochemical platform is focused on reducing the cost of converting lignocellulosic biomass to mixed dilute sugars and their further conversion to liquid transportation fuels. While ethanol is the Program's current fuel of focus, the Program is expanding its interest into other biofuel technologies which have the potential for development into successful integrated biorefineries. Biochemical conversion uses biocatalysts, such as enzymes and microorganisms, in addition to heat and chemical catalysts, to convert the carbohydrate portion of the biomass (hemicellulose and cellulose) into intermediate sugar streams which are then fermented to ethanol and other products.

Biochemical platform R&D will further improve the feedstock interface, pretreatment and conditioning, and enzymes and fermentation processes, in addition to process integration, in order to reduce ethanol costs. These economically viable technologies will act as a springboard for launching the next generation technology to produce ethanol and other products from a wide range of cellulosic feedstocks.

Platform Performance Goal

Reduce the estimated mature technology processing cost for converting cellulosic feedstocks to ethanol.

Objectives

- Short-term objectives are to reduce the modeled production cost of cellulosic ethanol to $1.33/gallon (2007$ estimated) by 2012.
  - By 2007, achieve a modeled cost target of $0.125 (2007$ estimated) per pound of sugars (equivalent to $2.43 per gallon of cellulosic ethanol) through the formulation of improved enzyme mixtures and pretreatments.
  - By 2012, develop improved saccharifying enzymes to meet the target of reducing the cost of enzyme systems to $0.10 per gallon of ethanol produced.
  - By 2012, validate integrated production of ethanol from corn stover at integrated scale at the NREL process demonstration unit facility.
  - Develop cross-cutting technologies useful for producing fuels (i.e., improved catalysts and biocatalysts)
- By 2017, validate integrated production of ethanol from switchgrass at pilot scale.

FY 2007 Accomplishments

- Creation of successful collaboration between the Feedstock and Biochemical Platforms with INL, NREL and ORNL as leading organizations. This group identified the most likely pioneer feedstocks to a biorefinery, analyzed how pre-processing methods could affect ethanol price, and developed an experimental plan for ensiled feedstocks.
- Continued operation of the Biomass Surface Characterization Laboratory (BSCL) at NREL. The relationships between pretreatment and the chemical/structural changes in corn stover stems that result in biphasic xylan hydrolysis have been better defined. Also, within this task, NREL has developed the first generation computational model of cellobiohydrolase I (CBH I) capable of describing structure and function, and verifying CBH I structure.
- The Consortium for Applied Fundamentals and Innovation (CAFI) is a university consortium, formed in 2001, of biomass pretreatment technology experts to investigate a wide variety of pretreatment processes (AFEX, Dilute Acid, Hot Water, Lime, etc.) for corn stover and hybrid poplar. Funding will continue through 2008 to expand pretreatment activities for switchgrass (CAFI 3).
- Increased xylose yield to 75% from 63%, in laboratory-scale high solids pretreatment reactor on corn stover.

- Issued a Funding Opportunity Announcement for improved ethanologens and selected five applicants to undertake R&D to develop microbial strains suitable for commercialization.
- Issued a Funding Opportunity Announcement for developing improved saccharifying enzymes that will allow for selection of potential awardees in FY 2008.
- Increased the platform range of technology options for meeting technical targets through advances:
  - Improved yields of ethanol from distillers dried grains; and
  - Production of value-added products from sugars.

Budget

The President's FY 2008 budget allows for the acceleration of research into cellulosic ethanol conversion from a wide range of feedstocks in order to meet the near and longer-term goals of the Biofuels Initiative. The FY 2008 budget is approximately $40MM.

2008 Plans

Ethanol cost reductions will reflect the results of work in the areas of pretreatment, conversion of cellulosic components of biomass to mixed, dilute sugar streams; and process integration. Specific objectives include determining which feedstock types will be used in pioneer plants, and reducing the severity (harshness) of thermochemical pretreatment while optimizing the digestibility of the pretreated material. Selecting optimal pretreatment chemistries along with improving the overall effectiveness of pretreatment processes; further reducing enzyme costs; and increasing the solids loading for the process to reduce equipment size, energy requirements, and reagent requirements will further reduce overall process costs.

In FY 2008, pilot-scale evaluation of one or more additional chemistries or configurations for thermochemical pretreatment will continue from 2007. Pretreated biomass will be reduced to simple sugars and residue by the action of hydrolytic enzymes. Further improvements are needed to: (a) increase the specific activity of cellulases; (b) exploit the synergy between cellulase and non-cellulase hydrolases that attack the hemicellulose, protein, waxes, perhaps lignin, and other compounds that contribute to recalcitrance; and (c) optimize the cellulase preparations to specific thermochemical pretreatments.

Specific planned activities include:

- Release a Funding Opportunity Announcement (FOA) soliciting applied R&D from the university system to address a wide range of topics related to improving biochemical processing.
- Select potential awardees from the FY 2007 issued FOA to undertake R&D to improve enzyme functionality leading to lower-cost enzymatic processing.
- Undertake a revised state of technology for the biochemical platform at NREL suitable for publication in FY 2009.
- Undertake an initial analysis of pretreatment options for switchgrass through the CAFI3 project with preliminary results available by the end of the fiscal year.
- Conduct multiple runs in the biochemical process demonstration facility at NREL to obtain operational data suitable for designing a fully integrated system available to process biomass to meet the 2012 cost targets.
- Participate in the Biomass R&D Board Biomass Conversion Science and Technology Working Group.

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Project Summaries

Biochemical Platform Support

Biochemical Platform Analysis

Andy Aden, National Renewable Energy Laboratory

Principal Investigator:	Andy Aden	Funding Partners:	N/A
HQ Technology Manager:	Amy Miranda	Sub-contractors:	N/A
PMC Project Officer:	Gene Petersen		

Goals and Objectives: The objective of this task is to perform analysis for the Biochemical Platform in order to support the on-going research in biochemical conversion of biomass. This task supports the following research areas: pretreatment and enzymatic hydrolysis, processing integration, feedstock/process interface and targeted conversion research. Specifically, the biochemical platform analysis goals are to:

1) Identify task level targets that will contribute to the overall critical project targets.
2) Track and report on overall progress to the goal of $1.31 per gallon ethanol (using $2007) via Annual State of Technology assessments
3) Perform quantified risk/uncertainty assessments to evaluate risk of project components and uncertainty in process parameters and costs.
4) Evaluate alternative processes that might improve the process economics/feasibility
5) Integration with other groups' activities including
   a) Strategic analysis of biorefineries and the bioindustry
   b) Systems Integration activities including protocol development
   c) OBP program activities including planning and reviews
   d) Thermochemical platform analysis

Relevance to 30x30 goals: Success in technology deployment hinges on technically viable, cost effective processes. This task translates R&D targets, achievements and milestones into quantitative performance and cost measures that help identify the cost sensitive parts of the technology and subsequently the priority R&D work to increase the technical and economic feasibility of the process under development. For the 2012 target, the analysis task provides annual evaluations of the state of the technology that play a role in determining whether the program is on schedule and if the plan should be altered based on findings during the year. For the 2030 goals, the analysis task develops advanced process designs that integrate current understanding of biomass conversion, possible learning curve improvements with advanced scientific concepts to get a picture of the ultimate potential of biomass.

Project Description: Platform analysis has historically either been part of the R&D projects or a separate project. Regardless of the program structure, analysis is closely tied to the R&D and program staff to provide information and guidance both to R&D projects and to program management. This analysis work is aligned with the planning documents for the program including multi-year program, technical and analysis plans. The goal of the techno-economic analyst is to have a closed loop communication with the researchers and OBP managers. The process-engineering analysts:

1) work with the researchers at the beginning of a project to determine what the targets should be and how they will be measured/reported;
2) provide process design, mass/energy balance modeling and economic analysis input to the project to direct and show progress; and
3) report analysis results to research staff and OBP management and work with both to keep the project focused.

This project is part of the NREL Biochemical Platform which conducts R&D across the breadth of fundamental, applied and integrated science to develop robust bioconversion technologies. Directed by rigorous process engineering and cost analysis, the R&D projects work together to address the key R&D barriers to technically feasible, cost effective ethanol production from biomass. Data and results from fundamental studies on biomass recalcitrance and enzyme action in the Targeted Conversion Research project are used to design improved pretreatment and hydrolysis technologies in the Pretreatment and Enzymatic Hydrolysis project. Those core technologies are tested in an integrated process to reduce the risk to commercial developers in the Biochemical Processing Integration project. The Feedstock/Process interface project in the platform ensures that the process technologies developed are complementary to feedstock collection and storage methods and vice versa. Additionally, the biochemical platform at NREL includes validation activities for the DOE ethanologen development projects to monitor progress to the platform's fermentation goals.

Summary of Work to Date - Accomplishments (FY05-current): The techno-economic analysis work to support the Biochemical Platform has been primarily focused on showing how research can affect the process to convert lignocellulosic biomass to sugars and ethanol. As such, many of the work products are incorporated into the researchers' milestones. Two major stand-alone reports are the design reports produced in 1999 and 2002, which detailed processes to produce ethanol from wood and corn stover, respectively. The annual State of Technology cases are other important work products, documenting the research progress and providing the basis for budget projections needed by OBP staff. State of Technology cases have been developed since 2000 to reflect technologies demonstrated in the lab and pilot plant. These cases address integration targets and document how well research is overcoming techno-economic barriers. Incremental developments required to achieve market target production costs have also been developed to aid OBP in developing their budget targets.

Other analysis of note in recent years includes:

- A Joule target completed in FY05 validated the cost of sugars from stover at $0.12/lb. This intermediate cost provides a more complete picture of the process economics for a biorefinery scenario (multiple products).
- Support to Pilot Plant's Pneumapress Operations. The Pneumapress experiments (in particular the hot wash experiments) were analyzed for component material balances and the resulting effect on the process economics determined. Hot washing the corn stover hydrolyzate did not have a significant effect on improving digestibility.
- Feedstock Study. Analysis was performed to determine the effect of corn stover variability on the minimum ethanol selling price in the market target case. This analysis was done using Monte Carlo

(uncertainty analysis) techniques developed in FY03. Variations in stover composition have a significant effect on the process economics of ethanol production.

- Liaisons to Enzyme Subcontracts. In FY05, a 4-year support effort concluded for the Novozymes and Genencor subcontracts to determine the impacts of the cellulase enzyme developments. Final enzyme preps were evaluated and the cost metric applied to determine the final almost 30-fold improvement from the contracts.
- High Solids Saccharification. Initial scenarios were run to determine if there are technical and economic benefits of performing saccharification at high solids and with high temperature cellulases. The effect of "process intensification" (running at higher solids) was found to be significant and further R&D work was planned in this area.

Schedule

Project Initiation Date:	Friday, October 01, 1999
Planned Completion Date:	Sunday, September 30, 2012

Preprocessing and Storage Systems Development/Qualification

Corey Radtke, Idaho National Laboratory

No project summary provided.

Biochemical Processing Core R&D

Pretreatment and Enzymatic Hydrolysis

Rick Elander, National Renewable Energy Laboratory

Principal Investigator:	Rick Elander	Funding Partners:	N/A
HQ Technology Manager:	Amy Miranda	Sub-contractors:	Hauser, Neoterics International, CICSCO, University of Georgia—Complex Carbohydrate Research Center, Oklahoma State University, Baylor University, Virginia Tech University, University of Maine
PMC Project Officer:	Gene Petersen		

Goals and Objectives: The objectives of Pretreatment and Enzymatic Hydrolysis Task include the investigation and evaluation of pretreatment approaches that are aimed at reducing the cost of pretreatment and increasing the enzymatic digestibility of residual cellulose and hemicellulose in pretreated biomass in a process relevant manner. Activities in this task are aimed at overcoming barriers associated with high capital and operating cost and sub-optimal sugar yields resulting from pretreatment and subsequent enzymatic hydrolysis of biomass. The effect of different pretreatment processes and chemistries on the enzymatic digestibility of pretreated biomass residues are being evaluated in terms of lowering the overall costs of saccharifying biomass that are associated with pretreatment and enzyme usage. Basic insights into the mechanisms of pretreatment catalyst transport and compositional and ultrastructural effects of pretreatment and enzymatic saccharification on biomass are continuing to be developed. Efforts are now expanding to include the investigation of how various pretreatment approaches and conditions affect hydrolyze toxicity properties and resulting hydrolyzate conditioning requirements and the associated response of ethanologens to various raw and conditioned hydrolyzates.

Project Description: This project is part of the NREL Biochemical Platform which conducts R&D across the breadth of fundamental, applied and integrated science to develop robust bioconversion technologies. Directed by rigorous process engineering and cost analysis, the R&D projects work together to address the key barriers to technically feasible, cost effective ethanol production from biomass. Data and results from fundamental studies on biomass recalcitrance and enzyme action in the Targeted Conversion Research project are used to design improved pretreatment and hydrolysis technologies in the Pretreatment and Enzymatic Hydrolysis project. Those core technologies are tested in an integrated process to reduce the risk to commercial developers in the Biochemical Processing Integration project. The Feedstock/Process interface project in the platform ensures that the process technologies developed are complementary to feedstock collection and storage methods and vice versa. Additionally, the biochemical platform at NREL includes validation activities for the DOE ethanologen development projects to monitor progress to the platform's fermentation goals.

More specifically, efforts in the Pretreatment and Enzymatic Hydrolysis Task are focused on understanding, developing and improving process concepts to achieve higher yields of monomeric sugars from important feedstock categories in pretreatment and enzymatic saccharification processes. The effects of pretreatment on enzyme requirements to achieve high sugar yields and on the properties of liquid hydrolyzates and their requirements for conditioning to allow for effective hydrolyzate fermentation are being investigated.

The proposed major activities in the Pretreatment and Enzymatic Hydrolysis Task for FY08 are listed below:

1. Understand pretreatment factors and implement equipment systems needed to achieve 2012 intermediate xylose yield and sugar degradation targets in continuous, pilot scale pretreatment systems.

2. Develop information on inhibitory compounds generated under different pretreatment processes and conditions and relate findings to hydrolyzate fermentability and conditioning requirements.
3. Further develop the concept of "fundamental reactivity" of feedstocks in order to achieve high sugar yields from pretreatment and enzymatic saccharification processes.
4. Develop improved knowledge of pretreated slurry rheological changes during enzymatic hydrolysis and relate findings to leading high solids saccharification process and equipment designs.
5. Apply findings from enzymatic oligomer saccharification systems to process concepts to reduce pretreatment capital and operating costs, lessen inhibitor product formation, and improve overall yields of monomeric sugars from less severe pretreatment conditions.

Summary of Work to Date - Accomplishments (FY05-current): In the period of FY05-FY07, the Pretreatment and Enzymatic Hydrolysis Task has been organized into 5 main subtasks:

- CAFI 2 Support Subtask
- Feedstock Qualification Subtask
- Enzymatic Hydrolysis Subtask
- Oligomer Saccharification (formerly Exploratory Saccharification) Subtask
- 30 x 30 Milestone Support Subtask

Activities of each of these subtasks are directly aligned with important intermediate milestones (as identified in the attached Project Milestone Summary Table) required to achieve the Biochemical Platform 2012 ethanol cost and process performance targets.

Key accomplishments in each subtask are discussed below:
<u>CAFI 2 Support Subtask</u>.
The Pretreatment and Enzymatic Hydrolysis Task has provided technical and logistical support to the Biomass Refining Consortium on Applied Fundamentals and Innovation "CAFI 2" project. We obtained and pre-processed corn stover and hybrid poplar feedstocks for all CAFI research teams and properly stored and distributed feedstocks to the CAFI research teams as requested. Compositional analysis of the raw feedstocks was performed and these results were provided to the CAFI research teams. The compositional analysis work revealed important lignin content differences in 2 different hybrid poplar batches, which translated into significant process performance differences and fundamental insights into pretreatment mechanisms for several of the CAFI pretreatment processes. Additionally, NREL provided dilute acid pretreated corn stover and hybrid poplar performance data and samples to various CAFI research groups for comparative enzymatic hydrolysis and hydrolyzate fermentability studies. The NREL dilute acid pretreated samples were generated in high solids bench-scale and pilot-scale pretreatment reactors and are therefore more process-relevant that pretreated samples available from the other CAFI research teams.

Most significantly, NREL, via a subcontract with Neoterics International, has been providing rigorous and comparative process economic models and analysis for each of the CAFI pretreatment processes on both corn stover and hybrid poplar. While the final process economic modeling finding are not yet complete, a number of general trends have become apparent across the various CAFI pretreatment approaches and the feedstocks being investigated in the CAFI 2 project. Acidic pretreatment processes are relatively insensitive to feedstock type (corn stover or hybrid poplar) and appear to perform reasonably well, although with some losses of sugars to degradation products. A greater sensitivity to feedstock type is seen with the hot water and alkaline pretreatment processes, with these processes generally achieving lower sugar and ethanol yields, and therefore higher predicted Minimum Ethanol Selling Prices (MESP) on the hybrid poplar feedstock. Differences in performance on some of the pretreatment process are also seen with the two different batches of hybrid poplar (low lignin and high lignin), which translate to different predicted MESP results. Some CAFI researchers have modified pretreatment process conditions in order to achieve better pretreatment and enzymatic hydrolysis performance on the high lignin poplar. As the final CAFI 2 pretreatment, enzymatic hydrolysis and fermentation data becomes available, the data will be used in the final updates of each respective pretreatment process economic model. These results will be presented as "current case" and "goal case" models for each pretreatment and each feedstock, including process yields and costs for any required hydrolyzate conditioning steps.

Feedstock Qualification Subtask

In the Feedstock Qualification Task, we have established a standard methodology for the systematic testing of selected important feedstocks across a range of pretreatment conditions using acidic, alkaline, or no-pretreatment catalysts. This is enabling the identification of appropriate pretreatment conditions for representative feedstocks and provides important information on the "relative reactivity" (defined as the total glucose and xylose yield achieved in both pretreatment and subsequent enzymatic hydrolysis) of the selected feedstocks. Initially, this work was performed in a multi-well MultiClave 10X pretreatment reactor and sand bath heating system, allowing for efficient screening of various feedstocks across a range of pretreatment chemistries and conditions. This work supported a FY06 Joule milestone to show that per pound minimum sugars selling prices of $0.11 to $0.135 for switchgrass and $0.105 to $0.125 for wheat straw from combined pretreatment and enzymatic hydrolysis resulting form this low-solids pretreatment screening apparatus was possible.

More recently, the findings from the low-solids pretreatment screening of switchgrass were applied to a more process intensive high solids ZipperClave pretreatment reactor. Combined pretreatment-enzymatic hydrolysis yields of greater than 75% xylose yield and greater than 85% cellulose to glucose yield resulting from pretreatment in the ZipperClave reactor under several process conditions was achieved. Performance between the low-solids MultiClave 10X pretreatment reactor system and the high-solids and the high solids ZipperClave reactor was compared. The pretreatment conditions were identical, except the ZipperClave was loaded at 25% solids versus 5% solids loading in the MultiClave 10X. Comparing the two reactor systems, both reactors showed similar trends of increased feedstock reactivity with increasing pretreatment severity. At lower pretreatment severity conditions, the MultiClave 10X achieved higher sugar yields than the ZipperClave. However, as pretreatment severity increased, the differences in overall reactivity decreased to less than 10% between the two pretreatment reactor systems.

These findings are now being applied to conduct more fundamental feedstock reactivity studies with the goal of further ascertaining factors that control the fundamental reactivity of various feedstocks. This work will highly leverage the chemical and biological processing fundamentals work being conducted within the Targeted Conversion Research Task. Additionally, work has been initiated to better understand how various combinations of feedstock and pretreatment approach affect the generation of potentially inhibitory compounds in hydrolyzate fermentation liquors. This work is primarily being conducted by university subcontractors to identify and quantify inhibitory compounds in hydrolyzates and to develop and implement genomic enrichment methods for use in revealing toxicity mechanisms of selected hydrolyzate compounds.

Finally, activities to support the capability enhancements and operational maintenance of the Biochemical Process Develop Unit (BCPDU) at NREL to service various programmatic activities associated with Biochemical Platform and Integrated Biorefineries Platform have been managed and supported by the Feedstock Qualification Subtask.

Enzymatic Hydrolysis Subtask

One key activity in the Enzymatic Hydrolysis Subtask has been to conduct experimental studies to quantify the effect of solids concentration and background sugars on enzymatic cellulose saccharification on dilute acid pretreated corn stover. Process economic analysis has indicated that operating the enzymatic hydrolysis under high solids conditions without separation and washing steps to remove soluble compounds in pretreated slurries are economically advantageous, but the effects of such a process intensive reaction environment for enzymatic hydrolysis is not fully understood. The results were compared to control conditions where the pretreated corn stover was washed to remove monomeric and oligomeric sugars and other soluble compounds there were released during pretreatment that could inhibit enzymatic saccharification performance. Experiments were carried out at different enzyme loadings, solids concentrations, and temperatures. It was found that the enzymatic saccharification performance was affected by both solids concentration and enzyme loading, as high solids loadings resulted in lower glucose yields, presumably to sugar product inhibition and/or mass transfer limitations under high solids conditions. Also, it was found that the unwashed pretreated slurries, where sugars and other compounds solubilized during pretreatment remain, achieved significantly lower enzymatic saccharification yields than the control experiments under identical conditions using thoroughly washed pretreated slurries. These findings indicate that there are significant challenges in applying commercially available enzyme systems to such process intensive reaction conditions that will require further understanding of enzymatic hydrolysis process and reactor design, along with improved knowledge of the inhibitory nature of compounds solubilized during pretreatment upon saccharification enzyme systems.

As motivated by process economic analysis findings, another key element of the Enzymatic Hydrolysis Subtask is to develop improved knowledge of pretreated slurry rheological changes during enzymatic hydrolysis and relate these findings to leading high solids saccharification process and equipment designs. Work has been performed to characterize how changes in rheological properties of slurries undergoing enzymatic saccharification relate to enzyme digestibility performance. Using pretreated slurries described in the high-solids pretreated corn stover enzymatic saccharification study described above, results from rheological measurements also showed that viscosity changes were more pronounced during digestions with the lower initial solid concentrations of 25% and 30%, when compared to digestions at higher initial concentrations of 35% and 40%. These results indicate that lower conversions at high solid concentrations are likely due to sugar inhibition of enzymes. At higher solid concentrations, it is likely that enzymes are inhibited either due to lack of sufficient free water or due to build up of sugars in the liquid phase. Further kinetic and rheological studies are required to better elucidate this decrease in digestibility. These advanced studies are being conducted using a new advanced rheometer system at NREL, along with two-university led subcontracts to more fundamentally characterize rheological properties of pretreated slurries and how those properties change during enzymatic hydrolysis. These findings are being applied to develop leading process and reactor design systems for high solids enzymatic saccharification. This aspect of work is led by an engineering design firm subcontractor.

Oligomer Saccharification Subtask

As motivated by programmatic drivers to lower the cost of the pretreatment operation and to achieve higher overall sugar yields with lower losses to inhibitory sugar degradation products, milder pretreatment approaches are being investigated in many aspects of the Biochemical Platform. In many cases, such pretreatment approaches may decrease the extent of hemicellulose hydrolysis that occurs during pretreatment and may result in greater proportions of oligomeric sugars from pretreatment that will ultimately need to be converted to monomers for fermentation. Such a process configuration will likely require a variety of enzyme activities to fully liberate monomeric sugars from cellulose, any remaining hemicellulose, and soluble oligomers resulting from such milder pretreatments.

Work in the Oligomer Saccharification Subtask is focusing on identification and application of enzyme systems to effectively convert oligomers released from such pretreatment conditions. Closely related work on insoluble hemicellulosic compounds in mildly pretreated biomass is being conducted within the Targeted Conversion Research Task in a highly leveraged manner (and was conducted within the Pretreatment and Enzymatic Hydrolysis Task in FY05 and FY06). This work has indicated that the addition of hemicellulase components (particularly xylanases) and in some cases, esterases, appear to work in a synergistic manner to improve the saccharification performance of both cellulose and hemicellulose. As specifically related to soluble oligomers in mild pretreatment hydrolyzates, a significant amount of advanced analytical work (LC-MS and MS-MS) has been performed to develop improved methods of complex oligomer identification, including identification of side-chain properties. These methods have shown that both the size and the complexity of oligomers is greater from milder pretreated conditions, and that there are fewer ester-linked side chains in mild alkaline pretreatments than in mild acid pretreatments. It has also been shown than xylanases, esterases, and in particular, xylosidases all demonstrate a significant impact on converting xylo-oligomers to monomeric xylose. To support these efforts, development of high-throughput enzyme-linked assays for glucose, xylose, and cellobiose determination is being conducted to improve the efficiency of the enzyme screening studies. Finally, university-led subcontracts have been awarded to generate enzyme genes for hydrolysis of recalcitrant biomass and oligomers, as well as to further identify structures for pretreatment hydrolyzate oligomers.

30 x 30 Milestone Support Subtask

The 30 x 30 Milestone Support Subtask was formed in FY07 to directly support FY07 and FY08 intermediate xylose yield milestones leading to the 2012 Biochemical Platform ethanol cost and process performance targets. Recently, the FY07 xylose yield milestone "Achieve 75% xylose yield in laboratory scale high solids pretreatment reactor on corn stem internode" was completed. In order to report results with greater process relevance, whole corn stover was used instead of a more narrow corn stem internode feedstock. These experiments were conducted using a variety of dilute acid conditions in two reactor systems (ZipperClave reactor and steam explosion reactor) at feedstock total solids loadings of greater than 45% using dilute acid pre-impregnated whole corn stover using two different feedstock particles sizes (¼ inch and ¾ inch milled corn stover). Eleven of the 14 experimental conditions exceeded 75% total yield of both monomeric and oligomeric xylose, with seven of the experimental conditions exceeding an 80% total xylose yield. These results were achieved in both reactors for both particle sizes. Four of the 14 experimental conditions exceeded a 75% yield of monomeric xylose, with two of the experimental conditions meeting or exceeding an 80% yield. The highest yield of xylan to total xylose was 87% at 180°C for 90 seconds using the steam explosion reactor. The 87% total yield value included a 5% oligomeric xylose yield and an 82% monomeric xylose yield.

There are significant challenges in achieving the higher xylose yield targets in continuous pilot-scale pretreatment reactor systems in 2008 and beyond. These include temperature control, feedstock heterogeneity and anatomical fraction segregation, less-than-ideal pretreatment catalyst impregnation, potentially detrimental feedstock compression in the plug-screw feeder, sensor calibration, process control, and residence time variability, any of which could contribute to lower xylose yields in such reactor system. To overcome the current limitations at larger scales, we must better understand both the fundamental reaction mechanisms and kinetics during pretreatment under process relevant operating conditions and the impacts that specific reactor equipment have on pretreatment performance. In future work, we propose to test hypotheses related to upstream processing operations on pretreatment performance. Some examples are the methods for pretreatment chemical impregnation and dewatering, feedstock milling, how feedstock is fed into the high pressure pretreatment reactor, reactor residence time and internal mixing, and pretreatment reactor discharge and decompression, among others. These factors will be studied in designed experiments at the bench scale and will provide guidance to future operations in continuous pretreatment systems.

Pilot-scale pretreatment equipment capabilities enhancements are currently being pursued that will increase the range of high solids operating conditions and upstream processing options that will be available in our efforts to achieve better pretreatment performance in the existing continuous pilot-scale pretreatment reactor systems at NREL. These enhancements include the procurement of a steam jacketed reactor shell for the 200 kg/day horizontal pretreatment reactor system, along with the design and installation of a non-compression feeder option (in addition to the existing compression screw feeder system) that will be integrated into the horizontal pretreatment reactor system. These equipment capabilities will be heavily utilized to achieve the FY08 (and beyond) pretreatment R&D area xylose yield milestone in continuous reactor systems.

Finally, while the xylose yield targets achieved in this milestone report were produced directly as a result of xylan hydrolysis in the pretreatment step, additional efforts both within and outside of the Biochemical Platform are investigating pretreatment approaches that may not achieve extensive xylan conversion to monomeric xylose in pretreatment. But such approaches, especially when combined with advanced hemicellulase and accessory enzyme systems, may provide for a cost effective means of achieving the higher overall xylose yields (ultimately, 90% monomeric xylose yields) resulting from both pretreatment and enzymatic hydrolysis steps for some feedstock types, including corn stover. These efforts are on-going in the Pretreatment and Enzymatic Hydrolysis Task (Feedstock Qualification and Oligomer Saccharification Subtasks), the Targeted Conversion Task, and the CAFI 2 project. Findings from these efforts will be evaluated and considered in strategies to achieve the higher xylose yield targets in intermediate milestones leading to the 2012 targets.

Schedule

Project Initiation Date:	Friday, October 01, 2004
Planned Completion Date:	Sunday, September 30, 2012

Novel Enzyme Products for the Conversion of Defatted Soybean Meal to Ethanol

Larry Allen, Lucigen Corporation

Principal Investigator:	Dr. Phillip Brumm	Funding Partners:	N/A
HQ Technology Manager:	Amy Miranda	Sub-contractors:	U.W. Dept of Bacteriology
PMC Project Officer:	Kevin Craig		

Goals and Objectives: The purpose of this work is to overcome the recalcitrance of cellulosic biomass by developing enzyme products capable of substantially degrading the carbohydrates in defatted soybean meal (DSM) into a fermentable substrate suitable for alcohol production.

Project Description: The purpose of this work is to overcome the recalcitrance of cellulosic biomass by developing enzyme products capable of substantially degrading the carbohydrates in defatted soybean meal (DSM) into a fermentable substrate suitable for alcohol production. This project will clone, express and characterize thermostable bacterial enzymes capable of degrading >70% of the carbohydrates in DSM into monosaccharides and disaccharides fermentable by yeast. The fermentability of the monosaccharides and disaccharides will be confirmed in alcohol fermentations using *Saccharomyces cerevisiae*. To achieve this goal, the following work will be performed.

Two thermostable cellulases will be cloned and over expressed in the *B. subtilis* system. Four thermostable *beta*-glucosidases will be identified either by screening of small insert libraries of thermophilic organisms on plates containing 4-methylumbelliferyl-β-D-glucopyranoside, or by *in silico* analysis of genome sequence information generated by JGI. The *beta*-glucosidases identified by *in silico* analysis will be recovered by PCR amplification from genomic DNA. At least two of these *beta*-glucosidases will be subcloned and expressed in the *B. subtilis* system for characterization and evaluation. Four thermostable *alpha*-galactosidases will be identified either by screening of small insert libraries of thermophilic organisms on plates containing 5-bromo-4-chloro-3-indolyl-α-D-galactopyranoside (X-α-Gal), or by *in silico* analysis of genome sequence information generated by JGI. The *alpha*-galactosidases identified by *in silico* analysis will be recovered by PCR amplification from genomic DNA. A minimum of two of these will be subcloned and expressed in the *B. subtilis* system for characterization and evaluation. Four to six thermostable hemicellulases will be identified by *in silico* analysis of genome sequence information generated by JGI. The hemicellulases identified by *in silico* analysis will be recovered by PCR amplification from genomic DNA. A minimum of four of these will be subcloned and expressed in the *B. subtilis* system.

The cloned and secreted enzymes will be purified and characterized for temperature and pH ranges, the range of substrates utilized, and the products produced. The enzymes will be evaluated for their ability to improve the fermentability of soy meal by *Thermoanaerobacterium saccharolyticum* B6A, both as individuals and as combinations of enzymes. The best enzyme combinations will then be evaluated in alcohol fermentations using *Saccharomyces cerevisiae*. A large fermentation will be performed using the best blend of enzymes, and the protein quality of the material remaining after fermentation will be determined.

Summary of Work to Date - Accomplishments (FY05-current):

Task number: A Host and vector construction

Subtask A1 Develop sporulation and protease negative strain of *B. subtilis*

The production strain was constructed via DNA mediated transformation of the low protease strain of *Bacillus subtilis* 1A751.

Subtask A2 Develop shuttle vector for *B. subtilis* and *E. coli*

Two *E. coli/B. subtilis* shuttle vectors capable of secreting cloned enzymes have been constructed. The first secretion plasmid was derived from pNW33N (obtained from the Bacillus Genetic Stock Center). This plasmid replicates in *E. coli, B. subtilis* and *B. stearothermophilus*. Chloramphenicol is the selectable antibiotic in all three bacteria. The second vector, pB7, was derived from the *E. coli* plasmid pSMART

LCKan (Lucigen Corp.) and pHCMC02. pHCMC02 replicates in *E. coli* and *B. subtilis*. An *E. coli* clone containing a 2 kb insert with a thermostable xylanase gene, its promoter and signal peptide was amplified using vector sequencing primers and blunt cloned into the SmaI site of the pB7 bacillus shuttle vector. The ligation waste transformed into *E.coli* and plated on agar plates containing 0.1mg/ml 4-methylumbelliferyl-β-D-cellobioside (MUC). Colonies that showed activity were confirmed by restriction analysis before transformation into *Bacillus subtilis*. Heat-treated supernatant from cultures was tested for secretion of active thermostable xylanase protein using AZCL-Xylan (Megazyme). Supernatants containing active thermostable xylanase enzyme were run on an SDS gel with purified xylanase; the SDS PAGE confirmed the expression and secretion of thermostable xylanase by *Bacillus subtilis*.

Task number: B Cellulase and *beta*-Glucosidase Cloning
A genomic library from the thermostable cellulase producing organism *Clostridium thermocellum* ATCC 27405 was prepared (*Cl. thermocellum* culture a gift of Dr. Paul Weimer) and used to transform electrocompetent *E. coli* cells. A novel soluble cellulase from *Clostridium thermocellum*, designated Cth10H6, was identified. Library clone Cth10H6 containing the cellulase enzyme was sequenced. The sequence aligns to a cellulase from *Clostridium thermocellum* (genbank accession AM62817). Primers were designed for the cellulase ORF without the predicted signal peptide and used to amplify the 1.6kb gene from library the clone Cth10H6. The cellulase ORF was ligated to pET vector. The ligation was transformed into BL21 (DE3) *E. coli* and activity was selected for on plates using 0.1mg/ml 4-methylumbelliferyl-β-D-cellobioside (Research Products International Corp.). Five expressing clones were analyzed for protein production using SDS gel and reducing sugar assays from lysate. The final clone was sequenced confirmed. Cth10H6 cellulase, was also transformed Lucigen OverExpress™ BL21(C43) cells; these cells have a history of improved production of lethal proteins. The gene was also cloned into BL21 Rosetta Stone (Novagen) to overcome any problems with rare codons. Cells were grown to log phase in a tryptone-free medium to prevent premature expression, induced with 1 mM IPTG for overnight, harvested by centrifugation, and lysed by sonication. Protein production levels were examined by enzymatic assay and SDS PAGE; no improvement in cellulase production was observed with either strain of *E. coli*.

In an effort to identify more cellulases the sequence of Cth10H6 cellulase (described previously) was blasted (tBlastx) against the completed genome sequence assembly of *Clostridium thermocellum*. Three high homology hits were identified: Cthe2872, Cthe0536, and Cthe2147. Cth10H6 and all three candidate cellulases are predicted to have signal peptide sequences in the protein. Primers were designed to amplify each of the four genes plus 400bp of flanking sequence on either side of the ORF. The cellulases plus flanking sequence were PCR amplified directly from *Clostridium thermocellum* genomic DNA. The PCR fragments were blunt cloned into the SmaI site of the pB7 *bacillus* shuttle vector. The ligations were transformed into *E.coli* and plated on agar plates containing 0.1mg/ml 4-methylumbelliferyl-β-D-cellobioside. Colonies of Cth10H6 were weakly active on the plates, Cthe2872 colonies were moderately active and colonies of Cthe0536 and Cthe2147 showed no activity. Restriction analysis confirmed cloning of fragments for Cth10H6, Cthe2872 and Cthe2147. Cthe0536 did not clone, only empty vectors were found. The three cellulase clones were transformed into *Bacillus subtilis* and tested for secretion of active cellulase protein on AZCL-HE Cellulose reagent (Megazyme). The Cthe2872 clone did produce active cellulase protein secreted into the growth media; Cth10H6 and Cthe2147 clones did not. A 2L culture of the Cthe2872 clone in *Bacillus subtilis* was grown, the supernatant was clarified by centrifugation, and proteins were ammonium sulfate precipitated. The crude cellulase is awaiting further purification/characterization.

Thermophilic organisms producing *beta*-glucosidase were identified by plating planktonic and biofilm samples from the hot springs at Yellowstone National Park on plates containing 4-methylumbelliferyl-β-D-glucopyranoside. Over 12 isolates were recovered using this method. Positive colonies were restreaked, grown in liquid culture, and preserved at –80°C. Four of these isolates were grown in 2 liters of clear medium, harvested and used for genomic DNA preparation. The DNA preparations were used to construct small insert libraries for whole genome sequencing by the Joint Genome Institute; sequencing of these genomes is currently underway. The results from genome sequencing will be used to generate primers for PCR amplification of the *beta*-glucosidase genes from these organisms. Genomic DNA was prepared from 12 additional hot springs isolates; 8 of the isolates were positive on plates containing 0.1%

4-methylumbelliferyl-β-D-glucopyranoside (MUG). The genomic DNA was transferred to the Joint Genome Institute for whole genome sequencing of these organisms as part of an ongoing project with the JGI. When sequencing is completed, the genomic sequences will be used to design PCR primers for amplification of the *beta*-glucosidase genes from these organisms.

An acidophilic, thermophilic organism was isolated from an environmental site in Wisconsin. Genomic DNA was used to prepare a small insert library in *E. coli*, and the library was screened for cellulases using plates containing 4-methylumbelliferyl-β-D-cellobioside. A positive colony was picked, grown, and the activity of the clone determined. Based on activity assays, the enzyme was shown to be a *beta*-glucosidase rather than a cellulase, and designated AAC-1. Library clone AAC-1 containing the *beta*-glucosidase enzyme was sequenced. The sequence aligns to a putative gene from *Alicyclobacillus acidocaldarius* described as having *beta*-glucosidase and *beta*-galactosidase activity (genbank accession DQ092439). Primers were designed for the *beta*-glucosidase ORF and used to amplify the 1.4kb gene from the library clone AAC-1. The *beta*-glucosidase ORF was ligated to the prepared pET). The ligation was transformed into BL21 (DE3) *E. coli* and activity was selected for on plates using 0.1mg/ml 4-methylumbelliferyl-β-D-glucopyranoside. Five expressing clones were picked and analyzed for protein production.

Task number: C *alpha*-Galactosidase

Over 20 thermophilic organisms producing *alpha*-galactosidase were identified by plating of either local environmental samples or planktonic and biofilm samples from the hot springs at Yellowstone National Park on plates containing 5-bromo-4-chloro-3-indolyl-α-D-galactopyranoside (X-α-Gal). Positive (blue) colonies were restreaked, grown in liquid culture, and preserved at –80°C. Two of these isolates were grown in 2 liters of clear medium, harvested, and used for genomic DNA preparation. The DNA preparations were used to construct small insert libraries for both whole genome sequencing by the Joint Genome Institute and for screening in a melA deficient strain of *E.coli*. Eight additional thermophilic organisms producing *alpha*-galactosidase were identified from the hot springs at Yellowstone National Park All eight of these isolates were grown in 2-4 liters of clear medium, harvested, and used for genomic DNA preparation. The DNA preparations were used to construct small and large insert libraries for whole genome sequencing by the Joint Genome Institute. Currently we are awaiting the results of sequencing by JGI to identify the *alpha*-galactosidase genes of these organisms; we will then amplify the genes directly from genomic DNA by PCR and clone the enzymes into pET vector .

Transposon mutagenesis and screening was used to identify a number of *E. coli* strains deficient in *alpha*-galactosidase activity (melA gene product); these strains give white colonies when grown on plates containing X-α-Gal. One of these clones was used to prepare high efficiency electrocompetent cells for library screening. Libraries from two of the isolates were transformed into the *E. coli* strain deficient in *alpha*-galactosidase activity. The transformants were plated onto plates containing X-α-Gal. Blue colonies were picked and restreaked three times to obtain colonies with stable inserts Sequencing of one of the two *alpha*-galactosidase positive clones was completed; the gene is highly homologous to the reported *Geobacillus kaustophilus alpha*-galactosidase gene. The gene has been cloned into a pET expression vector and produced at high levels. Characterization of this enzyme is ongoing.

The second gene could not be sequenced. Attempts to prepare plasmid containing the entire gene were unsuccessful; most plasmid recovered contained large deletions in the insert. The apparent cause of these deletions was the use of a high copy vector for the library construction. The library construction will be repeated using a low copy number vector, if necessary.

Task number: D Soy Hemicellulase Cloning
Work scheduled to begin July 1, 2007. We are awaiting whole genome sequencing results from JGI.

Task number: E Evaluate individual enzyme and enzyme combinations

Work scheduled to begin July 1, 2007. CRADA agreement with Paul Weimer of USDA Forage Research Center was written and submitted to the USDA for approval. Preliminary evaluation of enzymes on defined substrates and soy meal are underway.

Cost and Schedule

Project Initiation Date:	October 1, 2006
Planned Completion Date:	December 31, 2009

Energy Corn Consortium

Michael Blaylock, Edenspace Systems Corporation

Principal Investigator:	Michael Blaylock	Funding Partners:	NREL, Oklahoma State University
HQ Technology Manager:	Amy Miranda		
PMC Project Officer:	Fred Gerdeman	Sub-contractors:	

Goals and Objectives: As the principal member of the Energy Corn Consortium, Edenspace is working with NREL, Oklahoma State University, and several other partners on a recently funded USDA/DOE proposal "Energy Corn for Ethanol Production" (Funding Opportunity Announcement Number DE-PS36-06GO96002F). Edenspace is the primary partner in this consortium and is the focal point for work done by other consortium members. The primary research role of Edenspace is to implement technology developed in collaboration with NREL and Oklahoma State University into a commercially viable product, i.e. "Energy Corn^tm". As part of this effort, OSU is mining multiple bacterial genomes and cloning the genes of potentially useful enzymes into expression vectors. NREL will characterize and evaluate enzymes cloned by Oklahoma State University for their efficacy in biomass conversion. NREL, in collaboration with OSU, is developing a high throughput screening protocol for enzyme synergy testing on relevant substrates such as corn stover, switchgrass, and other potential biofuels feedstocks. Promising candidate genes will then be expressed in plants by Edenspace and evaluated by NREL. Edenspace will select the genes most effectively expressed in plants for incorporation into Energy Corn.

Project Description: The overall goal is the development and demonstration of a commercially viable line of Energy Corn^tm amenable to auto-digestion in a biomass-to-ethanol plant. Factors impacting this highly desirable function include selection/development of a suitable corn variety, *in planta* expression of the enzymes necessary to digest the biomass, development of a mild pretreatment or "enzyme activation" step to induce the autohydrolysis, and a pilot-scale demonstration of the technology. The project is broken down into discreet areas of research and integration according to the strengths of the partners.

Oklahoma State University will identify, clone, and express biomass hydrolyzing genes from a variety of sources in several expression vectors. These vectors, after transformation into suitable expression hosts, will be provided to NREL for expression, purification and evaluation of the enzymes. After expression of the desired activity, the active enzyme will be purified, assayed for activity on a suitable substrate or analogue, and then evaluated for efficacy in conjunction with other activities on biomass. Successful or promising enzymes and enzyme combinations will be reported to Edenspace for evaluation *in planta*. Edenspace will evaluate the genes with promising candidates transformed into corn for further development and evaluation.

Summary of Work to Date - Accomplishments (FY05-current):
<u>Identification of candidate enzyme gene sequences.</u> Oklahoma State University has initiated the genomic studies to isolate promising candidates. Several promising candidates have been identified and confirmed through initial screening procedures.

<u>Develop automated screening assay for enzyme efficacy testing (NREL).</u> NREL has been doing enzyme evaluation methods development using a 96 well microtiter plate format integrated into a Beckman FX robotics platform. Product (sugar) detection is currently being carried out by enzyme-linked sugar-specific assays.

Schedule
Project Initiation Date: October 6, 2006
Planned Completion Date: September 30, 2009

Lab Validation for Organism Development Solicitation Recipients

Kent Evans, National Renewable Energy Laboratory

Principal Investigator:	Kent Evans	Funding Partners:	N/A
HQ Technology Manager:	Amy Miranda	Sub-contractors:	N/A
PMC Project Officer:	Fred Gerdeman		

Goals and Objectives: DOE/GO announced an FOA for the development of robust, highly efficient fermentative organism. NREL's role and responsibility is to validate the organism performance, and to provide technical assistance in reviewing and evaluating various reports generated by the contractors. NREL will assist, as needed by DOE/GO, in evaluating the proposals. Since part of the proposal is for the applicants to perform fermentation experiments under specified conditions, we will perform on-site visits to the awardees to validate the data from those fermentation tests. We will prepare a detailed plan that will be used by the staff doing such validation. The plan prepared by NREL will be evaluated, modified and approved by DOE/GO. The audit will include the performance data on the microorganism and the overall ethanol production process that is being used by the contractors.

Project Description: This project is part of the NREL Biochemical Platform which conducts R&D across the breadth of fundamental, applied and integrated science to develop robust bioconversion technologies. Directed by rigorous process engineering and cost analysis, the R&D projects work together to address the key barriers to technically feasible, cost effective ethanol production from biomass. Data and results from fundamental studies on biomass recalcitrance and enzyme action in the Targeted Conversion Research project are used to design improved pretreatment and hydrolysis technologies in the Pretreatment and Enzymatic Hydrolysis project. Those core technologies are tested in an integrated process to reduce the risk to commercial developers in the Biochemical Processing Integration project. The Feedstock/Process interface project in the platform ensures that the process technologies developed are complementary to feedstock collection and storage methods and vice versa. Additionally, the biochemical platform at NREL includes validation activities for the DOE ethanologen development projects to monitor progress to the platform’s fermentation goals.

Summary of Work to Date Prior to FY07: In response to DOE/OBP's determination that improved microbial strains need to be available for an economic process for conversion of biomass sugars to ethanol, effort to date has focused in helping GFO to develop a Request for Information on developing robust ,highly efficient fermentative organism, and subsequently, to prepare an FOA for the same purpose. In order to identify the issues for the RFI, a thorough review and analysis of relevant public information on fermentative organisms was done and the suitable metrics for addressing the technical barriers of yield, titer, and rate for production of ethanol from biomass sugars were developed. The RFI responses from various companies, institutions and individuals were analyzed and summarized. This information and further analysis of the status of technology with respect to fermentative organisms for the conversion of biomass sugars to ethanol in process-relevant conditions were used to provide input to GFO for preparing an FOA on development of robust, highly efficient fermentative organisms for the conversion of lignocellulosic biomass to ethanol.

Accomplishments (FY07): NREL assisted DOE in developing the technical qualifications for applicants to follow in submitting proposals for review. The performance criteria were developed to provide guidelines for the organism performance and requirements that the applicant needed to supply to allow reviewers the opportunity to compare performance data from each proposal. The criteria were developed so that applicants could submit proposals to either research topics 1 or 2. Applicants needed to perform a series of qualification fermentations to demonstrate organism characteristics followed by a benchmark fermentation to show the best process conditions to date. Results were reported in tables with proposed performance targets through the period of performance. A third table was developed for the applicant to supply information on the proposed process including economics.

NREL staff was selected to contribute in selection of Topic and Topic 2 proposals during a group merit review discussion with other selected reviewers. A consensus review and score was placed on each proposal and submitted to DOE/GO staff.

NREL developed a draft plan outlining the requirements for validating the progress of the investigators research. The plan describes the procedure for conducting the initial verification, pre-Stage Gate, and final on-site audit required by the investigator. The plan will also describe the required documentation including procedures, experimental data, and final analysis that needs to be submitted during the on-site visit that shows performance and economic improvements. The researcher will be requested to perform a series of experiments to demonstrate the performance of the organism while the auditors are present. The experiments confirm the results submitted in the Fermentation Strain Performance Table A and B that was submitted in the original proposal. Intermediate and final validation performance will repeat the same series of experiments with confirmation of results based on the performance targets outlined in the original table. The NREL validation team will also confirm the Process Details and Costs Table C in the original proposal. Investigators will need to provide supporting information to show cost benefits to improved strains.

Currently, NREL and DOE/GO has completed the negotiation of confidentiality agreements with 2 of 5 total awards which will allow the initiation of the contract.

Schedule
Project Initiation Date: Sunday, October 01, 2006
Planned Completion Date: Thursday, September 30, 2010*
* Completion date is based on the 36 month period of performance once the final award is officially started.

Development of Applied Membrane Technology for Processing Ethanol from Biomass

Don Stookey, Compact Membrane Systems

Principal Investigator:	Stuart Nemser	Funding Partners:	N/A
HQ Technology Manager:	Melissa Klembara	Sub-contractors:	N/A
PMC Project Officer:	Gene Petersen		

Goals and Objectives: The program will focus on designing and developing a composite system (flat sheet or hollow fiber) that meets the chemical, thermal, and energy requirements for FGE. CMS will focus on testing at various temperatures and pressures consistent with operating conditions in ethanol plants. Initial testing related to screening and demonstration of feasibility will be done at one set of operating conditions (e.g. 95 oC,). Subsequent ruggedness tests and optimization tests in support of economic analysis will be done over a range of conditions (e.g. 110 oC, 45 psig). The excellent properties of the CMS membranes should provide the needed ruggedness to operate over this large range of operating conditions.

CMS will use above CMS membrane test results and do an economic evaluation in comparison to these controls. Milestones will show needed flux, selectivity and overall economics in combination with overall ruggedness.

The following tasks will be performed to meet the project objectives.
Task 1. Prepare Flat Sheet Porous Supports
Task 2. Prepare Hollow Fiber Porous Supports
Task 3. Coat Flat Sheets
Task 4. Coat Hollow Fibers
Task 5. Make Small Modules
Task 6. Membrane System Modeling
Task 7. Membrane Characterization
Task 8. High Temperature Gas Testing (Single Component)
Task 9. High Temperature Vapor
Task 10. Defect Repair
Task 11. Test Fermentation Ethanol System over Various Operating Ranges
Task 12. Economic Evaluation
Task 13. Design for Optimal Support and Module
Task 14. Multiple Component Evaluation

Project Description: CMS will adapt its membranes for making fuel grade ethanol (FGE) from fermentation based ethanol. The program will focus on designing and developing a composite system (flat sheet or hollow fiber) that meets the chemical, thermal, and energy requirements for FGE. This feasibility work will entail evaluating commercial porous supports, both flat sheet and hollow fiber (HF) materials. CMS will also do key modeling studies to identify the preferred design (e.g. flat sheet or (HF)). Overall design will address enhanced mass transfer and pressure drop and multi-stage features to make high purity (99.5%) fuel grade ethanol. Significant work will be done with commercial flat sheet materials. This will be followed by initial customization of process, product, or raw materials. Overall economics and basic data gathered from this research will lead to the eventual building of a prototype system (construction and testing of this prototype system is NOT included in the effort proposed here in).

Summary of Work to Date - Accomplishments (FY05-current): CMS is in the business of forming membrane devices from a family of chemically-resistant, perfluoro polymers. CMS polymers have very high membrane transport rates due to their high internal free volume, the spaces between the polymer molecules, which allow tiny molecules such as water to readily pass across the membrane while the larger molecules are blocked or hindered to membrane transport. CMS membranes are successfully used to separate air from volatile organic compounds, to dewater transformer fluids and hydraulic oils and to drive conversion by water removal from an esterification reaction involving an organic acid and alcohol mixture.

Such applications experiences suggest that drying of the ethanol water azeotrope to produce FGE would be a logical extension to CMS' platform technology. The perfluoro polymers themselves are known to be excellent for handling strong solvents, such as ethanol, giving further assurance as to their utility in FGE production. Thus the development of an ethanol-water separation membrane, the purpose of this project, involves the tasks of identifying membrane supports, sealing materials, and system components, membrane fabrication and application techniques that result in an efficient, long-life, membrane device that is compatible with ethanol and its mixtures in the intended operating environment.

The CMS polymers must be supported on a microporous sheet or on porous hollow fibers to form the membrane structure. This load-bearing structure must withstand the fluid pressure forces and separate the feed, for example the ethanol-water azeotrope, from the water-rich permeate stream that is removed in order to produce the dry FGE. Ethanol's incompatibility with the usual CMS membrane supports, such as polysulfone, led to an exhaustive search and screening of available microporous materials. CMS tapped eight sources and screened six different polymeric materials for their potential use. Key to this screening was the formation of trial membranes and characterizing the membranes for flux and selectivity. CMS has identified two prime candidates of differing materials, one a microporous sheet, the other a hollow fiber, that are now undergoing more extensive testing. CMS intends to carry both candidates into the FGE application to insure against unforeseen obstacles to either in downstream manufacturing and application related tasks.

During the period, CMS also formalized a supply agreement with a hollow fiber manufacturer who offers a variety of hollow fibers in varying dimensions, including the prime candidate identified in our screening. While we cannot disclose the supplier's identity, this major volume hollow fiber producer also has entered a licensing agreement, secured rights to producing and distributing other CMS products, and is making substantial investment in hollow fiber supply and the related CMS products. By insuring a product supply with an interested partner, CMS is assured the potential for carrying the FGE product under development into rapid, full commercialization.

Screening studies for the flat sheet materials lead to two other important developments, namely a tool for characterizing the membranes and a simple bench scale technique for screening five different membrane forming methods and the associated polymer solvents. Typically membranes have been characterized by their gas flux, the permeance, and their ability to separate gas species, their selectivity. Both parameters involve intrinsic polymer membrane properties and the gas species being separated. Thus, the usual membrane permeance and selectivity measures are simply a reflection of the membrane's thickness and any non-separating defects or leaks. The newly developed CMS tool utilizes permeation flux measurements at multiple pressures with multiple gases to quantify the membrane's thickness and its viscous and Knudsen pore defects, parameters that are more closely related to and influenced by coating and processing techniques. By quantifying the defects we have been able to more readily direct our research to formation of defect-free membranes, thereby avoiding need for a defect repair step common in gas separation membrane manufacture. This will also enhance the membrane service life since defects and repair techniques are common detractors and initiators for membrane failure.

CMS designed and installed a new hollow fiber coating line for forming membranes on the outside surface of the hollow fibers. Approximately 25 different conditions have been tested using three different hollow fiber types. The resulting fibers are being characterized and qualified candidates will shortly become available for testing in the ethanol-water mixture and for screening in the FGE application.

Traditionally, membranes are formed and applied to the microporous flat sheet or hollow fibers before their assembly into a cartridge configuration. We have recently shown that some of the materials can be successfully coated in the final processing step after the membrane cartridge has been formed. We are very encouraged by this accomplishment. By *in situ* coating any damage to the coating layer arising during membrane handling and cartridge processing are necessarily avoided, further insuring a defect-free product. Our partner is most interested in this potential, low cost method for forming the membrane and is now supplying small cartridges in support of our *in situ* coating trials.

CMS licensees form pleated sheet devices from CMS coated microporous flat sheet for non-FGE applications. One CMS partner has expressed interest in forming pleated sheet devices of the type material identified as a prime candidate for our FGE product. Thus, as noted previously for hollow fibers, we have accomplished another viable commercialization path to the FGE market.

Bench testing of candidate flat sheet and hollow fiber membranes has commenced with membranes operating at atmospheric feed pressures in pervaporation and vapor separation modes. Results are confirming preliminary tests that surprisingly showed CMS membranes, unlike polyvinyl alcohol (PVA) membranes, did not loose permeability at the low moisture levels necessary for the FGE application. Our investigation and research have now explained the fundamentals supporting these differences and validated our early permeation findings. Permeability is a combination of diffusivity and solubility of the permeating specie. PVA and other membrane dryers depend upon high moisture solubility for their permeation flux. Unfortunately, solubility is also related to the concentration of moisture in the mixture being separated for those materials leading to their marginal moisture removal near the dry FGE product conditions. To the contrary, CMS perfluoro polymers are hydrophobic and not influenced by the moisture. In contrast, the CMS permeability is high due to the extremely high diffusivity of moisture in the high free volume polymer and therefore remains unaffected by the low moisture levels required for FGE.

CMS has investigated several process schemes for incorporating the membrane in the FGE process. Replacement or augmentation of the cycling molecular sieve beds with a continuously operating membrane integrated into the FGE refinery show promise for substantial energy savings.

Schedule

Project Initiation Date: Friday, June 30, 2006
Planned Completion Date: Friday, June 29, 2008

Biochemical Processing Integration Core R&D

Biochemical Process Integration Task

Dan Schell, National Renewable Energy Laboratory

Principal Investigator:	Daniel Schell	Funding Partners:	N/A
HQ Technology Manager:	Amy Miranda	Sub-contractors:	Baylor University, Colorado State University, Membrane Science and Technology Center, Hauser Laboratories, Glenn Murray, Cheminformatics consultant
PMC Project Officer:	Gene Petersen		

Goals and Objectives: The goal of this task is to test integrated enzymatic cellulose hydrolysis-based biomass conversion technology using on a large-scale domestic feedstock. Corn stover is a model feedstock for much of the effort; however, we will also work with switchgrass and other lignocellulosic feedstocks. One overarching objective is to identify problems and showstopper issues relevant to the emerging biorefinery industry from an integrated process perspective. Another near-term objective is to demonstrate that the improved, lower-cost cellulase enzymes developed under cost-shared subcontracts by Genencor International and Novozyme Biotechnology reduces the cost and risk of enzyme-based process technology. Additionally, the improvement and development of both wet chemical and rapid analysis techniques also remains a major focus of this task to both improve the efficiency of in-house research activities and to support the emerging industry needs for accurate rapid analysis methods for quality monitoring and process control.

Project Description: This project is part of the NREL Biochemical Platform which conducts R&D across the breadth of fundamental, applied and integrated science to develop robust bioconversion technologies. Directed by rigorous process engineering and cost analysis, the R&D projects work together to address the key barriers to technically feasible, cost effective ethanol production from biomass. Data and results from fundamental studies on biomass recalcitrance and enzyme action in the Targeted Conversion Research project are used to design improved pretreatment and hydrolysis technologies in the Pretreatment and Enzymatic Hydrolysis project. Those core technologies are tested in an integrated process to reduce the risk to commercial developers in the Biochemical Processing Integration project. The Feedstock/Process interface project in the platform ensures that the process technologies developed are complementary to feedstock collection and storage methods and vice versa. Additionally, the biochemical platform at NREL includes validation activities for the DOE ethanologen development projects to monitor progress to the platform's fermentation goals.

Biochemical integration work will continue efforts to advance core process knowledge with emphasis on understanding factors affecting integrated process performance and producing process-relevant residues and waste streams for testing. Ultimately, this research reduces risk as well as capital and operating cost by overcoming technical barriers associated with high-solids processing, understanding the impact of feedstock variability, and developing a better understanding of the key interactions controlling process efficiency and performance (process integration).

In support of the 2012 goals, this task has been working and will continue work at the bench scale to demonstrate integrated process technology using the best available enzymes and microorganisms using an applied experimental approach. The results of this research will provide guidance to enzyme producers and microorganism developers on key technical performance parameters. It will also provide information that will be required to design pilot scale systems necessary to demonstrate good integrated process performance at the pilot scale and validate the 2012 technical target. As in any sophisticated conversion process, combining the individual unit operations into an integrated systematic process is a significant challenge. Individual pilot-scale operations to demonstrate the required performance of the unit operations as well as complete integrated pilot development runs will be required to demonstrate the $1.07 technology target. A specific challenge will be to demonstrate high solids processing at pilot scale to reduce capital costs throughout the entire process (at least 30% in pretreatment, 20% in hydrolysis).

Additional work is also needed to improve and further develop analytical methods to facilitate research efforts requiring accurate compositional information. Realizing the goals of the 30 x 30 initiative will require the development, standardization, and validation of hundreds of new analytical methods specifically for biomass feedstocks and intermediate process streams. The data generated by these analytical methods will be used to obtain accurate performance information to accurately evaluate process economics. This will improve the efficiency of R&D activities in the biomass community and support the emerging industry needs for accurate and rapid analysis methods for quality monitoring and process control.

Summary of Work to Date - Accomplishments (FY05-current): This project formally started in FY01 as a placeholder for commercial-track projects, completed Stage 2 activities and began Stage 3 work in FY02. The Gate 3 review held in January 2002 was extremely well attended by representatives from industry, academia, and government. The distinguished panel of external reviewers unanimously agreed that the project was ready to begin Stage 3 work. In FY03, the DOE awarded grants to a number of industrial/academic/national laboratory collaborations with the purpose of developing commercial bioenergy/bioproducts processes. Therefore, in the May 2003 interim review meeting, the review panel suggested that this task should become a research track project (in Stage B) that supports these and other commercially focused projects. In a September 2004 Stage B interim review, the panel recommended that the project continue its focus on identifying process integration problems and work to generate process relevant residues and waste streams for characterization.

In FY03, we improved our ability to perform high solids pretreatment and were able to produce initial performance data for dilute sulfuric acid pretreatments carried out at solids loadings as high as 35%. Other accomplishments included extending our understanding of corn stover compositional variability, performing a preliminary assessment of process economic uncertainties using Monte Carlo analysis, and improving rapid analysis methods for compositional analysis of corn stover. In FY04, we developed an empirical model of high solid pretreatment performance (i.e., hemicellulosic sugar yields and cellulose digestibility), demonstrated high solids enzymatic cellulose saccharification (80% cellulose conversion at 25% insoluble solids loading), gathered preliminary evidence indicating the potentially overriding importance of agronomic influences on corn stover composition, and further improved the accuracy of rapid corn stover compositional analysis. More recently, we performed first-of-a-kind integrated performance testing of a corn stover to ethanol process and demonstrated deficiencies with some of the currently available ethanologens. We also demonstrated that recycling a significant portion of the stillage for makeup water will be challenging and appropriate strategies will be needed to overcome these problems. We also completed the survey of corn stover composition began in FY02, and believe we have capture the extent of compositional variability inherit in this material. We also made progress in deploying rapid analysis methods as demonstrated by the successful installation of a NIR sensor in the pilot plant for on-line stover compositional measurement. We also improved the accuracy of methods for measuring biomass-derived sugars and developed an improved technique for measuring total solids of biomass slurries.

In FY06, we advanced efforts to transfer rapid biomass compositional analysis methods to industry. Specifically, a NIR/PLS method for rapid analysis of corn stover was successfully transferred to an instrument at INL as a prelude to transfer of the method to industry-based instruments. Additionally, we demonstrated that online analysis of corn stover in an industrially relevant setting is possible and ready for deployment to industry. A mass pyrolysis technique was used to demonstrate that conventional lignin analysis (i.e., lignin defined as the acid insoluble residue of a concentrated acid treatment) doesn't correctly measured lignin in corn stover. This problem is likely present, and perhaps to a greater degree, in herbaceous materials. Also in the analytical methods area, a subcontract with Baylor University was completed that developed methods for identifying and quantifying biomass extractives in corn stover. These methods will be extended to other feedstocks in the future. This year, we began work to test Genencor's advanced enzyme preparation by basing performance of a commercial enzyme. Our effort to complete work on the advanced enzymes was delayed due to unanticipated problems in receiving the enzymes. However, work completed this year supports an FY07 D milestone. We also installed a semi-automated centrifuge that will enhance future efforts to produce separated pretreated material to support core R&D activities.

In FY07, we tested an advance enzyme preparation from Genencor and have given the results to them for further analysis. We will begin shortly to test other enzyme preparations. We have also advanced knowledge of the conditioning process and have found that ammonia hydroxide-based conditioning has the potential to significantly reduce sugars losses that occur during this process, ultimately producing higher conversion yields based on initial sugars present in the hydrolysate liquor. We have also evaluated several ethanologens in preparation for selecting the best strains to demonstrate our September 2007 milestone target listed in the milestone table above. Higher conversion yields can be achieved by tailoring the conversion process to take advantage of the best characteristic of the enzyme and microorganisms. We will continue to build upon this work to fully understand the process and associated requirement that will be necessary to achieve the out year milestones to generate pilot scale data on an integrated process. Therefore, this task will take an active role in specify equipment for the new biochemical pilot facility and will ultimately heavily use this facility.

In the analytical area in FY07, we are continuing work to transfer rapid compositional analysis methods based on NIR spectroscopy (i.e., the calibrations equations) to stakeholders and to other manufacturer's instruments to facilitate widespread deployment of this technology. We are also improving current analytical methods for both speed and accuracy and have recently develop a HPLC method for analyzing ethanol and organics acids that reduced instrument run time to 25% of the normal time.

Finally, work is in progress to understand the impact of corn stover variability on process performance as measured by hemicellulosic conversion yields and enzymatic cellulose digestibility. Several varieties of corn we have received from various locations through out the U.S. are being pretreated in the pilot scale reactor and ANOVA will be used to determine the influence of various factors. This work is anticipated to be completed in early FY08.

Schedule

Project Initiation Date: Monday, October 01, 2001
Planned Completion Date: Sunday, September 30, 2012

Fundamentals and New Concepts

Targeted Conversion Research

Mike Himmel, National Renewable Energy Laboratory

Principal Investigator:	Mike Himmel	Funding Partners:	Genencor International
HQ Technology Manager:	Amy Miranda	Sub-contractors:	University of South Dakota, Colorado School of Mines, Vanderbilt University, Brookhaven National Lab, Cornell University, Colorado State University, Weizmann Research Institute, Oregon State University, University of Georgia, UC San Diego
PMC Project Officer:	Gene Petersen		

Goals and Objectives: The objective of the FY07 research proposed for the Targeted Conversion Research Task (TCR) is to conduct activities that ensure the success of the 2012 OBP goals of $1.31 ethanol technology. The TCR task also proposes to conduct OBP Translational Science designed to acquire new understanding of chemical and biological fundamentals underlying biomass recalcitrance. Specifically, this work will ensure the availability of new science knowledge needed by industry to develop future biorefinery processes. To achieve the DOE goals of enabling new technologies to provide 60 billion gallons of bioethanol by 2030, considerable improvement in enzyme saccharification of plant cell walls must be achieved. The correlative development of more active cellulases and improved energy plants will ensure attainment of DOE's post-2012 goals. This research utilizes the Biomass Surface Characterization Laboratory (BSCL) at NREL.

Project Description: This project is part of the NREL Biochemical Platform which conducts R&D across the breadth of fundamental, applied and integrated science to develop robust bioconversion technologies. Directed by rigorous process engineering and cost analysis, these R&D projects work together to address the key barriers to technically feasible, cost effective ethanol production from biomass. Data and results from fundamental studies on biomass recalcitrance and enzyme action in the Targeted Conversion Research project are used to design improved pretreatment and hydrolysis technologies in the Pretreatment and Enzymatic Hydrolysis project. Those core technologies are tested in an integrated process to reduce the risk to commercial developers in the Biochemical Processing Integration project. The Feedstock/Process Interface project in the platform ensures that the process technologies developed are complementary to feedstock collection and storage methods and vice versa. Additionally, the Biochemical Platform at NREL includes validation activities for the DOE ethanologen development projects to monitor progress to the platform's fermentation goals.

The recalcitrance of biomass to conversion processes has been related to the natural barriers that lignocellulosic materials present to saccharifying chemical and biological reagents. These barriers can be reduced via an adequate pretreatment. Pretreatment conditions are selected for their ability to modify the structure of biomass to increase the accessibility of the cellulose to enzymes, or the susceptibility to their action. The characteristics of pretreated biomass are also being measured to determine which have the greatest affect on the susceptibility of cellulose to enzymatic hydrolysis. The Targeted Conversion Research Task is subdivided into specific objectives that address key biorefinery technology barriers, listed as subtasks below.

The broad objective of the Chemical Processing Fundamentals subtask is to increase our understanding of the chemical and structural changes that occur in biomass during prehydrolysis over a range of treatment chemistries and severities through theoretical, modeling, and experimental studies. For example, under acidic conditions hemicellulose solubilization increases the accessibility of the remaining cellulose to enzymatic hydrolysis. A better understanding of the interaction of enzymes with biomass solids modified by dilute acid and other treatments is needed so that the rate and yields of sugars can be increased. In addition, as the hemicellulose is solubilized, mono- and oligosaccharides are released into the hydrolyzate. Under acidic conditions the solubilized sugars can be degraded into non-fermentable products and fermentation inhibitors resulting in loss of yield. Therefore, we wish to understand the relationship between pretreatment conditions and the chemical and structural changes that occur in pretreated biomass. The goal of the Biological Processing Fundamentals subtask is to advance the fundamental principles that underlie the complex biochemical mechanisms of the key enzymes used for biomass hydrolysis. Our approach is to use the tools of modern biochemistry and protein engineering supplemented with advanced imaging and computational models to solve how the cellulases work to degrade biomass. The action of processivity in the enzymatic degradation of recalcitrant polysaccharides is influenced not only by enzyme characteristics but by the nature of the substrate itself. Because of this we have focused not only on the properties of the enzymes but also on identifying key factors that improve substrate accessibility. Using this knowledge, the cellulose hydrolysis, pretreatment cost, and cellulase cost goals for 2012 technology will be more readily achieved. Specially, we are working towards understanding how CBH I, a principal part of cellulases, work to decrystallize and hydrolyze cellulose. The objective of Advanced Cell Wall Characterization research is to develop and apply cutting edge technologies for cell wall imaging. In FY07, our results from the characterization of native corn stover ultrastructure, as well as changes resulting from the bioconversion process, have revealed that plant cell wall biomass is highly complex at all length scales and especially chemically heterogeneous at the molecular level. However, the instrumental tools needed to analyze biomass at sufficiently small scale are not available. Thus, we will focus on developing and applying advanced imaging tools and associated theory to demonstrate efficacy with regard to the plant cell wall and its chemistry.

Summary of Work to Date - Accomplishments (FY05-current): The following milestones contribute to the 2012 platform target of cost competitive ethanol. D milestones discussed are listed in the table below. E milestones contribute to D milestones.

Chemical Processing Fundamentals: Progress to completion of D Milestone: *Define the relationships between pretreatment conditions and the chemical/ultrastructural changes in corn stover stems that result in biphasic xylan hydrolysis (Joint milestone with Plant Cell Wall Deconstruction).* This knowledge will allow us to improve pretreatment and/or enzyme processing to more easily convert the recalcitrant xylan fraction of biomass. This work is a continuation of research begun in FY06 in which we attempted to identify if there was a structural component, in plant cell walls, that was responsible for the biphasic kinetics of xylan hydrolysis. We found, as had other researchers, that hydrolysis of the xylan could be described as two first-order reactions, an initial fast reaction followed by a much slower reaction. That biphasic xylan hydrolysis was found even in this very select tissue type means that the reason for the biphasic kinetics must be at the cellular level or smaller and cannot attributed to a difference in hydrolysis rates between different tissue types, such as between leaves and stalk. Based on our experiments, it appeared that there was an increase in the fraction of fast hydrolyzing xylan as the temperature and acid concentration were increased, which implies that the biphasic kinetics was not due to the presence of xylans with differing chemical structures. The first of these is the use of linear and surface plots across cell wall profiles to characterize xylan localization in the cell wall, i.e., center versus edges, and how these change in response to various pretreatments. This year's work continues to test the validity of our hypothesis that the biphasic kinetics is linked to the migration of xylan, in close association with lignin, to the exposed surfaces of the cell walls. Fast xylan hydrolysis, then occurs when the xylan comes into contact with the liquid hydrolyzate. Slow xylan hydrolysis occurs when either xylan must be hydrolyzed directly from the secondary cell walls or when xylan migration becomes rate limiting. Methods for quantitating images and for tracking changes in xylan concentration and subcellular localization are developed by the PCWC subtask.

E MS: *Determine chemical pathways for oligosaccharide hydrolysis and reversion reactions using Carr-Parinello MD modeling.* It is important to maximize the hydrolysis of xylan into xylose and minimize the formation of intermediates (xylooligomers) and degradation products (furfural and reversion products). Our prior work has used quantum mechanical calculations and experiments to determine the relative rates of hydrolysis and dehydration of xylose, xylooligomers, and xylan. Calculations and experiments showed that the barriers for hydrolysis reactions were much lower than the barriers for dehydration processes. Experimental measurements also showed that xylobiose and xylan could be hydrolyzed at much lower temperatures than is required for dehydration. *These results indicate that dehydration reactions of xylooligomers should be of no concern during acid pretreatment.* In FY07, our research in this area is focused on the effects of mass transport on xylooligomer hydrolysis, and the mechanisms for the formation of unwanted reversion products from xylose. It has been observed that the temperatures needed for optimal yields of xylose from xylan and corn stover are much lower in bench scale experiments (110 to 130^{o}C) with low solids loading (1 to 10%) compared to the temperatures needed in larger scale pretreatment studies (140 to 200^{o}C) with higher solids loadings (10 to 30%) where mass transport is more restricted. There is evidence that the reason for the lower xylose yields is that there is a higher yield of xylooligomers at the higher solids loadings. Subcontract with Colorado State University to support this work placed 5/1/07.

E MS: *Define the critical substrate properties of corn stover stem tissue necessary for efficient cellulase enzymatic digestibility (Joint with Biological Processing Fundamentals).* Current pretreatment technologies utilize thermochemical processing to improve the accessibility of the cellulose fraction of biomass to cellulase enzymes. To improve current pretreatment regimes with more benign and thus less costly procedures, an in-depth understanding of barriers to cellulase enzymes becomes critical. Defining the complex interactions between enzymes and lignocellulose is critical to the deployment of both advanced pretreatments and improved enzymes. Prior work conducted by the Biological Processing Fundamentals and Chemical Processing Fundamentals subtasks, examined select biomass structural features that impact enzyme digestibility. Xylan content, sample drying, lignin and cellulose morphology were evaluated using a single highly purified cellulase component, the cellobiohydrolase (CBH I), obtained from a commercial *Trichoderma reesei* enzyme preparation. Our findings indicated that improving cellulose accessibility to enzyme attack is critical to efficient conversion and that factors which directly impact accessibility following pretreatment include xylan content, cellulose fiber interactions and hydration, and finally lignin content and morphology.

E MS: *Understand how pretreatment conditions impact lignin extrusion and deposition in corn stover stems cell walls.* This work is focused on identifying the fate of lignin under pretreatment conditions and the impact of changes in lignin distribution on the digestibility of pretreated substrates. Our previous work (FY06) was focused on the lignin fraction that made it into the aqueous phase of the pretreatment hydrolyzate and subsequently formed into droplets. This work demonstrated that these droplets were lignin-derived and that the free droplets may have a minimal affect on cellulose depolymerization (>12%) The major contribution from lignin to biomass recalcitrance is more likely with the lignin trapped in the residual cell wall structure. In FY07 we are defining and characterizing lignin movement in the corn stover stem as a result of thermal pretreatment in various process chemistries.

Biological Processing Fundamentals: Progress toward completion of the D MS *"Discover how cellulase enzymes move along the cellulose chain and the respective roles of the different enzyme substructures*." The following E milestones are underway in support of this D milestone.

E MS: *Model CBH I and the Family 1 cellulose binding modules using molecular simulations.* Enzymes acting on cellulose have the challenge of first associating with and then disrupting the crystal packing of an insoluble substrate followed by directing a single-polymer chain into the active site tunnel. Almost all biomass degrading enzymes have multiple domains and contain at least one carbohydrate binding module (CBM) that is thought to enable binding of the enzyme to the cellulose surface. CBMs are also thought to be important in the initiation and processivity of exoglucanases. Because of the importance of CBM's in biomass conversion we have begun using Computational Molecular Dynamics (MD) modeling to understand the contribution of CBMs on cellulose hydrolysis. This work is being done in collaboration with the San Diego Supercomputer Center. Recently a noteworthy discovery was made by NREL scientists showed that not only are Family I CBM's highly conserved in fungal enzymes but they may undergo an induced fit with a broken-chain cellulose surface. Part of this work was published in the journal *Protein Engineering Design & Selection (PEDS).* A visualization of the molecular model can be seen at: cover art movie. To experimentally confirm the induced fit model we are producing the CBM and several mutants by solid-state synthesis. These mutations have also been introduced into the gene by site-directed mutagenesis and are being produced in *Aspergillus awamori*. (Subcontract with UC San Diego, Cornell, and Vanderbilt are planned).

E MS: *Build Data Base of Cel7A Catalytic Domain Structure and Activity Using Crystallography And Kinetics*. We are using genomic sequences that have been generated in part by the DOE Joint Genome Institute to draw inferences on structural features of cellobiohydrolase enzymes that impart functional differences. Specifically we are interested in the conformation and size of the active site tunnels of these enzymes. Protein sequences are being compared using the algorithm PSI-BLAST which searches protein databases to determine close homologs. Sequence and structure conservation scores are then calculated using the web based program ConSeq. This approach allows for the identification of functionally and structurally important residues in protein sequences using the assumption that slowly evolving sites are biologically important. These highly conserved residues within the protein core are likely to have an important structural role in maintaining the protein's fold and will provide insight to the function of the enzyme. We plan to generate structural data on this enzyme using the new crystallography tools at NREL. As part of this study we have identified and successfully engineered an addition peptide loop into the *T. reesei* catalytic core and have removed the analogous loop from the *P. funiculosum* enzyme. Subcontract with Oregon State to support this work is planned.

E MS: *Assemble A Library Of Enzymes Necessary To Determine The Functional Relationship Between Application Of Defined Hemicellulases, Accessory Enzymes, Cellulosomes, And Cbms To Untreated Corn Stover Stems And The Required Relative Severity Of Dilute Acid Pretreatment.* Diferulate esters strengthen and cross-link primary plant cell walls and help to defend the plant from invading microbes. Phenolics also limit the degradation of plant cell walls by saprophytic microbes. We have shown that incubation of corn stover with a ferulic acid esterase and a xylanase improves its overall conversion. In order to evaluate the role of this class of enzymes two fungal ferulic acid esterases (faeA and faeB) were cloned and purified in *Aspergillus awamori*. We have determined many of the biochemical properties of the recombinant enzymes such as substrate specificity, thermal stability, and glycosylation. Subcontract with University of Georgia to support this work placed 6/1/07.

<u>Advanced Plant Cell Wall Characterization</u>:
This subtask has developed specific molecular probes, primarily CBMs, tagged with various fluorescent proteins for mapping pretreated corn stover samples. This project is also developing mutations of CBMs specifically recognizing polysaccharides for corn stover cell walls. Image pretreated corn stover cell walls using AFM, TIRF and Confocal Laser Scanning Microscopy. We will apply fluorescent labeling techniques to understand how pretreatment chemistry modifies the specific cell wall components such as cellulose and xylan. This project will particularly focus on developing and applying approaches for high (molecular) resolution imaging and quantitative analysis. Initiate a new imaging concept that combines spectroscopy and microscopy. This subtask has begun to evaluate Coherent Anti-stokes Raman Scattering (CARS) microscopy for biomass characterization. This project will be in collaboration with Prof. Sunney Xie of Harvard University (uncompensated collaborator). We also continue to develop the imaging capability of the BSCL. We recently completed the installation of two significant pieces of visualization equipment in the DISC (Data Interpretation and Simulation Center). The first system provides the capability for passive stereo 3D visualization by a working group using a single projector 3D projection system and shuttered 3D glasses. Also, we've implemented a high resolution collaborative visualization environment by tiling 6 high definition, LCD displays into a single 25 megapixel display. We are currently working on the software solutions that will allow us to fully utilize these image visualization tools with the full range of 2D, 3D, and video file types from multiple platforms in a collaborative work environment.

E MS: <u>Develop And Apply Biochemical Probe Technologies To The Characterization Of Chemically And Enzymatically Treated Corn Stem Cell Walls Using AFM And Total Internal Reflection Fluorescence Microscopy.</u> In support of the goals of the Biomass Program, NREL intends to explore the application of CBMs residing in the bacterial cellulosome as well as the cellulosome itself for labeling plant cell wall specimens for enhanced imaging. Subcontract with the Weizmann Research Institute is planned.

E MS: <u>Image Plant Cell Wall Degrading Enzymes Produced By Natural Biomass Degrading Communities Colonizing Corn Stem Cells To Identify Novel Conversion Paradigms</u>. Using bioinformatics and genomics tools provide new GH enzymes from mycorhizal and endophytic fungi associated with corn and poplar roots. The primary objective of this project is to gain an understanding of the composition and the metabolic potential of the lignocellulosic biomass degrading communities that decay poplar wood chips, corn stover and switch grass biomass under anaerobic conditions. Subcontract with BNL to support this work placed 6/1/07.

E MS: Develop Initial Concepts For New Biomolecular Imaging Methodologies Aimed At Generating Chemical Maps Of Corn Stem Cell Wall Structure At The Nanometer Scale. The primary objective of this effort is to develop new approach for achieving visualization of single cellulase enzyme acting on cellulose by single molecule spectroscopy. Development of a single-molecule photo-activated fluorescence imaging system: This task will involve development of a custom Total Internal Refelction Fluorescence Microscopy (TIRF-M) system for excitation and high-sensitivity detection of fluorescence. Subcontracts with South Dakota State University and Colorado School of Mines to support this work placed 7/1/07.

Schedule
Project Initiation Date: Sunday, October 01, 2000
Planned Completion Date: Sunday, September 30, 2012

Engineering Thermotolerant Biocatalysts for Biomass Conversion to Products

K.T. Shanmugan, University of Florida, IFAS

Principal Investigator:	K.T. Shanmugam	Funding Partners:	University of Florida
HQ Technology Manager:	Amy Miranda	Sub-contractors:	N/A
PMC Project Officer:	Fred Gerdeman		

Goals and Objectives: The objective of this study is to construct novel thermotolerant biocatalysts (second generation) that function optimally under environmental conditions that are also optimal for the activity of fungal cellulases (50ºC and pH 5.0). (I) Physiological and genetic characterization of selected second generation biocatalysts for optimum product production using the native lactic acid fermentation as a model system for future studies on ethanol production. (II) Metabolic engineering of selected biocatalysts to replace the native lactic acid pathway with a homo-ethanol pathway. (III) Metabolic and physiological characterization of engineered strains.

Project Description: The target is to develop technology that can support production of ethanol from biomass resources at a cost of $1.10 by 2010. The cost of cellulase enzymes for saccharification of feedstock has been identified as one of the critical cost factors in the production of fuel ethanol, from lignocellulosic biomass and this must be improved to reach this goal. With DOE support, two companies, Genencor and Novozymes, have reduced the cost of this enzyme to about 10-20 cents per gallon ethanol produced by optimizing cellulase production and activity. A parallel and synergistic approach to reduce enzyme cost is by developing improved biocatalysts that can operate at conditions that are optimal for these fungal cellulases. Present industrial biocatalysts function at temperatures that are 10-20 degrees below the optimal temperature for fungal cellulase activity (50ºC and pH 5.0). By developing second generation biocatalysts that are effective producers of ethanol under these conditions, the amount of enzyme needed can be reduced by more than half with corresponding reduction in cost. The production of these second generation biocatalysts for simultaneous saccharification and co-fermentation of both cellulose and hemicellulose hydrolysate is the focus of this study.

Summary of Work to Date - Accomplishments (FY05-current): The main objective of this study is to isolate bacterial biocatalysts that function optimally at the conditions that are also optimal for fungal cellulase activity towards reducing the amount of cellulase needed for SSF of cellulose and engineer these bacterial biocatalysts to produce ethanol as the main fermentation product using hexose and pentose sugars as the feedstock. Towards this goal we have accomplished the following.

1. **Isolation of thermotolerant microbial biocatalysts**. We have isolated over 400 bacterial biocatalysts that grow at 50-55 ºC and pH 5.0, conditions that are optimal for fungal cellulase activity. Based on 16S rRNA (DNA) sequence, many of the tested isolates were identified as *Bacillus coagulans,* which comprises a very diverse group of Gram-positive bacteria that has not been well studied. Based on various physiological characteristics, two isolates from this group, strains 36D1 and P4-102B, were selected for further analysis.

2. **Fermentation characteristics**. Strains 36D1 and P4-102B produced L(+)-lactic acid as the main fermentation product from both glucose and xylose at an optical purity of 97-100%. The lactic acid yield was about 90% from glucose and about 80-85% from xylose. The volumetric and specific productivities of lactate for strain 36D1 were, 0.86 (g/L.h) and 3.5 (g/h.g dry cell mass), respectively, during glucose fermentation. For comparison, the corresponding reported specific productivity value for *Saccharomyces cerevisiae* producing ethanol is about 2.0 g/h. g dry cell mass. On a molar basis, the specific productivity of respective products for *B. coagulans* and yeast were comparable. These bacteria also fermented sucrose and cellobiose in addition to other sugars normally found in various hemicellulose acid hydrolysates, such as galactose, mannose and arabinose. Ability of *B. coagulans* to ferment cellobiose would eliminate the need for β–glucosidase in the cellulase preparations during SSF of cellulose. Xylose was fermented by the *B. coagulans* strains using the enzymes of the pentose-phosphate pathway that convert all the xylose to pyruvate for further conversion to lactate or ethanol.

3. **SSF of cellulose**. Lignocellulosic biomass conversion to products depends on simultaneous saccharification of cellulose to glucose by fungal cellulases and fermentation of glucose to product by microbial biocatalysts (SSF). The cost of cellulase enzymes represents a significant challenge for the commercial conversion of ligncellulosic biomass into ethanol or lactate. In our experiments, the optimum temperature for the fungal cellulase from Genencor was found to be about 60ºC and the optimum growth temperature for *B. coagulans* strain 36D1 was 55ºC. The optimum cellulase concentration for SSF of crystalline cellulose with Genencor cellulases and *B. coagulans* strain 36D1 was determined to be about 7.5 FPU/ g cellulose at 50ºC. For highest volumetric productivity of the specific product in SSF of cellulose, *B. coagulans* required only 5 FPU/g cellulose at 55ºC while yeast required at least 20 FPU/g cellulose to reach the same level of volumetric productivity of strain 36D1. SSF with *B. coagulans* at 55ºC provides a 3 to 4 -fold reduction in the amount of fungal cellulase needed for optimum fermentation of cellulose to product with an associated savings in enzyme cost.

4. **Fermentation of hemicellulose acid hydrolysate**. Sugar cane bagasse acid hydrolysate (HCH) was overlimed and the pH of the overlimed hydrolysate was lowered to 5.0, the optimal pH for fungal cellulase activity. At this pH, *B. coagulans* fermented the HCH in mineral salts medium with only corn steep liquor (0.25% w/v). Lactate concentration peaked at 75% HCH in the fermentation to about 55 g/L and the yield was about 90% of the total sugars in the HCH. In addition, in an SSCF, simultaneous saccharification of cellulose (20g/L) with cellulases and cofermentation of the released sugars with 40% HCH, both cellulose and HCH were simultaneously fermented to lactic acid by *B. coagulans* at 50ºC and pH 5.0. These studies show that *B. coagulans* strains can ferment cellulose with less cellulases than yeast and also can coferment cellulose and HCH to products with savings in enzyme cost and equipment cost.

5. **Shuttle plasmid vector for gene transfer into *B. coagulans***. Although *B. coagulans* was first described in 1915, this bacterium is not a focus of intense study. Due to this lack of interest, gene transfer systems for this organism are not available. We found that only one *E. coli/ Bacillus* shuttle plasmids, pNW33N, function in *B. coagulans* strain P4-102B irrespective of the growth temperature. In addition, many of the antibiotic resistance genes from *B. subtilis* plasmids failed to provide resistance in *B. coagulans*. We constructed a shuttle plasmid using the replicon from a native plasmid found in strain P4-102B and chloramphenicol resistance gene (plasmid pMSR10). Using our electroporation protocol, plasmid pMSR10 was transferred into *B. coagulans* at about the same frequency as observed during *B. subtilis* transformation.

6. **Ethanol pathway for *B. coagulans***. Using plasmid pMSR10 as the backbone, we constructed plasmid pMSR40 that carries *Sarcina ventriculi pdc* (pyruvate decarboxylase) and *Geobacillus stearothermophilus adh* (alcohol dehydrogenase). Plasmid pMSR40 was stable in *B. coagulans* and the two genes of the ethanol pathway were transcribed. However, any increase in ethanol in fermentation broth or PDC activity was below the detection limit in the recombinant. Optimization of the expression of the ethanol pathway is in progress. Among the other *pdc* genes we tested (from *Zymomonas mobilis, Zymobacter palmae, Acetobacter pasteurianus* and Yeast), only the *pdc* from *Z. mobilis* produced detectable level of activity in a model Gram-positive host, *B. megaterium*. Using suicide plasmid vectors we are in the process of constructing mutants with deletions in the gene encoding L-LDH to shift the fermentation from lactate to ethanol while also optimizing the expression of active PDC in *B. coagulans*.

7. **An alternate homoethanol pathway**. Since the PDC activity was not detected in the *B. coagulans* recombinant, we developed an alternate pathway for production of ethanol as the main fermentation product. This development was in *E. coli* and utilized mutations in the pyruvate dehydrogenase complex (PDH). Although PDH is produced by wild type *E. coli* during fermentation, the enzyme activity is close to undetectable level. We introduced mutations in the gene encoding PDH that supported the enzyme activity in an anaerobic cell. In such a mutant, ethanol yield from glucose was close to 90%. Since the PDH of *B. coagulans* functions in a manner that is similar to that of *E. coli*, we are in the process of introducing analogous mutation in the *B. coagulans* gene encoding PDH. Introduction of this mutation into the chromosome is expected to yield a PDH complex that can support fermentation of sugars to ethanol

by this novel pathway. To increase the rate of ethanol production by this PDH-ADH pathway, we have cloned a native gene encoding ADH activity.

Summary. *Bacillus coagulans* grows and ferments all the sugars normally found in biomass to optically pure L(+)-lactic acid. Pentose is fermented by *B. coagulans* through the pentose-phosphate pathway to complete conversion to pyruvate and then to products. SSF of cellulose at 55ºC with *B. coagulans* requires only about 25-33 % of the cellulase needed for comparable SSF with yeast at 35ºC with a significant cost-saving on cellulase. An alternate homoethanol pathway has been developed for engineering *B. coagulans* for ethanol production. Towards this goal, gene transfer system and plasmid vectors for *B. coagulans* were also developed.

Schedule

Project Initiation Date:	April 1, 2004
Planned Completion Date:	March 31, 2008 (with one year extension)

Fungal Genomics

Scott Baker, Pacific Northwest National Laboratory

Principal Investigator:	Scott Baker	Funding Partners:	Poet, Novozymes, Verenium, Dyadic International, Mycosynthetix
HQ Technology Manager:	Amy Miranda		
PMC Project Officer:	Fred Gerdeman		
		Sub-contractors:	N/A

Goal and Objectives:

- Goal
    - Generate innovative fungal-based biotechnology to enable a robust biorefinery industry
- Objectives
    - Reduce the cost of biofuels and bioproducts
- Directly utilize complex biomass
- Enable processes with high concentration of end-product (for example, organic acids and enzymes)
    - Improve the overall tractability of filamentous fungi
    - Leverage industry needs and expertise to help guide research program

Project Description:

Our research is focused on generating basic understanding of fungal biotechnology. This basic understanding of the fungal systems will provide industry with enabling tools to rapidly and effectively develop new processes for the biorefinery industry.

Fungal biotechnology offers a promising set of technologies that are very important to the establishment of integrated biorefineries. These organisms have the potential for rapid, highly productive conversion of biomass resources to bio-based intermediates that bring economic benefit to industry. While fungal fermentations are currently used for a limited number of specialized products, the tools for a broader and more rapid implementation of these organisms are not yet available to industry. Current processes have been developed over many years without a clear understanding of the underlying ability to control and utilize fungal organisms.

To address the barriers to fungal fermentation, enabling R&D is needed in the following primary areas:

- **Morphology control**: the ability to control the morphology of the organism to increase both its productivity and the ability to functionally grow it in a fermentor
- **Genomics:** Application of genomics and proteomics tools to fungal species for selective modification
- **Hyper-productivity:** the ability to produce isolates with very high productivities of selected products, similar to those currently used for citrate production
- **Biomass to Product, Single Stage Processes:** enzyme production, biomass hydrolysis, biomass substrate utilization, cell growth, and generation of selected products
- **Filamentous fungal ethanol:** develop a model filamentous fungal ethanologen, targeted screening of a partner fungal collection for ethanol producers, metabolic flux modeling

Summary of Work to Date - Accomplishments (FY05-current):

The work has been divided into several subtasks:

1. Morphology control
2. Genomics
3. Hyperproductivity
4. Biomass to product
5. Partner Review Board
6. Filamentous fungal ethanol

Morphology control

Morphology of fermentation organisms is crucial for productivity. The most productive morphology for filamentous fungi is the pellet. Our model for a pelleted morphology in a fermentation process is *Aspergillus niger* in citric acid fermentation. In the citric process, *A. niger* forms hollow spheres wherein the whole surface area of the cell is made up of hyphal tips. Hyphal tips are “where the action is” with regard to fungal metabolism – they are the sites of secretion and growth. Pellets are also ideal for fermentation due to their low viscosity.

We have spent the first three years of this project dissecting the genetic control of pellet morphology in *A. niger* citric fermentation. Our goal has been to determine which cell biological processes are responsible for *A. niger* pellet morphology so that we can manipulate these pathways in other fungi that produce other products and ethanol. Our research has implicated the G-protein signaling pathway, the ubiquitin mediated proteolysis pathway at the genetic level. Reactive oxygen species (ROS) are produced by metabolism, and induced by the high glucose needed for citrate production, and have been implicated at the cell biological level. We have proposed a morphology control model linking these three pathways. This model forms a framework on which to base future experiments in *A. niger* and other fungi that will have future roles in the biorefinery.

Genomics
Since 2005, the Fungal Biotechnology Team at PNNL has led the *A. niger* Genome Project in collaboration with the DOE Joint Genome Institute (JGI). The availability of the genome has accelerated our research considerably. The genome sequence is now complete and has been mapped onto the eight known *A. niger* chromosomes. We have used the genome sequence information to rapidly target a number of gene families for genetic and transcriptome analysis. In addition, the genome has enabled high-throughput proteomic studies of the pelleted morphological state. Currently, we are comparing and analyzing the differences between the JGI *A. niger* genome (a citric acid producer) and comparing it to another recently published sequence from an *A. niger* strain that is a protein producer.

Hyperproductivity
We have chosen Aspergillus terreus and itaconic acid as our baseline organism and product. Our examination of the A. terreus genome sequence led to the identification of three genes of interest with regard to hyperproductivity on complex plant biomass. PCR primers for one of these genes, phyA encoding the phytase enzyme, have been designed and ordered. The primers will be used to construct a gene deletion cassette. Phytase is an enzyme that hydrolyzes phytic acid from corn and other plants to inositol and inorganic phosphate. Higher levels of phosphate appear to be correlated with low itaconic acid productivity in A. terreus. Our hypothesis is that deletion of the phyA gene may keep inorganic phosphate levels low and itaconic acid productivity high when A. terreus is grown on complex plant biomass sources.

The deletion cassette for phyA will be constructed and a deletion mutant of A. terreus isolated. This deletion mutant will be compared to the wild type with regard to itaconic acid production in shake flask studies using glucose media with or without phytic acid amendment, and enzyme treated ground corn. These studies will continue into FY08. Three 30L fermentation runs of A. terreus grown on glucose will be prepared and samples will be isolated at three time points. The times are before the onset of itaconic acid production, just after onset, and in the middle of the high productivity phase. These samples will be used for preparation of RNA for EST (expressed sequence tag) sequencing to be performed by JGI and for proteomics analysis to be performed at PNNL in FY08.

Biomass to product
Dry weight to image correlations work was continued to evaluate the potential for using this approach for analyzing process kinetics in consolidated biomass processing. Our baseline organism, A. terreus, was introduced successfully to the 30L fermentors. Repeated fermentations using glucose as the carbon source resulted in final titers of itaconic acid ranging from 50-60 g/L. This is an important accomplishment for supporting all of the other subtasks since A. terreus is our consolidated bioprocess model organism, the fungus to be used for transformation with morphology control genes identified in the Morphology task, and the target of proteomic and genomic studies to support the Hyperproductivity task.

Partner Review Board
A biorefinery industry Partner Review Board was formed with Poet, Novozymes, Verenium, Dyadic International and Mycosynthetix. We have prepared Annual Reports and held Annual meetings in 2005

and 2006. A SharePoint site was established so the PNNL Fungal Biotechnology Team and the Partners Review Board can exchange ideas, reports and other information relative to the project. Final arrangements are in process to provide the Board members and the PNNL Fungal Team access to this secure site.

Filamentous fungal ethanol

Like yeast, filamentous fungi possess the ability to produce ethanol when grown in low oxygen/anaerobic culture conditions. However in contrast to yeast, filamentous fungi are able to degrade lignocellulosic biomass, including cellulose and hemicellulose, as well as efficiently utilize xylose and other pentoses. Despite their positive characteristics and perhaps due to their inherent biological complexity compared with yeast or bacteria, filamentous fungi have only been explored as ethanol production organisms in a limited way. In previous experiments using Fusarium oxysporum grown on 10% glucose + 0.2% DDG we were able to generate up to 5.8% (w/w) ethanol. We have been authorized to add a task to our existing OBP supported Fungal Biotechnology research program to support characterization and optimization of filamentous fungal ethanol production from both simple sugars and directly from lignocellulosic biomass.

Schedule

Project Initiation Date:	Saturday, January 01, 2005
Planned Completion Date:	Monday, December 31, 2012

Chemicals and Products R&D

Integrated Biorefinery – Separations/Separative Bioreactor – Continuous Bioconversion and Separations in Single Step

Seth Snyder, Argonne National Laboratory

Principal Investigator:	Seth W. Snyder, YuPo J. Lin	Funding Partners:	Archer Daniels Midland Company
HQ Technology Manager:	Valerie Sarisky-Reed	Sub-contractors:	N/A
PMC Project Officer:	Fred Gerdeman		

Goals and Objectives: The objective is to identify and overcome technical hurdles and to demonstrate the technoeconomic feasibility for an integrated biorefinery to produce biobased chemicals. This project includes C-milestones for a pilot-scale process demonstration and economic analysis for commercialization. The D-milestones are focused on solving technical barriers for process development of the Separative Bioreactor. It includes energy efficiency and productivity of organic acid production; product purification; durability of process components; stability of biocatalysts without neutralization agents. The E-milestones are materials development and characterization of process parameters including: ion-exchange resin wafer development; automation of the Separative Bioreactor; biocatalyst immobilization; identification of key operational parameters.

Project Description: The Separative Bioreactor holds great promise for dramatically reducing the cost of production of many charged biobased products including organic acids and amino acids. The Separative Bioreactor integrates continuous bioconversions and separations into a single step. The DOE Office of the Biomass Program is interested in reducing technical barriers to production of biobased fuels and biobased chemicals. Technical analysis indicated that several organic acids are potentially "Top Ten" candidates for biomass-derived platform chemical intermediates. Overcoming the costs associated with acid neutralization and product separation was identified as a significant technical barrier to reducing the cost of production of organic acids.

Summary of Work to Date - Accomplishments (FY05-current): In initial bench-scale performance demonstrations of this electrically-driven membrane-based technology, the Separative Bioreactor produced and separated both lactic acid and gluconic acid. Initial calculations clearly show the economic advantages of using the Separative Bioreactor. Process economic calculations reveal that the Separative Bioreactor could produce organic acids at significant cost savings in comparison to conventional fermentation technology and even compete with petrochemical processes. Therefore, we believe that the Separative Bioreactor could 1) enable production of biobased chemicals as major platform intermediates and 2) facilitate the commercial success of the emerging integrated biorefinery industry. The scope of products that could be produced as well as long term bench scale and pilot testing are required to confirm the economic impact of this new technology.

Argonne developed an economic model to assess the production cost of biobased chemicals using our preliminary laboratory experimental results. Argonne selected the enzyme glucose fructose oxidase reductase (GFOR) for conversion of glucose to gluconic acid. The enzyme also converts fructose to sorbitol in a sequential reaction. Argonne completed 200 hours of continuous operation of single-stage enzymatic (GFOR) separative bioreactor to produce 18 wt. % gluconic acid without adding neutralization chemicals. The electrical energy consumption met the targets of the economic model.

Argonne and ADM developed a process to produce GFOR for full laboratory-scale separative bioreactor runs. Laboratory-scale, long-term continuous runs are in process. Pilot-scale demonstration are planned for the second half of FY2008.

ADM provided modified conditions for the whole cell fermentation using in-house strains to produce gluconic acid and lactic acid. Argonne conducted additional resin wafer screening to optimize product recovery under the modified conditions. The composition and dimensions of the resin wafer were optimized for the targeted fermentation pH and steady-state product titer. Argonne provided a redesigned separative bioreactor stack with the new resin wafers to ADM. The composition, fabrication and utilization of these resin wafers are protected by Argonne's background IP portfolio. The specific conditions and performance results are business sensitive patent and are protected by the Argonne-ADM CRADA. ADM performed a continuous integrated whole cell fermentation/separative bioreactor run for 240 hours (gluconic acid). Pilot-scale demonstration is planned for the first half of FY2008. Currently we are commissioning the pilot-scale equipments.

Argonne and ADM have initiated quarterly project reviews alternatively held on each location. To prepare for the pilot demonstration, the project team members have switched to monthly project meetings since March 2007.

To date, two US patents were granted and several patent applications were published and we also filed international patents. They are listed below.

Two US patents granted:
- US Patent 6,797,140 Electrodeionization Method.
- US Patent 7,141,154, Single-stage separation and esterification of cation salt carboxylates using electrodeionization

Four pending US patent applications:
- US Patent Application 20040115783, Immobilized biocatalytic enzymes in electrodeionization (EDI)
- US Patent Application, Retention of counterions in a separative bioreactor
- US Patent Application, 20040917, Electrically and ionically conductive porous material and method for manufacture of resin wafers therefrom
- US Patent Application, 20040917, 20040917,Devices using resin wafers and applications thereof
- Three international patent applications in Brazil, India & Australia, "Electronically and Ionically Conductive Porous Material and Method for Manufacture Of Resin Wafers Therefrom".

Beside the patents, the team received an R&D 100 award in recognition of the commercial promise of the Separative Bioreactor. Argonne and ADM are listed as co-developers of the technology. Chemical and Engineering News (January 09, 2006, pg. 32-33) published a story about ADM's "The ADM way of making chemicals". The story mentions the Argonne-ADM CRADA. Argonne also presented : a poster highlighting the project at BIO 2006; a seminars highlighting the work at the University of Illinois Symposium on Sustainable Bioenergy; a seminar to highlight part of the work at the North American Membrane Society (NAMS) 2006 Annual Meeting; a poster highlighting the project at 2006 AICHE Fall meeting.

Schedule

Project Initiation Date: Tuesday, June 01, 2004
Planned Completion Date: Tuesday, September 30, 2008

Advanced Catalyst Development for Polyols Production

John Holladay, Pacific Northwest National Laboratory

Principal Investigator:	John Holladay / Alan Zacher	Funding Partners:	UOP
		Sub-contractors:	Michigan State University
HQ Technology Manager:	Valerie Sarisky-Reed		
PMC Project Officer:	Fred Gerdeman		

Goals and Objectives:
The overarching goal of our work is to develop catalytic processes to displace petroleum with biomass for the production of commodity chemicals and fuels. To address this goal we have the following objectives:

- Develop broadly enabling catalyst technologies that will achieve catalyst life, specificity and activity targets while operating with actual feeds (rather than pristine feeds).
- Convert sugar alcohol waste streams to polyols. To do this better control of C-C and C-O bond scission is needed. Selective bond scission technology could be widely applicable in numerous applications, including fuels. Success will result in enhanced capability of extracting value from waste streams to improve the overall economics of biorefineries.
- The starting point for this work is to demonstrate the technology required to convert glycerol to propylene glycol.

Project Description:
The overarching objective of this work is to develop technology to control C-C and C-O bond scission reactions. Broadly enabling technology could have a wide range of applications in producing chemicals and fuels from sugar alcohol waste streams. In this stage of the work we are concentrating on an integrated process for the production of propylene glycol from sugar alcohols, specifically glycerol. PNNL has developed a number of catalysts for the production of propylene glycol from sorbitol. Sorbitol is derived from the hydrogenation of glucose. In order to make these technologies commercially viable, further improvements in the catalyst systems need to be developed. Improvements need to come primarily in the form of increased selectivity to propylene glycol. One of the major co-products from the conversion of sorbitol is glycerol. It is critical that a catalyst system be developed for converting glycerol to propylene glycol in high yields. In addition, other sources of glycerol are available and could be used for the production of propylene glycol. Glycerol is a co-product of bio-diesel production or from the transesterification of fatty acids. The utilization of glycerol from biodiesel production or fatty acid production could provide near-term commercial opportunities for implementation of the technology.

UOP has substantial interest in providing the engineering and catalyst manufacture for the conversion of glycerol into propylene glycol for use in high purity applications. The processes for biodiesel production and for the transesterification the fatty acids are very similar and it is expected that a single catalyst technology can be developed that will be applicable to both sources of glycerol to produce propylene glycol.[1]

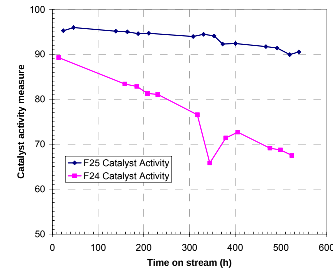
In this work PNNL and UOP have assembled a multi-disciplinary team with defined roles working closely together (see presentation slide 7). PNNL has primary responsibility in catalyst discovery and life-tests, process definition and optimization. Working with Michigan State University, PNNL is also tasked with fundamental kinetic and mechanistic studies. UOP has primary responsibility for commercialization, reaction engineering, and economic modeling; they are also responsible for catalyst characterization and commercialization. UOP maintains a web portal in which all data, notes and other information generated by either party is centrally stored and made available to the team. The team holds a joint web conference on the fourth Thursday of each month and hold informal discussions on a weekly basis. DOE funds are going to PNNL; UOP's research is being done as cost share.

[1] At the inception of the project in April of 2005 ADM was part of the cooperative research and development agreement (CRADA) along with PNNL and UOP. ADM opted out in August of 2006. UOP took over assignments held by ADM and the project was refocused for FY07 research.

Summary of Work to Date - Accomplishments (FY05-current):

Work flow: Catalyst development/process development culminating in techno-economic model

To understand the accomplishments in the last two years it is helpful to break down the work flow into ***catalyst development*** research and ***process development*** research which culminate in a detailed process flow diagram and ***process economics*** (See presentation **Slide 8**). In the presentation we have divided Catalyst development research into (1) determining what supports should be used, (2) defining optimal metals, (3) understanding interactions between support, metals and substrates, (4) defining catalyst activation its performance and (5) validating catalyst production by industry. Development of catalyst must be done in conjunction with process development and we have completed tasks to define the operational parameter space around pressure, temperature, space velocity (flow rates), concentrations, and pH. In the integrated process feed conditioning must be done as well as product recovery and purification. Since raw materials often predominant costs in biobased processes, minimizing feedstock processing is integral. Product separation and purification is essential to meet market acceptance. Accomplishments for each of these areas are summarized in the paragraphs that follow. In the Annual Operating Plan (AOP) milestones are based on process economics as related to cash cost of production (CCOP) and return on investment (ROI). This is presented in the Project Milestone Summary Table at the end of the report.



Brief summary of efforts through August 2005

At the time of the FY05 conference we had completed a significant amount of combinatorial / high throughput screening studies. These studies were aimed at identifying catalyst supports, metals, co-metals, and additives (pH modifiers). At the same time we initiated batch studies to validate findings from the continuous reactor and flow reactor studies to examine catalyst life. The initial flow study data was sobering; catalyst life was unacceptable. In both runs the drop of activity was unacceptable for a 500 h test. Further catalyst discovery work was implemented using high throughput techniques. While at the same time additional batch reactor work and flow reactor work using pristine feed was carried forth.

Where we are today: Technology demonstration for glycerol to propylene glycol

Catalyst development studies. Based on data obtained from extensive combinatorial research, carbon supports exhibited substantial promise. Catalyst activities were higher with carbon-based supports than observed for stable metal oxides such as monoclinic zirconium, rutile titania or carbon doped with metal oxides. Furthermore, a significant difference in performance was exhibited among different carbon supports that were examined. The greatest impact was on catalyst activity. Although the impact on selectivity was less severe, to meet the selectivity target (>90%) *one particular carbon was singularly effective* (see presentation slides 9 and 10).

The support plays many roles in the catalyst. For example it keeps the metal finely dispersed to prevent sintering and leaching. The support can modify catalytic behavior of the metals. In addition supports may also interact with the substrates and products. This is particularly true for activated carbon. Hence the local pore concentration of products and reactants can vary greatly from that of the bulk solution. One can consider the support as a delivery system of the substrate to active catalytic sites. We have found that propylene glycol (PG) competitively adsorbs on carbon compared to glycerol at both low and high temperature. However, the trend appears to be reversed in regards to the metal where glycerol is preferentially adsorbed on Ru sponge. One implication of this finding is that PG could have stability problems. Another is that reaching high conversion could be difficult. We are able to circumvent both problems through operating under continuous flow reactor (see presentation slide 11).

Although much work was done prior to August 2005 on identifying optimal metals, we ran a significant number of combi plates to further define metal composition. A portion of the work was designed to expand metal options and replace certain metals in bimetallic systems. We discovered new metal compositions that were effective in hydrogenolysis chemistry. Approximately 1000 individual runs were completed in the combi system during this study. From that work about ten catalysts carried on to flow reactors (see presentation slide 12), two of which were chosen to go forward (see presentation slide 13).

Flow reactor testing turned out to be integral to the program. Hydrogen mass transfer is better controlled in a trickle bed flow reactor resulting in higher selectivity (see presentation slide 14 and 28). Approximately 125 flow reactor runs have been completed since August 2005, ranging in duration from 24 h to 2000 h. The focus of the runs has been to demonstrate catalyst life, optimize catalyst activation procedures, define process operating parameters and determine impact of feedstock impurities. One key accomplishment from this work was reducing the total metal loading on the catalyst (slide 13). A second key accomplishment was completing a demonstration run of over a quarter year without loss of catalyst performance (slide 14). A third key accomplishment was determining the optimal method to activate the catalysts. To our surprise the two catalysts required different procedures to maximize activity (slide 15). Catalysts were examined by a battery of surface science tools which included testing at the Advanced Photon Source at Argonne National Lab (by Simon Bare of UOP). The work was used to direct activation studies and determine morphology changes on the catalyst over time. Catalyst research culminated with industry replication and scale-up of the two PNNL catalyst systems, a significant milestone (slide 16).

Process research. To optimize selectivity and conversion several experimental design sets were complete which examined pressure, temperature, liquid space velocity (flow rates), hydrogen to substrate ratio, substrate concentration, and pH. The work was completed in flow reactors. Statistical tools were used to analyze results (slide 17). Several surprises were found that are the basis for new intellectual property. The work culminated with industry validating the process at UOP in 150 cc flow reactors (slide 18). Industry validating the process in a scaled-up reactor system was a significant milestone.

An important aspect of flow reactor work was to reduce raw material costs. Initial work was done on purified feed. The impact of various impurities was tested by doping pure feeds and running for 24-48 h. At the same time process options for raw material processing were evaluated. We were able to remove several costly unit operations and two process options were down selected for raw material processing. We have achieved a key accomplishment of reducing feed costs while demonstrating catalyst life (slide 19).

Coming out of the catalytic reactor is a crude propylene glycol stream with various impurities. For the final process, the propylene glycol needs to be separated and purified. This work is underway driven by modeling along with experimentation. The goal is to minimize cost to produce proypylene glycol streams that will meet market acceptance (slide 20).

Process economics. The catalyst and process work, described in the paragraphs above, culminate in a detailed process flow diagram and a full technoeconomic model. Models of this sort are invaluable in determining sensitivity analysis to direct future research efforts. The CCOP and ROI have been determined. Although we are not publishing numbers in this document, the resultant numbers are the basis for an internal UOP Go/No-Go decision point. A technology review has occurred which received high marks. The primary show stoppers at this stage are market based and are listed on slide 21. In the longer term the knowledge gained from this work can be used to widen the range of feedstocks and products.

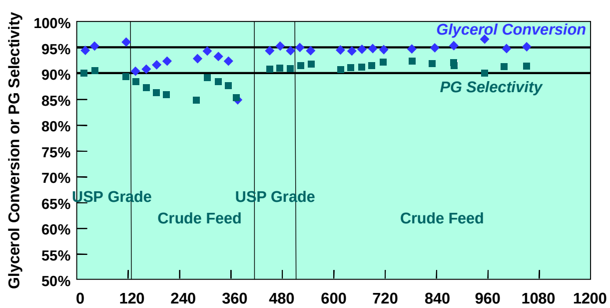


Figure 1. Accomplishments: met catalyst life and performance targets; industry validated

Schedule

Project Initiation Date: April 1, 2005
Planned Completion Date: September 30, 2008

Isosorbide, the Continuous Isosorbide Production from Sorbitol Using Solid Acid Catalysis

Rodney Williamson, Iowa Corn Promotion Board

Principal Investigator:	Norm Olson	Funding Partners:	The University of Iowa
HQ Technology Manager:	Valerie Sarisky-Reed	Sub-contractors:	N/A
PMC Project Officer:	Fred Gerdeman		

Goals and Objectives: The main objective of this project is to develop and/or enhance cost-effective methodologies for converting biomass into a wide variety of chemicals and products using supercritical fluids. Supercritical fluids will be used both to perform reactions of biomass to chemicals and products as well as to perform extractions/separations of bio-based chemicals from non-homogeneous mixtures.

Through this project we hope not only to empirically develop new paths for the conversion of biomass to chemicals but also to enhance the understanding of the science behind the nature of supercritical fluids.

Project Description: Supercritical fluids processing of biomass represents a very versatile and diverse path to the production of chemicals. Supercritical fluids can be used under a variety of conditions to quickly convert cellulose to sugar or to convert biomass into a mixture of oils, organic acids, alcohols and methane. Supercritical conditions exist when a fluid is pressurized and heated to conditions where the fluid behaves as neither a gas nor a liquid. This high pressure/moderate temperature zone is called the supercritical (SC) region. Most fluids exhibit significant changes in properties in the supercritical region, for example, water exhibits the characteristics of a high strength acid in the SC region while carbon dioxide exhibits solvent characteristics similar to hexane. Supercritical pressures and temperature are different for each fluid.

In this project numerous chemical reactions and extractions that take place when biomass is exposed to supercritical fluids will be investigated. With the exception of some well-known industrial processes the mechanisms underlying supercritical fluid interaction with solid biomass is not well understood.

This project will investigate several conversion reactions that may include 1) cellulose to sugars; 2) sequential dissolving and separation of cellulose, hemi-cellulose and lignin; 3) catalyst free biodiesel esterification; 4) other catalyst free esterifications; 5) direct biomass conversion to numerous chemicals; and 5) direct biomass conversion to hydrogen and CO.

The end result of many processes used to convert biomass to chemicals and fuels is often a somewhat complex mixture of products. This is true for many supercritical fluids reaction systems and most sterile and non-sterile fermentation systems. Supercritical fluids will be investigated with the goal of extracting key industrial chemicals such as furfural, organic acids (e.g. acetic acid and lactic acid) and alcohols (e.g. ethanol) from mixtures.

Summary of Work to Date - Accomplishments (FY05-current): Preliminary experiments and analysis on cellulose reactions to sugars in supercritical water have been performed using existing, old reaction equipment at the University of Iowa. Yields of approximately 50% sugars (glucose + fructose) have been demonstrated so far. Progress has been made in the development of reactor models for the hydrothermal conversion of cellulose to sugars. COMSOL Multiphysics finite element modeling software was used to model the temperature and flow patterns in the laboratory reactors. Accurate temperature- and pressure-dependent water properties were incorporated into the models, and the models yield results consistent with experiment. The reactor models will be used in interpreting experimental data for the determination of rate constants for cellulose hydrolysis and decomposition of sugars under hydrothermal conditions.

The work performed using the old reactor at the University of Iowa will be used to define starting conditions for the new reactor being installed at Iowa State University.

Reaction kinetic parameters were obtained for several reactions involved in the hydrothermal decomposition of cellulose. Specifically, activation energies and pre-exponential factors were obtained for the hydrothermal conversion of glucose, fructose, cellobiose, and cellotriose. Kinetic constants were calculated for the formation of 5-HMF, glyceraldehyde, levoglucosan, and erythrose during decomposition of monosaccharides, and for the isomerization reaction between glucose and fructose.

Preliminary experiments have been performed on catalyst free esterification of carboxylic acids in supercritical alcohols. The purpose of this research track is to demonstrate the use of supercritical fluids to make esters from soybean oil via a catalyst-free method.

A flow type reactor was designed and built to increase conversion of reactants. An esterification reaction was performed to test the new system. Technical grade linoleic acid purchased from Sigma was reacted with methanol. The solvent in the reaction products was removed under reduced pressure, then analyzed using NMR. The NMR spectrum of the esterification product does not indicate the presence of any unreacted linoleic acid, only methyl esters. Thus, the reaction appears to have proceeded to 100% conversion.

Work was started on setting up the reactor for organic acid esterification in supercritical alcohols and on developing protocols for chemical analysis

Schedule

Project Initiation Date:	May 31, 2006
Planned Completion Date:	June 30, 2008

Succinic Acid as a Byproduct in Corn-Based Ethanol Biorefineries

Susanne Kleff, Michigan Biotechnology Institute

No project summary provided.

Development of Sustainable Bio-Based Products and Bioenergy in Cooperation with the Midwest Consortium for Sustainable Bio-Based Products and Energy

Mike Ladisch, Purdue University

Principal Investigator:	Dr. Michael Ladisch	Funding Partners:	Michigan State University, University of Illinois, Iowa State University
HQ Technology Manager:	Valerie Sarisky-Reed		N/A
PMC Project Officer:	Gene Petersen	Sub-contractors:	Ames Laboratory, Competitive Pool-Recently Awarded, USDA NCAUR

Goals and Objectives: The work scope is based on the focus of this research on distillers' dry grains. Distillers' dry grains are co-products of dry-mills after starch in ground-up corn kernels has been fermented to ethanol. Distillers' grains contain cellulose (6 carbon sugars), pentosans (5 carbon sugars), residual starch (6 carbon sugars), some lignin, and protein. This composition provides opportunities to add value to the product mix from a dry-mill ethanol plant, reduce the net cost of ethanol, and support the DOE sugar platform. The proposed scope of work is defined by: 1) pretreatment of the distillers' grains; 2) hydrolysis of the resulting streams; 3) fermentation of the xylose and glucose in the hydrolysates to alcohols and chemicals and chemical intermediates; 4) analysis of composition of various streams for generating preliminary material balances and advanced separations to enhance overall process economics; 5) life cycle analyses to assess environmental impacts of new processes to allow for more rapid implementation of technology, and 6) economic assessment of the impact of process improvements resulting from this research on market potential. Participants for each area may come from any or all of the consortium members.

Our goal is to develop process technologies for (1) creating new markets for DDGS and (2) transitioning cellulose conversion technologies for use in existing corn to ethanol plants. The absence of a heavily lignified cell wall structure in DG makes DG particularly susceptible to pretreatment using either hot water or ammonia freeze explosion. The economic analysis compares added cost of conversion to the increased yields of fermentable sugars and ethanol in order to project the impact of cellulose conversion technology to increase income in dry grind plants.

Project Description: The new renewable fuel standards will push ethanol production to 7.5 billion gallons per year within two years. This project addresses processing that occurs post-fermentation and therefore minimizes impact on existing equipment in an ethanol plant, and facilitates retrofit of cellulose conversion capability into dry grind facilities. The project integrates multiple institutional capabilities to help solve a crucial problem: the proliferation of low value, fiber rich distillers grains (DG) now being produced in the corn dry milling industry.

The dry grind industry is growing rapidly, and the proliferation of the DG and DDGS has the potential to depress the market for this by-product and decrease the profitability of dry mills. This concerted effort will add value to distillers' grains by further processing them into additional fermentable sugars and ethanol, while leaving a solid that is reduced in weight and rich in protein. The project involves and integrates among members of the consortium: 1) advanced pretreatments to enhance the digestibility/reactivity of the fiber component (cellulose and hemicellulose) of DG, 2) enzymatic hydrolysis of pretreated DG to produce fermentable sugars and thereby remove part or all of the cellulose and hemicellulose, and thereby increasing the feed value of the residual unhydrolyzed solids, 3) fermentation of these sugars to ethanol and other biobased products, 4) analysis of composition and advanced separation methods applicable to ethanol and other products, 5) life cycle analysis to quantify key environmental features of these corn based biorefineries and the crop production systems that support them, and 6) comprehensive economic analysis of the processes, technologies, and markets, incorporating uncertainty in key technological and market parameters. As part of the Biomass Program within DOE's Office of Energy Efficiency and Renewable Energy, it is expected that this research will contribute directly to the multi-year technical plan particularly as related to the "Sugar Platform" and "Products," thus helping to ensure the department meets its targets to establish biomass as a significant source of sustainable fuels for the United States.

Summary of Work to Date - Accomplishments (FY05-current): The Consortium has worked together as a research team to obtain compositional analysis of DG and DDGS, to pretreat these materials, and then to systematically study their bioprocessing into sugars, ethanol, and other bioproducts. The results have been used to construct outlines of dry grind process flowsheets for untreated and pretreated DG so that compositional data, resulting from our experiments could be mapped onto the flowsheets to develop material balances, and to quantitate inputs and outputs for purposes of constructing an economic model.

The research has been carried out in close collaboration with industrial partners. One partner provided wet cake (DG) and DDGS, and insights on practical considerations for enhanced utilization of DG or DDGS. Genencor works closely with the Consortium to provide enzymes, expertise, and guidance on the types of enzymes that might be best suited for a specific set of processing conditions. These data, combined with an economic model that utilized current baseline capital costs, and cost of goods have enabled potential economic returns to be assessed if a dry grind facility were to incorporate cellulose conversion technology to reduce the volume of unfermented co-product, enhance ethanol yields, or produce other biofuels, while marketing the residual protein. While the scope of the work focuses on sugar and ethanol production, some effort was also made to analyze the composition, as well as the potential feeding value of a product that we have termed enhanced distillers' dried grains and soluble, since the processing of DDGS to additional ethanol results in a decreased mass and increased protein content of the DDGS that remain.

DDGS and wet distiller's grains are the major co-products of the dry grind ethanol facilities. As they are mainly used as animal feed, and a typical compositional analysis of the DDGS and wet distiller's grains mainly focuses on defining the feedstock's nutritional characteristics. With an increasing demand for fuel ethanol, the DDGS and wet distiller's grains are viewed as a potential bridge feedstock for ethanol production from other cellulosic biomass. The introduction of DDGS or wet distiller's grains as an additional feedstock for existing dry grind plants for increased ethanol yield requires a different approach to the compositional analysis of the material based on determining a detailed chemical composition. This is especially the case for the polymers cellulose, starch and xylan, which release fermentable sugars upon enzymatic hydrolysis. One accomplishment of this research is the detailed and complete compositional analysis procedure for DDGS and wet distiller's grains, as well as the determination of resulting compositions carried out independently by three different research groups. The compositions were comparable, thus giving an internally consistent basis for developing material balances, assessing the impact of pretreatment and hydrolysis, and developing an economic model.

One accomplishment is development of reproducible and accurate compositional analysis of DDGS and wet distiller's grains with a close to 100% mass closure. DDGS and wet distiller's grains are rich in glucan, xylan and arabinan. Total available sugars (glucan and xylan) of DDGS and wet distiller's grains for producing ethanol were measured to be 29.4% and 36.4%, respectively, based on total dry mass. Glucan includes both starch and cellulose in a ratio of approximately 1:3. Crude protein comprises 25% of the total dry mass of DDGS. Crude oil measured as ether extractives is 11.6%.

The second major accomplishment of this research is the use of controlled pH, liquid hot water (LHW) and ammonia fiber expansion (AFEX) pretreatments of DG and DDGS to enhance enzymatic digestibility of the distillers' grains . Both pretreatment methods significantly increased rates and extents of hydrolysis of distillers' dried grains with soluble (DDGS) as compared to untreated material, resulting in over 90% cellulose conversion to glucose within 24 hours of hydrolysis, at an enzyme loading of 15 FPU cellulase and 40 IU β-glucosidase per gram of glucan. Hydrolysis of pretreated wet distillers' grains at 13-15% (wt of dry distillers' grains per wt of total mixture) solids loading with the same enzyme dose resulted in approximately 70% glucan conversion to glucose within 72 hrs, regardless of the pretreatment methods applied. In addition a new approach to pretreating the DG was found. This approach forms phosphite esters of the oligosaccharides in DG and DDGS. This has been shown to be effective in dissolving the DDGS or DG in water.

A third major accomplishment is developing an understanding of how noncellulolytic enzymes act on pretreated substrates to enhance the hydrolytic efficiency of cellulases. This work was carried out with the input and assistance of Genencor. Supplementing the cellulase enzyme mixture with xylanase and feruloyl esterase for the high-solids digestion of the pretreated wet distillers' grains at 15-20% solids (w/w) enhanced the glucose yields up to 80% and xylose yields up to 50%. Fermentability of the hydrolyzed wet distillers' grains was tested by non-recombinant *Saccharomyces cerevisiae* ATCC 4124 strain, and close to metabolic (theoretical) yields of ethanol were obtained, for both LHW treated and AFEX treated wet distillers' grains. Enhanced DDGS refers to the final product of a modified dry grind process in which the distillers' grains are recycled and processed further to extract the unutilized polymeric sugars. Compositional changes of the laboratory synthesized enhanced DDGS have also been carried out and are part of an on-going activity.

The fourth major accomplishment was proving the fermentability of both glucose and xylose, derived from hydrolysis of pretreated substrates. Since industrial yeast strains are not capable of fermenting a major part of the sugars in this hydrolysate, non-traditional microorganisms were tested. These were: *Clostridium beijerinckii* BA101 for fermentation to butanol, and *Saccharomyces* 424A(LNH-ST) and *Escherichia coli* FBR5 for fermentation to ethanol. The yeast 424A(LNH-ST), under license to Iogen is in use at their new biomass/ethanol demonstration facility. Development of optimal fermentation conditions showed that all three microorganisms are capable of converting 80%, or more, of glucose and xylose to product. In the case of *E. coli,* acetic acid was found to be inhibitory, while some aromatic compounds derived from degradation of low molecular weight, lignin-like compounds in the DG could inhibit *Clostridium*. Overall, the formation of inhibitors due to the LHW and aqueous pretreatments was found to be minimal, and to have little effect on fermentation of the sugars to ethanol or to butanol.

The formation of oligosaccharides due to pretreatment led to a fifth accomplishment: the examination of a fixed bed (plug flow reactor) of meso-phase or solid catalysts. The results showed that current catalysts are capable of rapidly hydrolyzing cellobiose to glucose, but that the conversion of xylo-oligosaccharides and cellodextrins was not as efficient. While the results show a fixed bed catalyst has potential for rapidly processing aqueous streams containing soluble oligosaccharides, catalyst characteristics, including pore size, acid strength, and thermal stability need to be significantly improved for this approach to be feasible.

A sixth accomplishment was the development of an economic model, based on a process flowsheet in which pretreatment is added onto, or retrofitted to a dry grind facility. The concerted efforts of the Midwest Consortium Team enabled an integrated flowsheet to be developed, and the data on pretreatment, hydrolysis, fermentation, and co-product value to be mapped onto it in order to generate material balances around the process. The resulting flowsheets are being used to generate economic analysis, and to quantitate the value that is added by cellulose pretreatment and enzyme hydrolysis of DG and DDGS from a dry grind facility.

The seventh major accomplishment has been development of a peer reviewed, 10-paper compendium of the research results from this work. This work is being submitted to the journal, *Bioresource Technology*, to give an integrated assessment of the research results, obtained thus far, as well as a quantitative assessment of practical approaches to using cellulose conversion technology to enhance utilization of DG and DDGS in dry grind facilities. Work still remains to be done. However, the researchers in the Consortium wanted to inform colleagues and the industry of the status of this work, and the exciting potential of the near term application of cellulose conversion technology to dry grind, corn to ethanol plants. Annual meetings of the Midwest team and representatives from industry have also been carried out to communicate our results and receive feedback from a broad audience.

Schedule

Project Initiation Date: Friday, October 01, 2004
Planned Completion Date: Saturday, June 30, 2007

Iowa State University Biomass Energy Conversion Project

Norman K. Olson, Iowa State University

No project summary provided.

Thermochemical Platform

Introduction

The size of the U.S. bioindustry will, to a large degree, be determined by the cost, quality and quantity of biomass available. Equally important are the conversion technologies available to process these varying types of biomass. The Thermochemical Conversion (TC) platform is developing technologies that can fully utilize a wide range of biomass which may not be amenable to alcohol fermentation to produce fungible transportation fuels.

Our initial focus is on the available biomass as identified in the "Billion Ton Study" that will produce an alcohol fuel. Beginning in FY 2008, the platform has broadened its efforts to develop technology that can utilize the same wide range of feedstocks to produce hydrocarbon transportation fuels (e.g. gasoline, diesel, jet).

Platform Performance Goal

To reduce the estimated mature technology processing cost for converting cellulosic feedstocks to ethanol from $1.21 in 2005 to $0.82 per gallon by 2012 and $0.60 per gallon by 2017 (2007$), based on data at the bench scale.

Objectives

- By 2012, validate integrated production of ethanol from mixed alcohols produced from syngas at pilot scale, using agricultural residues and woody and energy crops (lignin or biomass) as feedstocks.
- By 2012, validate integrated production of biomass to gasoline and diesel via pyrolysis routes at pilot plant scale for woody biomass.

FY 2007 Accomplishments

- Completed TC design case
    - Industry validated (Feb)
    - Current ethanol cost goal is $1.33 per gallon
    - Low process water use: 1.9 gal water per gal ethanol
- Success in gasification
    - Developed correlations for tar yields from components of various types of biomass
- Success in gas clean-up/conditioning
    - Identified catalyst deactivation mechanism and metal-substrate interactions
    - Improved tar-cracking catalyst activity by 2.5 times (2010 target)
    - 2007 syngas clean-up solicitation issued
- Success in mixed alcohol catalyst to meet 2012 goals
    - Achieved space-time yield goal in mixed alcohol catalyst
    - Reached agreement in principal for DOW to supply their "Best In Class" mixed alcohol catalyst (key to meeting 2012 goal)
- Success in pyrolysis
    - Achieved 70 gal/ton (for gas/diesel fuel)
    - Obtained data for design case (due in FY 2008)
- Success in collaboration with government and industry
    - Co-lead (with NSF) to examine R&D needed for next generation of biofuels
    - Program peer (industry/university) review in July

Budget

The President's FY 2007 and 2008 budget requests include large funding increases for Thermochemical Conversion R&D from $4,723,000 in 2006 to $14,145,000 in 2007 and $17,537,000 in 2008.

2008 Plans

- 2008 Planned Solicitations
  - Pyrolysis oil to fuels ($1,000,000 in FY 2008 & $4,000,000 in out years)
  - Lab call for new ideas ($1,000,000)
    - Biomass substrate deconstruction and fuels synthesis
  - University call ($1,035,000)
    - Pyrolysis oil production and upgrading
    - Biorefinery residue gasification to fuels
    - Alcohol fuel synthesis catalysis
- FY 2008 End of Year (EOY) Joule Target
  - Modeled ethanol price of $1.92/gal from gasification
- FY 2008 Quarterly Milestones
  - By December 15, improve productivity of catalysts for mixed alcohol production from syngas (space-time yield = 800 g/l/hr).
  - By March 31, prepare and characterize two 75 kg charges of tar-reforming catalyst (pilot development unit).
  - By June 30, demonstrate 15 cumulative hours of thermochemical pilot operation

Paul Grabowski, Technology Manager – Thermochemical Platform
Department of Energy
Office of the Biomass Program, EE-2E
1000 Independence Avenue, SW. Washington, DC 20585-0121

Project Summaries

Thermochemical Platform Support

Thermochemical Platform Analysis

Andy Aden, National Renewable Energy Laboratory

Principal Investigator:	Andy Aden	Funding Partners:	N/A
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	N/A
PMC Project Officer:	John Scahill		

Goals and Objectives: The primary objective of thermochemical analyses is to accurately quantify the costs and benefits of thermochemical technologies in support of meeting the 2012 Minimum Ethanol Selling Price (MESP) of $1.07 per gallon and the 2030 renewable fuel production volume goals outlined in the 30x30 vision. In general, these targets will be met through improved feedstock-to-syngas conversion (i.e. tar reforming to yield more and cleaner syngas), process intensification (combining unit operations into a single operation) resulting in lower capital costs, and improved syngas-to-fuels productivity resulting in both lower capital costs and operating costs while increasing ethanol yields.

This task supports thermochemical research areas including tar reforming, gas cleanup, and mixed alcohol synthesis. Its goals are:

1) Identify task level targets that will contribute to the overall critical project targets,
2) Track and report on progress to the goal of $1.07 per gallon ethanol in annual State of Technology assessments,
3) Evaluate alternative processes and scenarios that might improve economics, feasibilities, or other factors such as environmental impacts (e.g. water usage),
4) Integration with other groups' activities including
   a) Strategic analysis of biorefineries and the bioindustry
   b) Systems Integration activities
   c) OBP program activities including planning and reviews
   d) Biochemical platform analysis
5) Technical Targets (i.e. cost, yield): Analysis is primarily focused on helping to demonstrate $1.07/gal ethanol by 2012.

Project Description: The goal of analysis is to help set technical and cost targets for the thermochemical platform and guide the research towards meeting these targets. Conceptual process designs are developed based on input from researchers and other engineers for converting biomass feedstocks into liquid fuels. These designs are modeled using software such as Aspen Plus to develop mass and energy balance information that is subsequently used in economic analyses. Many times, a discounted cash flow rate of return economic analysis is used to calculate the minimum ethanol selling price (MESP) need to meet a certain hurdle rate, 10% IRR in most cases for a net present value of zero.

However, the appropriate level of engineering rigor is used for each project. For example, if a project is in a very early stage of development, a simplified cash flow analysis may be all that is needed.

Using these models, analysts can also track research progress towards the goals through what are known as "State of Technology" assessments, where data achieved at the laboratory or pilot scale is used in the model to predict what the economics might look like at the commercial scale. As the science and research advances technically, these advancements can be quantified economically as progress towards a cost goal.

Accomplishments (FY05-current): Since FY05, the thermochemical platform has changed focus. While a syngas intermediate used to be the focus (with hydrogen as a model product), it has shifted instead to a focus on the end fuel product, where ethanol is now being targeted. As a result of an extensive literature search, a fixed bed MoS2-based fuel synthesis catalyst was chosen for this process because of its potential for high ethanol selectivities. Initial process designs and economics for the production of mixed alcohols from biomass gasification were developed, but these initial designs suffered from low ethanol yields and relatively poor economics.

It soon became clear that a detailed design report was necessary for several reasons. First of all, the biochemical platform had used such a report as a successful means of establishing a benchmark against which all process improvements could be quantified. A detailed design report represents one technology package that can meet the cost objectives. It by no means is meant to be considered the “optimal” design, but simply establishes a baseline. In addition to documenting a sound basis behind quantifiable targets, it also functions as a means of establishing better collaboration with industrial and academic partners.

In a short period (approximately 4 months), a design report was generated to document the process for converting wood chips into fuel ethanol via indirect gasification and mixed alcohols synthesis. Several steps for cleanup and conditioning were used, including tar reforming (with catalyst regeneration), quench, syngas compression, and acid gas scrubbing. In addition to detailed documentation of the process design assumptions and economic parameters used, a set of process flow diagrams were also developed. This report described where the research parameters needed to be to achieve “economic” ethanol; it did not reflect where state of the technology was at present. The initial report was extensively reviewed during the thermochemical platform workshop held in Washington, DC in January, 2007.

The gasifier in the model was based on the Battelle Columbus Labs (BCL) design and data from their 9 ton/day gasifier from which correlations were built. The syngas tar reforming conversions used in the model did not reflect what had actually been achieved at pilot scale, but rather were conversion targets to achieve. Syngas cleanup requirements were based on the catalyst system chosen with advice and support from Nexant Inc. The mixed alcohol fuel synthesis data was also a depiction of necessary targets for CO conversion, selectivity, and productivity. Liquid alcohols were condensed from the reactor outlet, and purified into two products: fuel grade ethanol and a “higher alcohol” co-product made predominantly of C3- and C4- linear alcohols. Methanol was recovered and recycled back to the synthesis reactor to increase the yields of ethanol and higher alcohols. Unconverted syngas was primarily recycled back to the tar reformer.

An MESP of $1.01/gallon was shown for a 2000 dry metric tonnes per day facility with a yield of 80 gal/dry ton of ethanol. The overall project investment was on the order of $190MM. The overall energy efficiency of the process on an LHV basis was 46%. Overall, the economics clearly showed that the cleanup and conditioning section of the process was one of the most expensive, and therefore should be targeted for research. Sensitivity analyses were also conducted in order to show which process variables had significant economic impact.

Two primary design considerations implemented during this period were: energy self-sufficiency and water usage minimization. The design used a small slipstream of “dirty” unreformed syngas to provide the heat needed to run the process. While this allowed for the requirement of no external fuel (i.e. natural gas), it did come with a price; a small loss of alcohol yield. Realizing that water sustainability is a key consideration in today’s ethanol industry, engineers implemented several design changes to minimize the water needed for cooling. For example, forced air cooling was used in place of cooling water heat exchangers where appropriate. The resulting water demand for the process was 1.9 gallons per gallon of ethanol produced.

Schedule

Project Initiation Date: October 1, 2002
Planned Completion Date: September 30, 2012

Gasification

Gasification Process Modeling and Optimization Task

David Dayton, National Renewable Energy Laboratory

Principal Investigator:	David Dayton	Funding Partners:	N/A
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	N/A
PMC Project Officer:	John Scahill		

Goals and Objectives: Mixed alcohol production from biomass-derived syngas is the leading thermochemical technology option for meeting the Advanced Energy Initiative's goal of producing ethanol for $1.07/gal by 2012. Thermochemical gasification technology is essential to fully exploit the diverse biomass resource base available for biofuels production. This is because the performance of thermochemical conversion technologies is relatively insensitive (compared to biochemical conversion) to the carbohydrate composition of biomass feedstocks and as such can utilize a wide variety of regionally specific materials exhibiting a broad range of chemical and physical properties. Biomass feedstock types being specifically targeted for thermochemical conversion are those not suitable for biochemically-based ethanol production. Ultimately lignin-rich residues from the biological conversion of lignocellulosic feedstocks will be used as thermochemical feedstocks to maximize biofuel production in integrated biorefineries.

Using wood as a model feedstock, the goal of the gasification fundamentals task is advance our understanding of thermochemical conversion mechanisms, particularly how processing conditions influence reaction behavior. In FY07, we performed detailed studies of lignin devolatilization kinetics using lignin model compounds. The objective of these studies is to identify reactor independent reaction mechanisms that can be used to model the formation and evolution of tars and heteroatom impurities in syngas. The kinetic models will then be used to explore and define process parameters that minimize tar formation (thermally or catalytically) as well as sulfur, chlorine, and nitrogen release during biomass gasification. The models will be tested/validated using a range of biomass feedstocks spanning woody and herbaceous types as well as biochemical process residues over a statistically robust set of gasification conditions to evaluate the effect of feedstock type (particularly ash content and composition) on product gas composition.

The ability to control the biomass gasification step to reduce the levels of syngas tars and other impurities offers the potential to significantly lower the cost of downstream cleanup and conditioning process steps. This approach is ultimately expected to increase overall conversion efficiency and decease capital and operating costs for an integrated process.

Technical Targets (i.e. cost, yield):
- Validate the technical and economic feasibility of generating syngas from low carbohydrate feedstocks
- Quantify the impact of feedstock composition on the cost of thermochemical ethanol production
- Develop a chemical mechanistic understanding of thermochemical biomass conversion

Biomass Gasification Targets for pilot-scale demonstration of 2012 cost-competitive ("$1.07") TC Ethanol Technology:
- 78% syngas efficiency
- H_2/CO = 1.0
- $CH_4 \leq$ 5vol%
- Tars $\leq$ 1 g/Nm^3
- benzene $\leq$ 0.04 vol%
- $H_2S \leq$ 20 ppm
- NH_3 and HCl to be determined

Project Description: The goal of this project is to develop tools to understand fundamental mechanisms and reaction kinetics that can be applied to developing thermochemical biorefinery technologies. The focus is on fundamental chemical kinetic measurements of trace product formation in biomass thermochemical processes including tar formation and destruction, transformation of S, N, Cl, and alkali metal release rates. The thermochemical conversion of model compounds of relevance to biomass pyrolysis and gasification will also be investigated. Some candidates for detailed study are furans, guiacols, phenols, anisole, and levoglucosan. These are all important compounds in the pyrolysis of lignocellulosic materials. The thermal conversion rates of model tar compounds (benzene, naphthalene, phenol, toluene, etc) will also be measured under relevant gasification atmospheres. Tar formation and conversion will be investigated as a function of temperature and gasification atmosphere (steam and partial oxidation). Fundamental kinetic rates for the thermal decomposition, steam reforming, and partial oxidation of these models compounds will be determined and compared to literature values when available. Extrapolation of results obtained from these bench-scale experiments to larger scale systems will be facilitated.

Accomplishments (FY05-current):

Title of task, subtask or milestone	**Status of Progress in Task or Milestone**	**Approved Updated Completion Date**	**Task or Milestone Completion Criteria (to include cost and performance metrics)**
Pilot-scale parametric gasification of wood, lignin-rich residues, switchgrass, and wheat straw to develop correlations for input in process models.	On schedule, progress positive or work completed	9/30/07	Biorefinery residues - Indirect (atm) gasification : corn stover; switchgrass; wheat straw; lignin - 78% syngas efficiency: $H_2/CO = 1.0\text{-}1.5$; $CH_4 \leq 15$vol%; Tars ≤ 30 g/Nm3; benzene $\leq$ 1vol%; H_2S = 50-600 ppm; NH_3 and HCl to be determined

The work in this project will be conducted in 3 related subtasks that explore the range of syngas compositions produced from various feedstocks including biorefinery and agricultural residues and future energy crops. Pilot-scale parametric gasification studies will provide the basis for developing correlations between feedstock composition and fundamental process parameters such as temperature and steam: biomass ratio that can be used as input for biomass gasification to mixed alcohols process simulations. Combining the pilot-scale experimental results with thermochemical analysis will be used to update technoeconomic analyses for thermochemical ethanol scenarios developed for the near term $1.07/gallon 2012 cost target and longer-term 30x30 vision.

The three tasks associated with this project are as follows:

1) Lignin Production – In collaboration with NREL's Targeted Conversion Research task, a sufficient amount of biochemically-derived lignin rich residues will be produced to satisfy the feedstock requirements for bench-scale and pilot-scale gasification and catalyst testing studies.

2) Parametric Gasification Studies – Process variables in NREL's TCPDU will be varied according to a statistical design to measure syngas composition, tar concentrations, and impurity levels (H_2S, and NH_3) with selected feedstocks; including lignin-rich residues, wheat straw, and switchgrass as a function of process conditions. These pilot-scale experiments will provide the data needed to develop correlations for use in Thermochemical Process Analysis.

3) Fundamental Thermochemical Conversion Kinetics – This task will conduct fundamental kinetics measurements in a bench-scale, variable temperature laminar entrained flow reactor (LEFR). These measurements will help validate chemical kinetics mechanisms that can be used for reactor designs by gasification developers.

Technical Feasibility and Risks: A Benchmark thermochemical process designed for achieving $1.07/gal ethanol by 2012

Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass (NREL-TP-510-41168) http://www.nrel.gov/docs/fy07osti/41168.pdf was completed and used to develop specific, quantitative R&D targets for overcoming identified technical barriers to successful technology demonstration. This project is to provide the technical feasibility needed to advance, demonstrate, and validate gasification performance of appropriate feedstocks meeting process design targets.

The benchmark process design also quantifies the relative capital and operating costs associated with process unit operations highlighting the economic benefit of overcoming specific technical barrier areas to help guide R&D efforts to maximize the economic impact of research by optimizing performance and identifying process integration opportunities. Integrating unit operations provides opportunities for process consolidation to improve technical and economic feasibility and brings about a systems-level approach to identify relative importance of identified technical barriers.

All of these R&D activities are focused on process improvements at the scale of projected biomass systems, roughly 2000 tpd as benchmarked in the Mixed Alcohol Design Study. At this scale there are limited cost-reductions from increased economy of scale and costs associated with feedstock collection, processing and handling are significant.

The challenges directly associated with this project are to 1) develop laboratory-scale correlations that apply to larger-scale systems, 2) incorporate detailed chemical kinetic mechanistic modeling to explore biomass thermochemical conversion, and 3) develop computationally-tractable CFD models of thermochemical biomass conversion systems.

Schedule

Project Initiation Date:	October 01, 2002
Planned Completion Date:	September 30, 2011

Catalytic Hydrothermal Gasification for Eastman Kingsport Chemical

Chris Lindsey, Antares Group Incorporated

Principal Investigator:	Ed Gray	Funding Partners:	Eastman Chemical
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	N/A
PMC Project Officer:	John Scahill		

Goals and Objectives: The objective of the project team's Phase-I research and development effort is to advance a low-temperature catalytic gasification concept for use with wet biomass feedstocks, such as biosludges. The effort will leverage efforts already undertaken by PNNL in developing LTCHG and verify reactivity and treatability for various key byproducts. The endpoint of this Phase is a design for the first commercial application for the LTCHG process. This work is expected to lead to the first chemical synthesis application for a broad class of biomass resources with very high moisture contents including biosludges and stillage from ethanol production.

Technical Targets (i.e. cost, yield): This project contributes to the technical targets for the Corn Stover to Ethanol process, as LTCHG can be used to treat wet residue streams from the biorefinery. In particular, the lignin by-product of lignocellulosic ethanol production can be converted into a high value fuel gas which can then be used to generate energy. As LTCHG does not require the energy-intensive drying step necessary for combustion or air-blown gasification, it will be the technology of choice for converting wet byproducts to energy in and integrated Biorefinery.

Project Description: Substantial amounts of biomass are available in high-moisture or slurry waste streams generated Biorefineries and municipalities and industrial facilities. These include cellulose and hemicellulose hydrolysis byproducts, animal manures (especially dairy and swine), pulp mill sludges, food processing sludges, and municipal wastewater sludges. The high moisture content of these streams makes them problematic for conventional thermochemical conversion since water removal (either mechanical or thermal drying) puts a significant strain on project economics. Using the raw byproducts as a boiler fuel is a frequently used disposal application that has no energy benefit for the process. As a result, there is substantial industry interest in thermochemical technologies to convert waste streams into added-value products.

Low-Temperature Catalytic Hydrothermal Gasification (LTCHG) offers the potential to access the carbon trapped in these streams using a less energy intensive process that works with, rather than against the high moisture contents of these resources. The process is a thermocatalytic gasification concept, which converts wet organic residues to a medium-Btu gas. The system is operated as a liquid-phase, heterogeneously catalyzed process at nominally 350ºC and 20 MPa to produce a methane/carbon dioxide product gas from the water solutions or slurries of organics. The LTCHG system operates with streams containing as little as a few percent dry solids by weight. In contrast, conventional gasification systems are generally inoperable with feedstocks containing more than 50 weight % moisture.

The development efforts undertaken to date have included characterization of numerous feedstocks, including recent work characterizing waste biosludge streams at Eastman's Kingsport Chemical Plant and materials from existing dry corn ethanol mills. Characterizations have included detailed chemical analyses as well as process tests in batch reactors, bench scale continuous flow processing evaluations, and finally testing in a continuous flow reactor in a mobile Process Development Unit (PDU). With the knowledge gained in the PDU testing of the Eastman biosludges Antares is proposing to restructure the industrial arrangements focusing on Biorefinery partners whose byproducts of hydrolysis better fit the range of treatability. Antares intends to work with several partners providing confidential results to each company on the treatability of the byproducts. Partners with strong interest in the technology and high byproduct treatability will be selected as the basis for completing a conceptual pilot plant design.

Accomplishments (FY05-current): The development efforts undertaken to date have included analysis and characterization of waste biosludge streams at Eastman's Kingsport Chemical Plant. Characterizations have included detailed chemical analyses as well as process tests in batch reactors, bench scale continuous flow processing evaluations, and finally testing in a continuous flow reactor in a mobile Process Development Unit (PDU). A summary of the accomplishments to date by task is given below.

Task A: Biosludge Analysis and Assessment: PNNL completed chemical analyses of Eastman biosludge samples collected approximately monthly for more than a year. A deliverable report was issued on January 19, 2005. The analyses show the expected levels of the various elemental components and confirm the similarity of composition of the biosludge with other biomass feedstocks. This similarity also suggests the broader applicability of the pretreatment technology being developed in this project to other wet biomass feedstocks, including biorefinery residues. While the basic organic components of the biosludge were very consistent the results indicated highly variable concentrations of key contaminants including sulfur.

Task B: Batch and Continuous Flow Reactor Testing: PNNL completed a set of process tests with the biosludge samples in its batch reactor to evaluate catalyst activity and reaction conditions. The effect of different catalysts and solids concentration of the feed streams were evaluated. Tests confirmed the expected high activity of the catalyst with this feedstock, particularly for the ruthenium on carbon catalyst. From the results it was determined that Eastman wastes can be gasified in the catalytic gasification system at levels equivalent to or better than other wet biomasses. PNNL also tested Eastman feedstock in a bench-scale continuous reactor process, which confirmed the expected high activity of the catalyst and the high-pressure feeding of the biosludge at up to 5 wt% dry solids. Optimization of the mineral capture system operation was evaluated, and the sulfur capture system was expanded to include both reduced sulfur and sulfate separation.

The scaled-up reactor system (or Process Development Unit – PDU) was modified to include biosludge feeding, mineral matter separation and recovery, and sulfur removal (both sulfate and sulfide) to protect the catalyst bed. Several process tests were performed in the PDU, which confirmed the high-pressure feeding of the biosludge at up to 5 wt% dry solids. A high level of gasification was accomplished in the catalyst bed. Plugging in the heat-up portion of the system was overcome by a pressure stabilization modification to the reactor system. Subsequent operations confirmed significant losses of carbon in the solids separation step.

Task C: Process Modeling and Economic Analysis: Antares developed a detailed mass balance spreadsheet which tracks the relevant composition and properties (temperature, pressure) through each process element. This model was used to determine equipment requirements and sizes, and to estimate the end products of the process. PNNL analysis results were used for the initial composition of the biosludge and post-reactor gas composition. Estimates of equipment costs were gathered from vendor quotes and cost-estimating software. Antares generated a pro forma preliminary economic analysis based on the Eastman process and a switch from a negative or neutral value boiler fuel disposal option to a positive value high BTU methane production option. Sensitivity analyses were performed for the key factors in the process, including capital cost, catalyst lifetime and LHSV. Significant capital and O&M costs were included fur sulfur and mineral treatment for the Eastman feedstock. These costs were shown to have a large impact on the project economics. A preliminary evaluation of the process using feedstocks with minimal sulfur loading indicates very favorable economics.

Task D: Conceptual Pilot Plant Design: The project team determined that a biosludge composition with approximately 5 wt% solids is preferred for Eastman feedstock, based on economic and pumping considerations. The project team made preliminary decisions about equipment type, size, and materials from economic and technical analysis. Several possible pumping systems were identified, including screw, reciprocating, and syringe pumps. Screw pumps are currently the favored option. Due to the importance of effective sulfur removal before the catalyst, the project team has incorporated a pre-process sulfur trap, to remove the bulk of sulfur.

Technical Feasibility and Risks: LTCHG has the ability to turn industrial process liabilities (low or negative value byproducts) into assets – a clean medium-Btu fuel gas. While much attention is being poured into partial oxidation gasification, particularly on the gas clean-up side of the equation, limited effort in the US has focused on gasification in an aqueous medium – hydrothermal catalytic gasification. Although there are advantages to both gasification approaches, the benefits particular to LTCHG include:

- Alkali metals at concentrations typically found in biomass pass through the reactor in aqueous solution;
- Tars are efficiently converted to gasification products over the reactor bed;
- Wastewater cleanup of organic byproducts is not an issue;
- Reactor effluents are not airborne but are in solution making it relatively easy to separate out the clean product gasses;
- Chlorine is in dilute ionic form and passes through the reactor without problem;
- The medium-BTU gas comes available at high pressure (around 3000 psi), which facilitates (semi) selective removal of CO2 resulting in a high-BTU fuel gas and separate CO2 product stream.

These advantages combined with the very active hydrothermal environment aids the pretreatment of feedstocks and the post-treatment of byproducts. As this technology can be applied to a wide range byproducts from industrial and municipal customers (ethanol Biorefineries, pulp & paper mills, municipal or industrial WWT), it ensures that there will be a place for LTCHG even if markets shift.

The primary challenge for hydrothermal gasification is to adequately clean the feedstock prior to the catalyst bed in the gasifier reactor. As feedstock contaminants (such as sulfur and minerals) are detrimental to catalyst life, the feedstock composition is a key to project success. In addition to selecting feedstocks based on compositional requirements, effective low cost pretreatment options and polishing steps for sulfur and mineral removal need to be developed. Carbon losses (with mineral precipitation) also need to be minimized.

Schedule

Project Initiation Date: October 01, 2004
Planned Completion Date: March 31, 2008

Mississippi State University Sustainable Energy Center

Mark Bricka, Mississippi State University

No Project Summary Provided.

Fuel Chemistry and Bed Performance in a Black Liquor Steam Reformer Project

Kevin Whitty, University of Utah

No Project Summary Provided.

Clean-Up and Conditioning

Biomass Gas Cleanup Using a Therminator
Santosh Gangwal, RTI International

No Project Summary Provided.

Engineering New Catalysts for In-Process Elimination of Tars

Larry Felix, Gas Technology Institute

Principal Investigator:	Rachid B. Slimane	Funding Partners:	Alfred University; Ohio State University; NexTech Materials, Ltd.
HQ Technology Manager:	Paul Grabowski		
PMC Project Officer:	John Scahill		
		Sub-contractors:	N/A

Goals and Objectives: The primary goal of this project is to develop a new and more efficient method for engineering and economically producing optimized catalysts for the reduction or elimination of tars in biomass gasification. A second project goal is to determine if waste materials of little (or negative) value that contain potential catalysts can be converted into attrition-resistant refractory catalyst substrates and tar-cracking catalysts. All work will be performed by GTI and our partners on this project (NexTech Materials, Alfred University, and Ohio State University).

Accomplishments (FY05-current): In FY2007, work will first focus on assessing the information gained from intensive studies by Ohio State University (OSU) of new Ni-based tar-cracking catalytic materials produced on this project and samples of these catalysts that have been exposed to surrogate biomass tars both by GTI in its Catalyst Test Facility in Des Plaines, IL and by Dr. David Dayton in his catalyst testing facilities at NREL in Golden, CO. Samples of Ni-based catalysts developed at NREL will also be evaluated by OSU to compare with the catalytic materials developed on this project elucidate the underlying mechanisms that these catalysts share. GTI and NREL will also conduct exposure tests of new catalytic material made on this project with syngas made by gasifying corn stover and biorefinery wastes supplied by NREL. Samples of materials tested at GTI and NREL will be forwarded to OSU for in-depth analysis and characterization.

As part of its techno-economic analysis of catalysts, NexTech Materials is determining the costs for producing these materials by two routes: first, by taking the process used at GTI to a commercial scale, and second, by determining the costs associated with producing these catalysts in a submerged combustion melter. In this work, NexTech will produce small amounts of the types of catalysts that have been produced at GTI, but with commercial equipment to establish basis for cost. GTI will provide economic cost information for incorporating submerged combustion melting. Alfred University will investigate formulating high-temperature glasses that exhibit catalytic activity.

Title of task, subtask or milestone	**Approved Updated Completion Date**
Concept Feasibility	14-Oct-05
Performance Optimization	15-Mar-07
Develop waste-based catalyst	1-Jun-07
Techno-economic analysis	31-Dec-07
Large-Scale Test	1-Dec-07
Large-scale test of baseline catalytic bed materials	4-Nov-05
Evaluate existing materials	4-Nov-05
Produce new catalytic materials	1-Jul-07
Evaluate new Catalysts	1-Dec-07
Demonstrate feasibility of concept	14-Oct-05

Schedule

Project Initiation Date:	October 1, 2004
Planned Completion Date:	December 28, 20-07

Catalyst Fundamentals

Dave Dayton, National Renewable Energy Laboratory

Principal Investigator:	Kim Magrini	Funding Partners:	N/A
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	N/A
PMC Project Officer:	John Scahill		

Goals and Objectives: Technoeconomic analysis has shown that cleanup and conditioning of biomass-derived syngas to remove chemical contaminants such as tar, ammonia, chlorine, sulfur, alkali metals, and particulates has the greatest impact on the cost of clean syngas. To date, gas cleanup and conditioning technologies and systems are unproven in integrated biorefinery applications. Catalytic steam reforming of tars produced during biorefinery residues gasification will be investigated in bench-scale reactors. Surface analysis and fundamental catalyst screening studies using Micro-Activity Test Systems (MATS) will be used to assess the impact of sulfur release from biorefinery residue gasification on the long-term activity and regenerability of developing tar reforming catalysts. The collective catalyst activity and lifetime measurements from these experimental investigations and ongoing catalyst deactivation kinetic determinations will be used to aid in the preliminary design of a regenerating catalytic tar reforming reactor that can be implemented in thermochemical conversion processes that are integrated into current and developing biorefinery process concepts.

Accomplishments (FY05-current): Developing an optimized fluidizable tar reforming catalyst for gas cleanup and conditioning in a biomass gasification/mixed alcohol synthesis process has been the focus of these efforts. Correlating bench-scale results from micro-activity test systems with pilot-scale catalyst performance has led to improved catalyst regeneration procedures and better catalyst formulations. The methods and protocols developed should benefit catalyst manufactures in the future as these catalysts become commercial.

Additional improvements in catalyst performance could be realized by taking a much more fundamental approach to developing improved catalyst formulations and optimized regeneration protocols to maintain high tar reforming activity for long periods of time. The three tasks below will increase the core knowledge of tar/catalyst interactions.

1) Catalyst Surface Science – A detailed, fundamental understanding of catalyst surface chemistry as is impacts initial catalyst deactivation and long term catalyst activity will be developed. Utilizing the capabilities in NREL's Biomass Surface Characterization Laboratory (BSCL). Correlating catalyst surface analysis with metal dispersion, elemental composition, crystal growth, active site poisoning, etc. is the goal of this effort. Alternatively, we will collaborate with Argonne National Laboratory to explore the effectiveness of using existing in-situ catalyst reactor cells and on-line analysis equipment available in ANL's Advanced Photon Laboratory to perform TPR, EXAFS, and XANES. This work should provide quantitative of nickel species during preparation and reaction and insight to catalyst morphology changes with composition, sulfur adsorption, and deactivation.
2) Bench-scale catalyst testing – The micro-activity test systems and slipstream 2" fluidized bed catalyst reactor will continue to be utilized to evaluate the performance of developing catalysts. Catalysts will include new formulations on alternative supports plus catalysts being developed in other Biomass Program projects.
3) Computational Catalysis – Computational methods will be developed and applied to guide catalyst design and related experimental work to explore/validate basic molecular interactions occurring on metallic and metal oxide surfaces. Ni-based tar reforming catalysts are the basis for developing initial computational methods. First principles methods will be used to comparatively investigate and rank the catalytic activity of different metals, metal-alloys and nano-structured catalyst systems. The experimental capabilities for catalyst activity screening and catalyst evaluation developed in this will be used to test and validate key computational results.

The arrangement of the various components in these multi-functional catalysts at the nano-scale may be critical. As postulated in the literature, at least two metal atoms (typically nickel) are needed to adsorb the hydrocarbon and break the C-C bond while the alumina support provides hydroxyl moieties to react with the carbon to form hydrogen and oxides of carbon. Computationally, the arrangement, size, and orientation of these components could be modeled to develop a better understanding of how these catalysts work and guide the synthesis of new catalysts which could be tested to verify the approach.

Schedule

Project Initiation Date:	August 1, 2001
Planned Completion Date:	September 30, 2011

Integrated Catalyst Testing

Calvin Feik, National Renewable Energy Laboratory

No Project Summary Provided.

Fuel Synthesis

Thermochemical Conversion of Corn Stover

James L. Gaddy, Bioengineering Resources, Inc.

Principal Investigator:	James L. Gaddy	Funding Partners:	Bioengineering Resources, Inc.; Chippewa Valley Ethanol Company; Katzen International, Inc.; Burns & McDonnell Engineering Company, Inc.; University of Arkansas
HQ Technology Manager:	Paul Grabowski		
PMC Project Officer:	John Scahill	Sub-contractors:	N/A

Goals and Objectives: The overall objective of this project is to develop an economical gasification/fermentation process to produce ethanol from corn stover. Process variables will be optimized and a detailed cost projection prepared for the integration of a conventional grain alcohol plant with the stover and ethanol facilities.

Technical Targets (i.e. cost, yield): Gasification of corn stover and subsequent gas cleanup to provide a fermentable syngas. Fermentation productivity of at least 50 g/L/day is sought. An overall process ROI of 15 percent is targeted.

Project Description: The overall objective of this project is to develop an economic gasification / fermentation process to produce ethanol from corn stover. Process variables will be optimized and a detailed design and cost projection prepared for the integration of a conventional grain alcohol plant with the stover and ethanol facilities. Stover gasification experiments will be conducted in the BRI Gasifier where conditions to maximize the CO and H_2 concentrations in corn stover syngas will be sought to optimize ethanol production by fermentation. Syngas produced from stover gasification will be used in the gas fermentation. Fermentation subtasks include syngas clean-up, the fermentation experiments, emissions measurement and by-product utilization. Economic projections will be prepared, including a process design and economic analysis and a detailed energy balance.

Accomplishments (FY05-current):
Task A. Stover Gasification. The current method utilized by farmers is to bale the stover for alternative cattle feed. They use round bales and square bales. We have utilized round bales bound either with string or with wrap. The wrapped bales are easier to handle and are co-fed with wood chips into our grinder, which reduces the size and mixes the two feeds. This mixture has proven to flow without much difficulty through our feed conveyors and dryer.

The cost of delivered corn stover has been investigated by CVEC to be about $35 to 40 per ton delivered within a 30 mile radius. Recently we have priced early summer square baled stover to be $40 per ton before delivery costs.

Gasification in our pilot 1 ton per day gasifier (120 lbs/hr) works best with the stover after rough grinding. The grinding serves to reduce the variation in size to provide a more dense feed. Wood chips are being added at a ratio of 50 percent by weight. Stover availability seemed to be in short supply, so the chips extend the life of the stover without adding much volume. By volume, the stover to chip ratio is 3 to 1. The chips may also help alleviate bridging within the gasification bed. Experience with sugar cane bagasse required considerations for bridging and stover may also.

Therefore, at this time, the focus has been on long operating periods with the stover / wood chip mix to refine gasifier operating parameters to maintain high CO concentrations and to ferment the gas generated. Carbon monoxide concentrations of over 30 percent have been demonstrated during the last two month period.

This task is scheduled to be completed by September 2007.

Task B. Syngas Fermentation. Gas clean-up by water scrubbing has permitted successful fermentation of syngas generated from wood chips, sugar cane bagasse, corn stover and mixtures thereof. The focus of the fermentation has been to maintain a productivity of 40 g/L/day or higher and doing so over long periods of time to demonstrate the suitability of the gas, reaction to gas contaminants and changes in gas composition. Theoretical productivity of over 50 g/L/day has been demonstrated over the last two months.

This task is scheduled to be completed by April 2008.

Task C. Economic Projections. This task is being delayed until sufficient data from the pilot plant is available to pursue preliminary design and cost projections.

This task is scheduled to be completed by August 2008.

Technical Feasibility and Risks:
Technical Risks

Dilute Syngas requires large downstream equipment. Air leakages into the gasifier cause syngas dilution due to the nitrogen in the air. Heat losses result in higher CO_2 concentrations and subsequently lower CO concentrations. These two causes can be alleviated by using oxygen enriched air and by the reduced surface to volume ratio in the larger units.

The fermentation process is continuous, therefore the gas supply must also be continuous. Downtime due to tar/soot deposition must be resolved or minimized. Mechanical failures of equipment must also be minimized.

The Fermentation productivity impacts the size of the fermentation vessels. The syngas must also be adequately scrubbed to remove materials toxic to the bacteria.

Process emissions must at a minimum, satisfy environmental regulations.

Business Risks

Raw Material cost and availability constraints require that the raw material be available and that the delivery cost be in an acceptable range. Alternative feedstocks will likely need to be considered due to uncertainty of annual availability.

The Scale-up uncertainties are centered around the gasifier and the fermenter. The gasifier has been in mechanical operation at the unit size envisioned (150 tons per day). The difference is that we will be operating the second stage with starved air (oxygen or oxygen-enriched air feed) to just crack the tars, not burning all the gas to completion. The fermenter scale-up will be a 10 to 1 scale-up based on reactor diameter. This is a normal scale-up ratio.

The Fuel Market needs to continue to support ethanol production. The potential market is 100 billion gpy to replace all imported liquid fuel. An ethanol price of $2 per gallon will help ensure the financial success of the process.

Schedule

Project Initiation Date: October 1, 2004
Planned Completion Date: September 30, 2008

Small Scale Biomass System (BioMax)

Robb Walt, Community Power Corporation

No Project Summary Provided.

Biomass-Derived Syngas Utilization for Fuels and Chemicals

Santosh Gangwal, RTI International

No Project Summary Provided.

Syngas Quality for Mixed Alcohols

Jim White, PNNL

No Project Summary Provided.

Pyrolysis

Core Pyrolysis R&D

Doug Elliot, Pacific Northwest National Laboratory

Principal Investigator:	Douglas C. Elliott	Funding Partners:	collaboration with VTT (Finland) is under development
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	N/A
PMC Project Officer:	John Scahill		

Goals and Objectives: Pyrolysis is an effective method for converting solid biomass or biomass-processing residues into liquid that can be directly used in stationary power generators, can be upgraded to gasoline-like fuel or can be used as feedstock for producing syngas by gasification. Each of these applications adds value and improves economics of the biomass to ethanol process by utilizing the whole biomass and not only the carbohydrate fraction.

Technical Targets (i.e. cost, yield): This project is focused on fundamental research to support the main pyrolysis barrier to develop "new methods to control the pyrolytic pathways to bio-oil intermediates in order to increase product yield and recovery." As this is a new area for research, the specific targets have not been instituted for pyrolysis and will be developed as part of the FY07 effort in this project.

Project Description: The objective of this work is to develop improved pyrolysis systems for production of liquid fuels from biomass. PNNL will evaluate the use of innovative catalysts and processing conditions for modifying bio-oil composition. The research will also examine products from bio-oil through modified pyrolysis techniques including in-situ catalysis. Research will also examine pyrolysis oil components which can be recovered in an aqueous phase.

The experimental work will use innovative catalysts and processing conditions to produce higher quality biocrude oils during biomass pyrolysis. The high oxygen content and reactivities of current technologies require significant stabilization and upgrading of the biocrude before it can be used as a refinery feedstock. Improved methods to create higher quality oil during the pyrolysis step would result in a product that could be fed directly to petroleum refineries with little or no stabilization or pretreatment.

The project includes tasks for development of a base-case design of pyrolysis to liquid fuels, experimental work in a bench-scale unit, participation in the IEA pyrolysis activity, and support for standards development.

Accomplishments (FY05-current): A base-case design study in underway and should be completed by the end of FY07. It will provide a basis for comparison with other biomass conversion systems and a means to assess the utility of this processing option and to evaluate the process options to allow a means to focus on parameters of importance.

A bench-scale fast pyrolysis reactor will be assembled at PNNL for production of modified bio-oils for analysis and evaluation for products recovery. The unit is currently under construction with final design of remaining elements to be completed shortly.

This project also includes participation in the IEA Bioenergy Pyrolysis Task. The semiannual meetings include the PI in workshops with European experts in the field. The PI is also the lead of an element on Biorefinery within the international collaboration. The Biorefinery effort includes preparation of technoeconomic assessments of 4 scenarios for a pyrolysis-based biorefinery and organization of a lignin pyrolysis round-robin, which is underway.

In addition, the project includes a task to support the establishment of standards for bio-oil within the ASTM structure. The draft standard, produced by the industrial participant Dynamotive with input from the national labs and others, has been reviewed by ASTM and is being revised.

Technical Feasibility and Risks: Benchmarking Pyrolysis processes to produce hydrocarbon liquid fuels designed for achieving $1.07/gal ethanol-equivalent by 2012 will be a goal using a basecase design study, which is being drafted. Through experimental work we hope to demonstrate and validate pyrolysis performance of appropriate feedstocks meeting process design targets.

Process integration options should provide opportunities for process consolidation to improve technical and economic feasibility. A systems approach will be used to identify relative importance of identified technical barriers.

Scakles of operation will be evaluated from 200 to 2000 tpd. Potential exists for cost reduction of biomass pyrolysis systems through economy of scale incorporating petroleum refinery infrastructure. Feedstock cost, handling, processing, and bio-oil cost, handling, processing elements will all play a role.

Specific to this project, bench-scale studies provide fundamental data for relatively low cost and low risk and can explore a wide range of experimental conditions in a reasonable time frame to focus process optimization of demonstration projects.

Remaining challenges to be assessed include:

- Variability of bio-oil composition,
- Inorganic impurities,
- Long-term catalyst performance.

Schedule

Project Initiation Date: October 01, 2006
Planned Completion Date: September 30, 2010

Core Pyrolysis R&D
Doug Elliot, PNL

Principal Investigator:	Stefan Czernik	Funding Partners:	N/A
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	N/A
PMC Project Officer:	John Scahill		

Goals and Objectives: Pyrolysis is an effective method for converting solid biomass or biomass-processing residues into liquid that can be directly used in stationary power generators, can be upgraded to gasoline-like fuel or can be used as feedstock for producing syngas by gasification. Each of these applications adds value and improves economics of the biomass to ethanol process by utilizing the whole biomass and not only the carbohydrate fraction.

Technical Targets (i.e. cost, yield): Technical targets for pyrolysis R&D are being developed in collaboration by NREL and PNNL. A draft document proposes the following FY2007 targets for bio-oil: yield of 53%, oxygen content 35%, acid number 150, carbonyl content 5 mol/kg, and hydrocarbon fuel yield of 75 gal/ton biomass. For 2012 these targets are respectively: 67%, 15%, 25, 2 mol/kg, and 90 gal/ton biomass. Pyrolysis design case report to provide benchmark baseline technology for cost targets and R&D goals will be completed by the end of FY2007.

Project Description: The goal of this project is to improve the quality of biomass pyrolysis oil (bio-oil) that will result in more efficient converting biomass to gasoline-type fuel. The main barriers for using bio-oil in refineries (adaptation of hydrotreating process to bio-oil being developed by UOP) are its instability and high acid content. Therefore, at present, only the lignin-derived bio-oil fraction (1/3 of the whole bio-oil) is considered an acceptable refinery feedstock. This effort focuses on improving bio-oil properties that will make possible using the whole bio-oil in the hydrotreating process, which will produce more biomass-based gasoline.

The pH of bio-oils is about 3 and results from the presence of organic acids of which acetic acid is the most abundant. 1 kg of bio-oil includes 1.5-2 moles of carboxylic acid groups. The acidity implies corrosive behavior to mild steel and promotes unwanted reactions of polymerization and condensation that lead to increase in molecular weight and a consequent increase in viscosity on storage. The most abundant compounds in bio-oil are aldehydes and ketones, with 5-6 moles of carbonyl groups per 1 kg bio-oil. Those compounds readily react between themselves and with other bio-oil components, especially in the presence of acids, to form unwanted large molecules. The destruction of acidity and prevention of molecular weight growth is the goal of the proposed upgrading process. The idea is to react organic acids and aldehydes in bio-oil with small molecular weight alcohols (methanol, ethanol) and convert them respectively in esters and acetals. This will remove acidity and improve chemical stability by preventing further reactions between functional groups attached to larger molecules. The reaction of bio-oil with alcohols can be carried out both in liquid phase using condensed bio-oil and in vapor phase using pyrolysis vapors before condensation of bio-oil. The first approach is compatible with the existing pyrolysis processes (Ensyn, DynaMotive) and will require an additional reactor for upgrading bio-oils as currently produced. The second approach involves a modification to the pyrolysis system with a catalytic gas-phase reactor installed before the condensation train, which may be more challenging but more innovative and potentially more advantageous.

Accomplishments (FY05-current): This effort will focus on the effectiveness of reacting selected alcohols (methanol, ethanol, glycerol, etc.) with high temperature pyrolysis vapors to convert acids to esters. A review of the literature will validate this approach and identify other potential chemical reactions that can be targeted. In addition, supporting experiments will be conducted with molecular beam mass spectrometer systems in conjunction with variable, high temperature flow reactors. The goal is to evaluate the effect of pyrolysis temperature, reaction temperature, alcohol (methanol, ethanol, and glycerol) addition, and feedstock cellulose, lignin, poplar, and corn stover). One hypothesis that will be tested is whether the carbohydrate fraction of biomass pyrolysis vapors reacts with alcohols to make esters and whether or not the lignin-derived pyrolysis products are unreactive or inhibit the carbohydrate reactions.

Task 1. Literature Review to evaluate reactions of methanol, ethanol and glycerol. Explore other potential additives to concentrate species in modified bio-oil
Task 2. Preliminary scoping experiments with bench-scale flow reactors to determine the effects of high temperature alcohol addition on biomass pyrolysis products

Title of task, subtask or milestone	Status of Progress in Task or Milestone	Approved Updated Completion Date	Task or Milestone Completion Criteria (to include cost and performance metrics)
Opportunities for Biomass Pyrolysis - Scenario Analysis	On schedule, progress positive or work completed	30-Sep-07	Develop Quantitative Technical R&D Targets for Biomass Pyrolysis Technologies through 2012 - This analysis will provide the basis for developing R&D Targets for out-year milestones

The literature review was conducted to determine the existing state-of-the-art methodologies that are currently known for esterification and acetalization reactions. These reactions are expected to remove unwanted acidity and improve stability of bio-oil. Our experiments with a mixed hardwood bio-oil so far have shown that the acidity can be reduced by more than 60% during the simple azeotropic removal of water from the crude bio-oil, while over 30% of volatile carbonyl compounds were also removed from the oil. Treatment of the bio-oil with lower alcohols, *i.e.* methanol, ethanol and butanol, using acid catalysts such as *p*-toluenesulfonic acid (a homogeneous acid) or Amberlyst-15 (a solid acid resin) led to near-quantitative removal of the carboxylic acids, and also up to 70% reduction in free carbonyl compounds. While this clearly surpasses our initial goal, we decided to further expand our 'proof-of-concept' to the use of polyols such as glycerol and ethylene glycol. Preliminary experiments showed that these polyols not only promoted near-quantitative removal of the acidity of the bio-oils, but also removed up to 90% of the free carbonyl concentration. The use of glycerol is particularly interesting because this polyol is in need of large market outlets as it is an abundant by-product of the biodiesel industry. We are currently focusing on the analysis of the various distillates and oil residues in order to better understand the underlying chemistry of the reactive distillations.

Technical Feasibility and Risks:
At present, unknown is a potential impact of feedstock composition variability, especially of inorganic impurities on the pyrolysis yields and on the upgrading catalyst performances.

Schedule
Project Initiation Date: October 01, 2006
Planned Completion Date: September 30, 2007

Pyrolysis Oil to Gasoline

Richard Marinangeli, UOP

Principal Investigator:	Richard L. Bain (NREL), Doug Elliott (PNNL), Richard Marinangeli (UOP)	Funding Partners:	N/A
HQ Technology Manager:	Paul Grabowski	Sub-contractors:	N/A
PMC Project Officer:	John Scahill		

Goals and Objectives: In the DOE report "Opportunities for Biorenewables in Oil Refineries," refined pyrolysis oils were shown to have the potential to replace a significant portion of transportation fuels. This thermal processing route can effectively utilize a vast majority of the 1 billion tons of biomass projected to be available in the United States, including those feedstocks unsuitable for fermentation. The pyrolysis pathway therefore provides the opportunity for increasing the impact of biofuels while leveraging existing processing and distribution systems. The short term option produces gasoline and refinery fuel, while longer term advanced thermal conversion configurations may have the potential to produce both gasoline and ethanol. The project supports the 30 x 30 goal of replacement of 30% of 2005 gasoline with renewable fuels by 2030 and supports the $1.07 goal by investigating alternative higher value uses of lignin rich streams in a biochemical biorefinery.

Thermochemical Pyrolysis (Gasoline) Targets:

- Pyrolysis Oil to biocrude (58 wt% conversion) (2009)
- Stabilization of Dry biomass by hydrotreating (TAN < 100)
- Upgrading to Finished Fuel 82 galHC/ton (2009)

Project Description: The objective of this project is to upgrade biomass pyrolysis oils to petroleum refinery feedstocks in a cost-effective manner. Pyrolysis-derived biooils are relatively inexpensive to produce, but there is little market for the resulting crude bio-oil. Selective hydroprocessing will be used generate a higher value biocrude and the biocrude will be converted to biofuels.

Accomplishments (FY05-current):

- Bio Oil prepared from mixed wood and corn stover
- Four bio-oil feedstocks have been processed through hydrotreating and hydrocracking process steps to examine processing conditions and determine product yields and composition.
- Intermediate stabilized bio-oil has been recovered and analyzed
- A fungible fuel product has been made from lignocellulosic waste
- Data base developed for pyrolysis, hydrotreating, hydrocracking and fuel properties
- Detailed results from these tests provide the basis for assessment of the process concept and the determination of process costs.
- LCA in progress

Technical Feasibility and Risks:

Potential Issue:	Mitigation
Yield loss to char and gas:	Improved T control, Metals removal, Catalyst development
Corrosion:	Stabilization of raw oil, Improved metallurgy
Unknown deactivation mechanism:	Analysis of deactivated catalyst during development stage
Poor fuel quality:	Use as feedstock to upgrading process

Schedule

Project Initiation Date: April 01, 2006
Planned Completion Date: Dec 31, 2007

Developing Thermal Conversion Options for Biorefinery Residues
Vann Bush, Gas Technology Institute

Combine with Previously Reviewed Project – Page XX.

Mississippi State University Sustainable Energy Center (MS)
Phil Steele, Mississippi State University

No Project Summary Provided.

Applications of Thermo-Depolymerization Technology
Thomas Butcher, Brookhaven National Laboratory

No Project Summary Provided.

IBR Platform

Introduction

The Integrated Biorefinery goal is to foster new industries converting lignocellulosic biomass into a wide range of products, including ones that would otherwise be made from petrochemicals. As with petrochemical refineries, the vision is that the biorefinery would produce both high-volume liquid transportation fuel (meeting national energy needs) and high-value chemicals or products (enhancing operation economics).

The integrated biorefinery is a conceptual framework that capitalizes on the core R&D carried out in the other technical elements of the Program and the synergies of integrating these technologies. The majority of projects in this area are expected to be cost-shared public-private partnerships. Intellectual property and geographic and market factors will determine the feedstock and conversion technology options that industry will choose to demonstrate and commercialize. Government cost share of the final integrated stages of biorefinery development is essential due to the high technical risk and capital investment involved.

The Integrated Biorefineries element is organized around the seven biorefinery pathways, Wet Mill Improvements, Dry Mill Improvements, Oil Seed Mill Improvements, Agricultural Residue Processing, Perennial Energy Crop Processing, Forest Resources Processing, and Post Consumer Waste Processing. The Program biorefinery pathway framework was evolved to support the following needs:

- Recognize the diversity of feedstocks and their specific associated issues from production through conversion.
- Highlight the need for integration between the feedstock production, feedstock logistics and conversion elements of the overall biomass supply chain.
- Identify the complete set of technologies required up to and including those in the biorefinery and the connections, or interfaces, between the individual technology parts, especially those from fundamentally different technical areas or disciplines.
- Clarify how new technologies could fit into the existing bioindustry market segments.
- Identify current and future synergies within existing bioindustry market segments.
- Envision the transition from today’s bioindustry to the future.

In 2007, EERE completed a significant revision of the Biomass Program’s objectives by focusing on demonstration and deployment activities for moving technologies beyond bench scale to pre-commercial demonstration and pioneer biofuels production plants, and facilitating growth of biofuels distribution infrastructure and biofuels-compatible vehicles across the U.S. into the marketplace. These demonstration and deployment efforts directly align with the biomass-to-biofuels supply chain.

Platform Performance Goal

To demonstrate and validate integrated technologies to achieve commercially acceptable performance and cost pro forma targets.

Objectives

The 2012 performance goal of the Integrated Biorefineries platform is to demonstrate the successful operation of three integrated biorefineries across various pathways. By 2017, mature[1] technology plant model[2] will be validated for cost of ethanol production based on pioneer plant performance and compared to the target of $1.33/gallon.

The performance goals for the pathways currently under investigation are as follows:

- Corn Dry Mill Improvements Pathway
  - Demonstrate and validate economical corn-fiber-to-ethanol setup in a corn dry grind mill by 2012.
- Agricultural Residue Processing Pathway
  - Demonstrate and validate integrated agricultural-residues-to-ethanol process at demonstration or commercial scale by 2012.
  - Demonstrate and validate production of ethanol from mixed alcohols produced from agricultural residues (lignin- or biomass-derived) syngas at demonstration or commercial scale by 2012.

FY 2007 Accomplishments

- Three of the 932(d) selected projects were awarded but may not cost until some conditions are met, primarily the production of a risk mitigation plan satisfactory to DOE. The three awardees are Abengoa Bioenergy of Kansas, Poet Project Liberty, and BlueFire Cellulose to Ethanol plant.
- The Range Fuel project was not under award at the end of the fiscal year but FY 2007 funds were reserved and reobligated such that the construction or Technology Investment Agreement was able to be signed November 5, 2007 by DOE.
- The project “Making the Industrial Biorefinery Happen!” has been managed by NatureWorks. Cargill has spun off a joint venture with another company which will now be comprised of the NatureWorks commercialization efforts. The R&D effort that constituted this project will now become part of Cargill. The formal transfer of personnel and project responsibility will be completed in the first quarter of FY 2008.
- Fermentation organism work at DuPont and NREL was concluded this quarter. A strain was demonstrated to meet the milestones for the rate of ethanol production, final ethanol titer, and extent of glucose and xylose conversion. This task was thus completed and a milestone report will be submitted next quarter. This strain is not yet adequate for production.
- Abengoa held a public ceremony on October 12 in York, Nebraska to herald the formal opening of a 1-ton-per-day cellulose pilot plant. It was attended by the Governor, the Congressman from that District, the Nebraska State Senator from that District, the Mayor of Lincoln, the CEO of Abengoa Bioenergy, DOE personnel, and local citizens.

Budget

The President’s FY 2008 and 2009 budget requests include increased funding for integrated biorefinery technologies and will continue to support industry’s efforts to commercialize biorefineries for the production of transportation fuels and co-products (such as materials and chemicals) as authorized by

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[1] The ethanol production cost targets are estimated mature technology processing costs which means that the capital and operating costs are assumed to be for an “nth plant” where several plants have been built and are operating successfully so that additional costs for risk financing, longer startups, under performance, and other costs associated with pioneer plants are not included.

[2] The modeled cost refers to the use of models to project the cost such as those defined in the NREL design reports:

1) “Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover,” NREL TP-510-32438, June 2002.
2) “Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass,” NREL/TP-510-41168, April 2007.
3) Feedstock Logistics Design Report, final editing in progress as of 09/27/07.

EPACT 2005, Section 932(d). The cost-shared projects selected for award in FY 2007 will launch the plant commercialization phase of the Biofuels Initiative, which is critical to validate the near-term biorefinery pathways for production of cost-competitive cellulosic ethanol. Additionally, the funding increase supports the technical and economic validation of additional biomass conversion technologies and feedstocks in biorefineries at approximately 10 percent of commercial scale.

2008 Plans

- Cargill and its partner PNNL were able to show economical production of secondary products from the 3 hydroxlypropionic acid platform; however, they are still unable to biologically produce the 3HP economically. They will refocus the R&D accordingly and have brought on a new partner to help with that process.
- A key economic driver is lowering capital cost. NatureWorks did achieve some success in producing lactic acid and ethanol yeast strains tolerant to acetic acid and operating at low pH. They will focus on fully demonstrating and validating this with Abengoa at the pilot plant scale but also on biomass-derived sugars in addition to starch-derived sugars.
- NatureWorks plans to operate pilot-scale unit for all the steps from pretreating corn stover to production of ethanol from C6 (glucose) and C5 (xylose) sugars. These findings would provide the basis for demonstrating and validating the process in a full-scale facility.
- Initial Award 1 was made to Abengoa. Projects are on track to complete work scope of Award 1 leading to a construction award or Award 2. Agricultural residues include wheat straw, corn cobs, and switchgrass.
- Range Fuels signed an Award 2 Technology Investment Agreement, Nov 6, 2007 using FY 2007 funds. Work will proceed toward completion of the initial phase of construction by the end of calendar year 2008.

Larry Russo and Neil Rossmeissl
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1000 Independence Avenue, SW. Washington, DC 20585-0121

Project Summaries

Corn Wet/Dry Mill Improvements

Sugar-based Ethanol Biorefinery: Ethanol, Succinic Acid and By-Product Production.

Donal F. Day, Louisiana State University Agricultural Center, Audubon Sugar Institute

Principal Investigator:	Dr. Donal Day	Funding Partners:	MBI International
HQ Technology Manager:	Neil Rossmeissl	Sub-contractors:	MBI International,
PMC Project Officer:	Gene Petersen		Lansing, Michigan

Goals and Objectives: This project is focused on increasing the number of marketable product options of sugar mill industries through a biorefinery alternative that converts biomass (i.e. bagasse, CLM and molasses) to refined biofuels and biochemicals. Our efforts in this project have been directed towards addressing some of the major components of the sugar based biorefinery including:

1) Developing an appropriate and scaleable fermentation process for the production of ethanol from biomass such as bagasse and CLM. Molasses will be added as a fermentation supplement to boost ethanol yields.
2) Investigate potential products other than ethanol (i.e. lignin-derivatives, cellobio-oligosaccharides, succinic acid, glycerol, aconitic acid, fiber mats) that may result in higher income for mill operators and develop appropriate and scaleable processes for production of these proposed value added products.
3) Demonstrate the effects of the biorefinery concept on the economics of the sugar mill industry by creating a model for a Louisiana sugar based biorefinery producing both sugar and ethanol from sugar cane.

Objectives under Preliminary Investigation Stage

1) Evaluate lignin-based by products from stillage.
2) Evaluate other potential by products from stillage.
3) Determine the effect of synchrotron radiation on the cellulase production from selected microorganisms for the improvement of the simultaneous saccharification and fermentation (SSF) process.

Objectives under Detailed Investigation Stage

1) Develop appropriate and scaleable fermentation process for the production of ethanol from bagasse, CLM, and molasses.
2) Evaluate the effects of a model biorefinery on the economics of a sugar mill.

Project Description:

1) MBI further investigated AFEX treated bagasse and CLM for the production of ethanol. Fed batch SSF on pretreated biomass and ethanol yields will be evaluated at a 10 L capacity. The results were to be compared to data gathered in the previous year from similar experiments using a 3 L fermentor. The composition of the resulting stillage was also to be studied for the evaluation of potential byproducts.
2) The impact of biorefinery on the economics of a sugar mill was to be evaluated by developing models of an existing sugar mill (Raceland Raw Sugar Corp., LA) and its product streams to be used as the feedstock for an ethanol fermentation model. The two were to form an integrated model of a biorefinery that can produce alcohol and sugar. Projections of sugar market pricing and quotas were to be incorporated to this model.
3) In an effort to select the most advantageous process for ethanol production, Audubon continued with a task from the previous year to evaluate SSF on pretreated bagasse at a 20 L capacity. The target was to maximize solid loadings of pretreated biomass. The supplemental feed of molasses to the biomass was to be assessed for improved ethanol yields and the stillage was to be analyzed for lignin degradation products, cellobiose, etc. These fermentations were to be conducted to provide sufficient stillage for further investigations on the separation of stillage components. Fractionation into a solid and a liquid stream was to be followed by an attempt to distill the monophenols and separate the cellobiose from the stillage and produce a trisaccharide using the hydrolyzed bagasse and sucrose. It was also planned to demonstrate the production of methane from stillage using anaerobic digestion.
4) Audubon was to explore the potential of mutating *Pichia stipitis* for the simultaneous fermentation of xylose and glucose.

Summary of Work to Date - Accomplishments (FY05-current):

1) The primary focus at the inception of this grant was to identify existing pilot equipment that could be used to carry out pilot scale biorefinery investigations. These equipments were identified and their functionalities assessed. Most had to be refurbished to operating conditions for the processing of sugarcane biomass. One of the tasks was conducted in tandem with another task undertaken in GO-14236, whereby AFEX treated pith and CLM received from MBI were further pretreated at Audubon with water and sodium hydroxide using a 1-5 L Parr reactor. Aqueous extractions were found to contain primarily lignin and smaller quantities of hemicellulose. Experimental results indicated that an alkali pretreatment favored the saccharification of AFEX-treated pith and CLM. MBI was not very successful in providing Audubon with enough AFEX-treated biomass in the pilot plant implementation at 20 L. Therefore, to continue with our task a dilute alkali pretreatment process on bagasse was developed taking into consideration the difficulty of degradation of this material. The dilute alkali process must undergo a wash step to remove saccharification and fermentation inhibitors that may be formed during pretreatment.
2) Characterization of the lignin stream was performed. The results were presented in a comprehensive report as a deliverable showing the identification of various compounds from streams obtained through varying treatments. The conclusions reported were as follows:
    i) A two step treatment (caustic, oxidant or organosolv followed by a caustic wash) of sugarcane biomass was required for the release of at least 50% of the lignin.
    ii) A 50% lignin removal correlated with at least 80% cellulose conversion.
    iii) Approximately 30% to 50% of the lignin was removed as phenolic compounds.
    iv) Vanillin, 2-methoxy-4 vinyl phenol (4-vinylguaiacol), benzofuran 2, 3 dehydro (coumarans), and benzaldehyde-4-hydroxy (syringaldehyde) were the most abundant compounds extracted from sugarcane biomass.
3) MBI completed their work that involved proprietary information to investigate the production of succinic acid and its derivatives from sugars derived from sugarcane biomass and other waste streams such as molasses and stillage by studying fermentations with *Actinomyces succinogenes* and by developing second generation organisms. Results and conclusions were reported in detail as part of their deliverable.

Schedule

Project Initiation Date: July 01, 2005
Planned Completion Date: December 31, 2007

Improved Biorefinery for the Production of Ethanol, Chemicals, Animal Feed and Biomaterials from Sugar Cane.

Donal F. Day, Louisiana State University Agricultural Center, Audubon Sugar Institute

Principal Investigator:	Dr. Donal Day	Funding Partners:	MBI International
HQ Technology Manager:	Neil Rossmeissl	Sub-contractors:	MBI International, Lansing, Michigan
PMC Project Officer:	Gene Petersen		

Goals and Objectives: The objective of this project was to evaluate scalable and integrated technologies for the production of fermentable sugars and ethanol. A sugar-based biorefinery will use bagasse, molasses, CLM and sucrose for the production of ethanol, chemicals, biomaterials and animal feed. The overall objectives were as follows:

1) Develop a fully integrated process using bagasse, CLM and molasses from sugar mills in Louisiana for the production of fuels, chemicals, and other value-added products.
2) Demonstrate the feasibility of such a biorefinery and generate design and economic data for an integrated plant.

Project Description:

1) A preliminary study on the gasification of sugarcane bagasse was to be done to produce syngas. A small scale gasifier was to be constructed for experimental measurements to validate simulations on Aspen® and Femlab. From the simulations, Audubon was to develop a predictive model to design and optimize scaled up gasifier systems.
2) A 5 L pressure reactor purchased from Parr Instrument Company was to replace the 1 L reactor used for post AFEX-treated biomass extractions. This scaled up version was to be installed to (i) verify the optimal AFEX parameters for treatment of bagasse and CLM; and also (ii) identify the AFEX parameters for mixed biomass or whole plant.
3) With the scaled up AFEX reactor, MBI was to produce kilogram quantities of AFEX treated material for both Audubon and MBI to perform other tasks in GO-14236 and GO-85007.
4) Audubon was to continue studying the viability to produce ethanol using combined pretreatments and hydrolysis processes. Efforts were focused on validating the integration of dilute alkali-treated bagasse with SSF to convert cellulose to ethanol with a minimum target performance to be met. This was to be performed at a pilot scale of approximately 100 pounds of bagasse. Mixtures of bagasse with molasses as feedstock were to be explored for improved product yield.

Summary of Work to Date - Accomplishments (FY05-current):

1) Preliminary studies began as an evaluation of the based-catalyzed thermochemical conversion of sugarcane biomass yielding results that led to a decision point of investigating uncatalyzed conversions instead. It was concluded that the composition of pyrolysis liquids was highly aromatic; consequently, it was susceptible to naphtha reforming leading to gasoline fractions as fuel. The composition of the gas phase was mainly carbon dioxide. Thus a rich syngas for chemical synthesis would be the next step for gasification. The results indicated that both pyrolysis and gasification must make use of water-mediated reactions to achieve a competitive advantage over drier substrates. Simple hot water and near supercritical water may offer sufficient chemical reaction power to produce both syngas and pyrolysis liquids with specific characteristics without toxic chemicals. Efforts on pyrolysis liquids were scaled back to increase our focus on gasification using hot and near supercritical water to produce syngas.
2) Use of a 1-gal Parr AFEX reactor continued from YEAR 1 through the end of YEAR 2 to produce limited quantities of AFEX-treated materials. The process parameters were optimized and experimental data obtained to correlate AFEX performance with the production of glucose and xylose during enzyme hydrolysis. The fermentation of AFEX treated bagasse using SHF was conducted achieving complete utilization of the glucose and xylose to yield ethanol. The combination of AFEX pretreatment with SSF also demonstrated the ability to produce ethanol from bagasse.
3) AFEX treated pith and CLM received from MBI were further pretreated at Audubon with water and alkali. Aqueous extractions were found to contain primarily lignin and smaller quantities of hemicellulose. Experimental results indicated that an alkali pretreatment favored the saccharification

of AFEX-treated pith and CLM. In the pilot plant implementation, it is recommended that pretreatment of biomass be followed by a step to remove saccharification and fermentation inhibitors that may be formed during pretreatment.

4) The task to evaluate the physical properties of sugarcane fibers, delignification of sugarcane fibers and development of marketable products from sugarcane fibers was completed at the end of YEAR 2 to produce a simple mechanism to make fiber mats of 4 feet in width which are awaiting performance testing for use as erosion control. The goal was to develop a continuous manufacturing process for sugarcane bagasse mats that can be implemented in the local sugar mills to provide an economical benefit to both the sugarcane and the road construction industries.

Schedule

Project Initiation Date: July 01, 2004
Planned Completion Date: December 31, 2007

Integrated Corn-Based Bio-Refinery (ICBR)

Mike Sanford, DuPont

Principal Investigator:	Mike Sanford	Funding Partners:	N/A
HQ Technology Manager:	Neil Rossmeissl	Sub-contractors:	NREL, Diversa, Michigan State University
PMC Project Officer:	Gene Petersen		

Goals and Objectives: Since 2003, DuPont has been leading a team under a DOE cost-shared cooperative agreement (#1435-04-030CA-70224) to develop and demonstrate an economically viable, scalable Integrated Corn Biorefinery (ICBR) to convert corn grain and stover to fuel ethanol and value-added chemicals.

Key goals for the project are to develop base technology for pretreatment, enzymatic saccharification and fermentation to produce ethanol economically from corn derived cellulosic biomass. Additionally, we seek to apply process modeling to define an economically favorable integrated process. Key unit operations of the process will be demonstrated on the semi-works scale in a final demonstration campaign, and the data utilized to provide a complete technology package suitable for piloting the complete process. Furthermore, we will utilize life cycle assessment to fully understand the impacts of the proposed process.

Project Description: To complete this project, DuPont assembled and leads a team including Diversa, the National Renewable Energy Laboratory, Michigan State University and Deere & Co. Under DuPont's leadership and direction, each participant has brought specific capabilities and expertise in the areas of enzymology and protein engineering, metabolic engineering, chemical process technology, and agricultural practices to provide a holistic approach to developing an economically viable and sustainable solution.

There are four main components, or Tasks, to the DuPont ICBR program: Process Design Economics and Testing; Pretreatment and Saccharification Development; Ethanologen Development; and PDO Production. Substantial progress has been made in each area to advance the state of technology towards commercial readiness. These tasks are summarized below.

Task 1 Process Design, Economics and Testing: The ultimate objective of Task 1 is to produce a technology package which can be used as the design basis for an ICBR pilot plant, as well as to develop economic and life cycle analysis models to compare various process options vs conventional dry-grind ethanol and the benchmark NREL acid hydrolysis process.

Task 2. Saccharification: The purpose of Task 2 is to develop a commercially scalable process to convert the cellulose and hemicellulose in the preferred stover feedstock into fermentable sugars – primarily glucose and xylose.

Task 3. Ethanologen Development The objective of Task 3 is to develop an ethanologen strain and fermentation process capable of high conversion of both glucose and xylose monomers in the presence of process hydrolysate to produce ethanol at economically viable rates and titers.

Task 4. PDO Production The purpose of Task 4 was to demonstrate the capability to utilize the glucose stream from a dry grind or mill wet mill to produce value adding chemicals and assess the economic viability. This task was completed in 2004 **.**

Summary of Work to Date - Accomplishments (FY05-current):

Task 1 Process Design, Economics and Testing:
To address the inherent issues with respect to capital intensity associated with the prior art "standard" cellulosic ethanol process which involves acid pretreatment, DuPont proposed a process involving mild

alkaline (ammonium hydroxide) pretreatment of the corn stover feedstock, followed by enzymatic saccharification, fermentation then product isolation and purification. Recycle of ammonia and water streams as well as integration of heat flow within the biorefinery are critical elements of the process to optimize the energy balance and minimize cost.

Utilizing NREL's stover to EtOH Aspen and techno-economic model as the basis, the team developed an Integrated Aspen Model and a Life Cycle Analysis (LCA) model for a grain plus stover manufacturing facility. This model is used to test various process options and trade-offs, and to compare our proposed process, incorporating experimental results, with NREL's acid process and the rest of the industry. We continually update the model as the process design evolves and as new process data is generated.

Utilizing the Aspen and LCA model, we developed Key Metrics and Goals necessary for an economically and environmentally favorable ICBR. These are utilized to guide research effort and gauge progress. (i.e. yields, titers, rates, and process energy used). The key factor for an economically favorable process include overall high yields and high % solids in pretreatment, as well as high titers in fermentation, which requires high solids in saccharification and the elimination of process separation steps (such as over-liming) which add capital and process time.

Based on our process modeling, as well as laboratory experimentation, the team has defined equipment functional specifications and or process requirements for scale-up. Task 1 will culminate with a semi-works scale Milestone Demonstration run, MD07, which is intended to demonstrate the scalability of the various process elements and serves as the basis for scale-up to a future pilot facility. Final constructrion of the pilot facility is in progress and commissioning and startup are expected this month.

Task 2. Saccharification:
The purpose of Task 2 is to develop a commercially scalable process to convert the cellulose and hemicellulose in the preferred stover feedstock into fermentable sugars – primarily glucose and xylose.

Pretreatment Process: At the start of the program, acid pretreatment was the most developed process for converting lignocellulose to EtOH. In an effort to improve the economic viability of the process, the ICBR team explored milder pretreatments and discovered that low levels of ammonia in pretreatment, along with the appropriate enzymes, works as well as the more severe pretreatments without the concurrent generation of high levels of inhibitors. This effort led to the development of a high solids, low residence time, mild pretreatment process that gives high yields with reasonable capital equipment cost. DuPont has filed patent applications on this novel process.

Saccharification Process: DuPont and NREL developed a roller-bottle system with attrition media as a development tool to evaluate pretreatment conditions and various enzyme efficacies at high solids process conditions. Based on the need to process high solids (up to 30%), and the recognition from roller bottle data at NREL that particle size reduction enhances saccharification yields, we developed a scaleable fed-batch saccharification process using a low cost reactor system (tank + agitator) with in-line grinder. This system has been tested and demonstrated on the lab scale using pretreated solids.

Enzyme Development: Enzyme development for saccharification has focused on enzymes developed and provided by Diversa. The program has met the early milestones in the ICBR project including discovery of 95 novel endoglucanases, 28 novel cellobiohydrolases and 89 novel beta-glucosidases for cellulose. Diversa has also developed an enzyme cocktail, which met early milestone goals for glucose and xylose monomer release. However we have fallen short of later milestone monomer sugar conversion goals using reduced enzyme loadings and DuPont pretreated corn stover. The hemi-cellulase has been shown in the lab to approach target goals for consumption of xylan, but does not fully convert the soluble sugars to xylose. Diversa has however discovered potentially useful oligomerases, which cleave solubilized oligomers to monomer glucose and xylose – this offers potential for achieving the milestone target for xylan conversion.

To begin to address the gap between current enzyme performance and the milestone objectives, DuPont has implemented an internally funded enzyme evaluation program to assess enzymes and cocktails from several sources. This will allow us to evaluate and possibly develop a range of cocktails/specific enzymes, saccharification conditions, which will drive us towards ICBR commercial goals.

Task 3. Ethanologen Development

To optimize fermentation performance, DuPont and NREL focused on developing an ethanologen strain which performs well with the sugar streams produced from the pretreatment and saccharification processes developed in Task 2. The initial strain was Zymomonas mobilis ZW1. The first step in the program was to develop an improved genetic toolbox for more efficient genetic engineering and scouting for new genes. In this effort, the DuPont team developed a combination of new tools and methodologies, which decreased the new strain construction cycle time from months to weeks.

Using these tools, the team has made significant advances in both the strain and the fermentation process conditions which allow us to improve both the utilization of xylose in clean sugars and the tolerance of the strain to the challenging environment of process hydrolysate.

By combining these improvements, we have achieved commercial targets for rate and titer on clean sugars, milestone rate, titer, and yield on clean sugars plus acetate, and are very near 2007 milestone targets on hydrolysate.

Schedule

Project Initiation Date:	April 01, 2003
Planned Completion Date:	December 31, 2007

Separation of Corn Fiber and Conversion to Fuels and Chemicals Phase II: Pilot-Scale Operation

Nathan Fields, National Corn Growers Association

Principal Investigator:	Nathan Fields	Funding Partners:	Archer Daniels Midland
HQ Technology Manager:	Neil Rossmeissl	Sub-contractors:	NREL, PNNL
PMC Project Officer:	Gene Petersen		

Goals and Objectives: The multidisciplinary project team from the National Corn Growers Association (NCGA), Archer Daniels Midland (ADM), and Pacific Northwest National Laboratory (PNNL) intend to economically derive high-value chemicals and oils from lower value corn fiber. In the process, starch is recovered as glucose, which is then converted to ethanol. The hemicellulose fraction is hydrolyzed to yield the 5-carbon sugars, arabinose and xylose. The xylose is converted to ethanol, and the arabinose is catalytically converted to ethylene glycol, propylene glycol, and glycerol. In addition, high-value oil components, sterols and stanols, are recovered. The residual fiber (~50% by weight of the original corn fiber) contains primarily cellulose and protein. The protein concentration of the residual fiber is approximately double that of the starting material and, therefore, has an increased value (i.e., corn fiber value is roughly proportional to protein content).

The subject of this project is pilot-scale testing to validate the process prior to full-scale commercial implementation. The pilot-scale testing phase will entail bench-scale process optimization testing, system design, system procurement and fabrication, system construction, shakedown testing, actual testing, and an economic evaluation of the integrated process. Piloting of the process is necessary so that the technical (i.e., processing and operation of key equipment) and economic aspects of the process can be more thoroughly evaluated prior to commercialization of the process.

Project Description: The focus of the Phase I work was to develop an economical, integrated process for the recovery of the key components of corn fiber. This has involved an extensive analytical characterization of corn fiber and of the components recovered from corn fiber, as well as an evaluation of recovery processes. When Phase I was initiated, target goals were established for recovery of the key components from corn fiber. All of the target goals have essentially been satisfied, resulting in the development of a process flowsheet.

Most process schemes proposed for corn fiber are focused on the complete conversion of the cellulose and hemicellulose to fermentable sugars (or to sugars of sufficient purity to be converted catalytically), and ignore the minor components present in the fiber stream (e.g., recoverable oils). The approach being taken under this project is to recover valuable carbohydrate components as well as other valuable components such as oil. The recovered carbohydrate fractions are converted to ethanol and polyols. The recovery of the high-value oil components for use as nutraceuticals (e.g., sterols and stanols) is key to making the process economical. The cellulose portion is not being targeted for hydrolysis, rather it is being utilized as a carrier for the protein-enriched corn fiber residue. The end result of the process is utilization of ~50% of the original corn fiber as a new source for value-added products, and the production of a higher-value animal feed supplement.

Piloting of the process is necessary so that the process economics can be more thoroughly developed, and also so that the operation of key equipment and the overall process can be evaluated more realistically. Pilot operations were split onto all of the research sites during the second half of phase II. PNNL focused on hydrolysis testing, NREL with initial fiber processing, and ADM testing processed fiber, optimizing conditions, oil extraction, and fermentative systems.

Summary of Work to Date - Accomplishments (FY05-current):

1) University of Illinois Projects: Meetings occurred between ADM and the University of Illinois staff subcontractors regarding the DOE project. The following projects were completed to complement the goals of the original work plan in lieu of building and utilizing a pilot facility. The pilot facilities at NREL and ADM were utilized instead.

Dr. Zhang –.Experiments in continuous reactor hydrolisis were completed. Continued experiments in their Parr reactor have also been completed. Continuous reactor design of experiments on corn fiber hydrolysis was completed.

Dr. Blaschek – Concentrated corn fiber hydrolysate screened for fermentability of the hydrolysate with several organisms, including Clostridium beijerinckii BA101. Optimization of corn fiber hydrolysate fermentation with Clostridium organisms to produce acetone-butanol –ethanol (ABE) complete, with final report.

Dr. Fahey –Completely analyzed corn fiber samples from each stage of the process. Completed corn fiber 2-stage digestion and 3-stage fermentation *in situ* digestion trials. Pet food evaluation of four separate corn fiber samples, including as-is and residues have scaled up to a feed trial to evaluate digestibility. Pet food has been produced and trials are completed. A report is expected in the near future. The project is nearly complete. Pet food evaluation of four separate corn fiber samples have concluded and the final report has been received.

Dr. Mackie – Enzyme hydrolysis of the corn fiber, with twenty rumen enzymes cloned and produced. Goal is to produce a blend of enzymes that can be commercially produced for use on corn hemicellulose, project complete with final report pending.

2) NREL Corn Fiber Hydrolysis Experimentation: NREL has been contracted by ADM to conduct continuous hydrolysis experiments on corn fiber in their Pilot Development Unit (PDU). The work plan includes conducting small scale experiments based on a 2 factor central composite experimental design. The factors are time and temperature. After the small scale experiments were completed, a large scale experimental design was executed. The fiber used in the experiments was supplied by the ADM corn wet mill in Columbus, NE.

A pilot scale trial of corn fiber hydrolysis occurred on Feb. 16th at the NREL PDU. During the testing three conditions were evaluated. The corn fiber was used as a feedstock for the continuous reactor. 300 grams (dry weight basis) of each condition was returned to ADM and the remaining material from the three conditions was dewatered and washed in the Pneumapress to form a corn fiber cake, which was shipped back to ADM for oil extraction experimentation.

NREL analyzed the corn fiber hydrolyzed solids and solubilized hydrolysates from the three conditions in the PDU. The pretreatment conditions were designed to overlap what had previously been attempted a small scale Zipperclave reactor experiment. The amount of solubilized sugars in the hydrolysate nearly equal the amount of corn fiber solubilized, which gives a good mass balance.

4000 pounds of corn fiber were processed through the NREL continuous pilot development unit on July 27th and 28th, 2006. The corn fiber extract and washed fiber were shipped back to Decatur, IL for further processing.

Corn fiber hydrolysis test data reported by NREL for 16 small-scale and 3 pilot-scale corn fiber hydrolysis tests were evaluated by PNNL to develop empirical predictive correlations for the yields of glucose, xylose, arabinose, furfural, and solids solubilized. The effects of hydrolysis time and temperature, in the small-scale tests, on the total glucose and xylose yields could be predicted with a good degree of confidence, and for total arabinose, monomeric xylose and soluble solids yields with a fair degree of confidence. In general, the pilot scale total glucose, total xylose, monomeric xylose, and soluble solids yields were comparable to those predicted for the small scale tests. Pilot scale total and monomeric arabinose yields were significantly lower than those predicted from the small scale tests, while the furfural yields were significantly higher.

Twenty thousand pounds of corn fiber were hydrolyzed at NREL. The corn fiber hydrolysate and wash from the centrifuge were concentrated in their evaporated and two drums of concentrated hydrolysate were shipped to ADM. The hydrolysate was tested with secondary acid hydrolysis as well as enzyme hydrolysis using experimental enzymes.

The final report has been received from NREL for the work completed at that location.

3) Corn Fiber Fermentation-Screening of Ethanologens: Several strains of organisms were adapted on the new hydrolysates from the NREL runs in February and July, 2006. Shake flask fermentations were also run to validate the fermentability of the new hydrolysates. Batch fermentations were carried out utilizing the NREL and ADM-produced hydrolysates

4) Corn Fiber Hydrolysate Processing: The concentrated liquid fraction of the hydrolyzed corn fiber processed at NREL in February was utilized in fermentation experiments. The new hydrolysate from the NREL July run was also used in these experiments

   The liquid fraction of the hydrolyzed corn fiber processed at NREL was concentrated in preparation for use as an ethanol fermentation media. The concentrated corn fiber hydrolysate was treated with sulfuric acid to hydrolyze the oligosaccharides to monosaccharides.

   The corn fiber hydrolysate was processed by secondary acid hydrolysis and concentrated by evaporation. The corn fiber hydrolysate concentrate was fermented by microorganism strains in two fermentation media blends. The spent fermentation media was centrifuged and the solids were removed. The liquid portion was evaporated in a forced circulation, long-tube vertical evaporator.

   Samples of this distilled, spent corn fiber hydrolysate concentrate fermentation media were sent to PNNL for catalysis testing for converting the remaining sugars to polyols.

5) Hydrolyzed Corn Fiber Extraction and Analysis: An additional pilot-scale, counter-current extraction was conducted at ADM on the pretreated corn fiber from the NREL pilot-scale hydrolysis. Over 50 kg of corn fiber were extracted.

   Oil extraction and recovery testing was completed at PNNL The oil extraction and testing results have been compiled and will be incorporated into the final report for the project.

   Oil and sterol/stanol yields from nine filtered hydrolyzed fiber samples received by PNNL from small-scale hydrolysis testing conducted at NREL were completed. These samples were dried and twice extracted with solvent, followed by a final extraction with hexane and the oil and sterol/stanol yields were determined.

   The analytical data were used to prepare empirical models to investigate the separate effects of hydrolysis time and temperature on oil and total sterol/stanol yields for the NREL test. These models, which showed very good correlation with the data, indicated that the oil and sterol yields, with respect to the dry corn fiber weight prior to hydrolysis, increased in a regular manner, with respect to both hydrolysis time and temperature (for a given reactor system).

   A direct saponification procedure carried out with fiber samples hydrolyzed under moderately severe conditions, showed that a significant amount of oil remains in the fiber following the solvent and hexane extractions.

   A second set of hydrolyzed fiber samples from seven small-scale and three pilot-scale hydrolysis tests were received by PNNL from NREL underwent drying and extractions. The extractant was then evaporated and the remaining extracted oil (and residue) was saponified and analyzed. Gas

Chromatograph (GC) analyses of all of the samples have been completed to determine the yields of oil and selected sterols. The effects corn fiber hydrolysis time and temperature on oil and sterol yields for this set of samples were generally similar to those observed for previous samples analyzed. A separate set of extraction tests were conducted, using corn fiber from one of the pilot plant tests, to examine the effect of the extraction temperature on the oil and sterol yields. It was found that there was an effect of the extraction temperature.

Four oil extraction samples were received from ADM for subsequent saponification and sterol analysis using a gas chromatograph (GC). The results of the analyses of the ADM samples are shown in the Table 1. As can be seen the sterols content for these samples ranged from 5.81% to 18.82% (saponified oil basis).

Experiments were also conducted using hydrolyzed corn fiber samples from a pilot plant test to examine the effect of combining two key steps involved in the extraction process into one step. The experiments showed that under certain conditions the one-step process resulted in the recovery of significantly more oil and total sterols as compared to the two step process.

Table 1. Composition of ADM Oil Extraction Samples.

Sample Label	ADM-1-	ADM-2-	ADM-3-	ADM-4-
Sample weight, g	**0.710**	**0.699**	**0.699**	**0.720**
Saponified Oil weight, g	**0.501**	**0.105**	**0.202**	**0.520**
Campesterol Concentration, Wt % of Saponified Oil	1.75	1.41	0.67	1.57
Campestanol Concentration, Wt % of Saponified Oil	2.02	1.07	0.60	2.02
Stigmasterol Concentration, Wt % of Saponified Oil	0.73	1.18	0.39	0.84
Sitosterol Concentration, Wt % of Saponified Oil	5.93	5.70	2.18	7.15
Sitostanol (Stigmastanol) Concentration, Wt % of Saponified Oil	6.21	3.93	1.97	7.23
Total Sterol Concentration, Wt % of Saponified Oil	**16.63**	**13.30**	**5.81**	**18.82**

Experiments efforts continued using hydrolyzed corn fiber samples from a pilot plant test to examine the effect of combining two key steps involved in the extraction process into one step. These tests confirmed what had been reported prior, that the one-step process resulted in the recovery of significantly more oil and total sterols as compared to the two step process. Tests have focused on optimizing the one-step process, in particular reagent concentrations have been evaluated. The results suggest that reagent concentrations can be reduced while maintaining the same recovered oil yields.

The results suggest that the one-step process is effective in recovering up to ~25% more oil and 37% more total sterols (dry hydrolyzed fiber basis) as compared to the two-step process.

6) Pretreatment/Catalyst Testing: Conversion of sugar components (e.g., from fermentation broth) to value-added products is accomplished by a two-step catalytic processing, involving 1) conversion to the sugars to sugar-alcohols (hydrogenation), followed by 2) conversion of the sugar alcohols to the final products (hydrogenolysis) – propylene glycol (PG), ethylene glycol (EG) and glycerol.

The results from testing demonstrated that ultrafiltration is required as a pretreatment step to allow for catalytic conversion to products.

Additional micro-scale combinatorial testing generated good hydrogenation and subsequent hydrogenolysis of fermentation derived feedstock. Material was ultrafiltered and demonstrated good performance approaching the model compound results.

With fermentation derived feed, ultrafiltration treated feed results in 41% conversion and 9% selectivity of C5 and 17% conversion and 97% apparent selectivity of C6. The addition of a heat treatment followed by carbon adsorbent column prior to hydrogenation results in 53% conversion and 42% selectivity of C5 and 25% conversion and 93% selectivity of C6 under similar conditions.

The results indicated that for fermentation broth, both catalysis steps were enabled by the following pretreatments: ultrafiltration followed by a carbon adsorbent treatment. While enabling catalysis, pretreatment also resulted in removal of desirable substrates (e.g., sugars) along with the inhibiting compounds. For acid hydrolysate, both catalysis steps were enabled by ultrafiltration and carbon adsorbent treatment. Again, this pretreatment resulted in removal of desirable substrate.

Table 2 shows some representative results from the hydrogenolysis batch testing (2nd catalysis step) for the fermentation broth and acid hydrolysate as compared to xylitol and sorbitol model compound work. All batch reactor tests shown were performed at the 100ml size except for fermentation broth which was at 10ml.

Table 2. Summary of Hydrogenolysis Results.

Conv / Carbon Molar Select.	C5 (xylitol)			C6 (sorbitol)			Actual	
	Theoretical	Best Flow	Best Batch	Theoretical	Best Flow	Best Batch	Best Batch	Best Batch
		Model Cpd	Model Cpd		Model Cpd	Model Cpd	Acid Hydrol	Ferm. Broth
C5 Conv	100	99	---	0	0	0	84.4	72.2
C6 Conv	0	0	0	100	100	93.2	94.8	80.9
EG	40	27.8	35.3	0	15.7	17.5	21.3	11.9
PG	60	39.8	30.4	100	46.8	32.2	26.7	9.1
Glycerol	0	7.7	13.7	0	8.1	8.1	20.9	0
Lactate	0	5.2	8.9	0	4.1	2.9	6.0	7.2
Total	100	80.5	88.3	100	74.7	60.7	74.9	28.2

Schedule

Project Initiation Date: April 30, 2003
Planned Completion Date: June 30, 2007

New Sustainable Chemistry for Adhesives, Elastomers and Foams

Scott Boyce, Rohm and Haas Company

Principal Investigator:	Thomas Kauffman	Funding Partners:	N/A
HQ Technology Manager:	Valerie Sarisky-Reed	Sub-contractors:	Virginia Tech, Eastman Chemical Company, USDA Eastern Regional Research Center
PMC Project Officer:	Fred Gerdeman		

Goals and Objectives: Our project focused on the goal of providing commercially-viable adhesives for flexible packaging (primary) and structural (secondary) applications that exhibit equivalent performance to that of polyurethanes yet with the advantages of:

- faster cure thereby reducing the working capital and increasing production agility;
- elimination of the handling of isocyanates in adhesive production;
- elimination of the handling of isocyanates in production facilities using adhesives;
- elimination of aromatic amine formation in food packaging;
- increased price stability due to lessened dependence on petrochemical feedstock;
- reduced greenhouse gas emissions.

A secondary goal was to extend the research to determine the technical feasibility of developing bio-based, non-isocyanate-based foams and elastomers with many of the same expected benefits as for adhesives.

Project Description: Polyurethane adhesives utilize methylene diisocyanate (MDI) with various petrochemical-derived polyols (polyesters and polyethers). MDI is a known chemical sensitizer. Solventless polyurethane adhesives are typically two-part systems in which one part (A) contains an isocyanate-based pre-polymer derived from MDI and the second part (B) is a hydroxyl-containing pre-polymer or polyol. Polyurethane foams and elastomers are closely related technologically to polyurethane adhesives and, not surprisingly, share common raw materials.

This project utilized Carbon Michael chemistry, a non-isocyanate technology, in which the reactants, which are bio-based, form polyester compositions which rival polyurethanes in performance. The work initially involved synthesis of bio-based reactants, such as acetoacetates and acrylates of a mono- or disaccharides and other bio-based materials such as castor oil, glycerol, and crop oil derivatives. These reactants were then formulated at levels from 20-60% to produce non-isocyanate bio-based adhesives, foams, and elastomers. Proprietary, low toxicity catalysts were used to promote the reaction. Desirable bio-based reactants were then scaled-up to pilot plant scale. The hazards associated with acetoacetates and the acrylates chosen for the work were demonstrated to be lower than those for MDI based reactants.

Summary of Work to Date - Accomplishments (FY05-current):
Accomplishments

1) Synthesis and characterization of over 50 bio-based raw materials were conducted in Rohm and Haas' Spring House, PA laboratories to determine the most suitable candidates for the various applications.
2) Advice on the future supply and cost projections of various biorefinery outputs was received from Dr. Thomas A. Foglia of the USDA Eastern Regional Research Center in Wyndmoor, PA to guide the bio-based raw material selection process.
3) Extensive toxicology testing was carried out at contract laboratory facilities on a preferred raw material, glycerol tris acetoacetate, to ensure a low toxicity profile and to allow formal submission to the EPA for TSCA listing. These data may also be useful for future TSCA submissions on related biobased acetoacetates.

4) Rohm and Haas applied to the US EPA for the TSCA listing of glycerol tris acetoacetate. The EPA has issued a Consent Order to allow limited commercial use of the material, pending the completion of additional toxicity testing, based on the relatively low hazard level of the material.
5) Formulation optimization and extensive end-use testing have resulted in several adhesive prototypes for the flexible packaging market, These rival the performance of 2-part polyurethanes. One key performance attribute, however, was still deficient and was not satisfactorily resolved by the completion of funding. Similar work on structural adhesives also resulted in interesting prototypes with performance rivaling that of polyurethanes. However, the prototypes could not match the performance of epoxies.
6) Raw material specifications were established for glycerol tris acetoacetate and communicated to two potential suppliers. Scale-up of glycerol tris acetoacetate and other preferred raw materials has taken place to allow sufficient materials for customer trials and in-house high-line-speed optimization trials.
7) High-line-speed trials of optimized formulations for flexible laminating were conducted at Rohm and Haas' Ringwood, IL facility using several bio-based non-isocyanate prototypes for lead customer qualification. Excellent coating quality, clean processing and acceptable cure rate were observed on key substrate combinations during these runs.
8) Commercialization of bio-based flexible packaging adhesives has been delayed due to a shortcoming in one key performance test. Work is ongoing beyond the scope of the DOE funded work to resolve these issues and to reintroduce an improved version of the product when appropriate.
9) Commercialization of bio-based structural adhesives has been abandoned for the present time, despite solid technical results, due to an unattractive value proposition.
10) Technical feasibility of technology for foams and elastomers was established. The former work was done at Rohm and Haas' Spring House, PA research facility while the latter was carried out at Virginia Tech in Blacksburg, VA under the direction of Dr. Timothy E. Long.
11) Two US patent applications were filed and a total of 15 concept documents (indicating patentable inventions) were created and communicated to the DOE over the course of the 2 year project.

Schedule

Project Initiation Date: October 1, 2004
Planned Completion Date: December 30, 2006

Oil Mills Improvement

National Agricultural-Based Industrial Lubricants Center Project

Wes James, University of Northern Iowa's National Ag-Based Lubricants Center (NABL)

Principal Investigator:	Dr. Lou A.T. Honary	Funding Partners:	Iowa Department of Economic Development
HQ Technology Manager:	Valerie Sarisky-Reed	Sub-contractors:	N/A
PMC Project Officer:	Fred Gerdeman		

Goals and Objectives: This project's overall objective is to firmly establish the National Agriculture-Based Lubricants (NABL) Center. NABL will be the premier source of fundamental biolubricants research, credible, independent biolubricants and biofuels testing, biodegradability and toxicity research, and general support for stakeholders in the bioproducts industry.

As the use of bio-products increases, scientific and technical support is required to ensure that new discovery continues, that improvement of existing products continues (to achieve performance gains and price parity), and that environmental impact is examined. Expert support is needed to demonstrate that renewable lubricants - manufactured using crop-based oils - meet performance specifications, quality, certification and labeling requirements, and applicable regulatory measures. In addition, education and outreach are needed to encourage the widespread adoption and use of biobased products.

Benefiting from more than a decade of bio-lubricant research and development, the National Ag-Based Industrial Lubricant (NABL) Center is uniquely positioned to play a key role in the development of the nation's bio-lubricant industry. Having established a basic foundation for the NABL Center through the expansion of biobased research and test capabilities, this investment will better establish the NABL Center as a point-source of knowledge, support, and testing services. The end result of this project will be a reduction in the nation's reliance on petroleum imports, with a corresponding decrease in the impact of petroleum lubricants on our nation's environment.

Project Description: Continued improvements in the Center's scientific and laboratory capabilities will provide the year's largest project activity. Additional scientific equipment will be chosen for acquisition, based on research by NABL technical staff members and feedback from stakeholders. This equipment will be purchased and preparations completed for equipment operation – including staff training and any appropriate laboratory modifications necessary for equipment installation. Existing test stands will be modified as required to meet ASTM standards, and new biolubricants test stands may be constructed by NABL staff.

New and continued biolubricants research will account for 25% of the Center's efforts. Anticipated projects include laboratory study of the oxidation stability (shelf life) of vegetable-based components of biofuels, laboratory study of the cold temperature behaviors of vegetable-based oils, and laboratory investigation of potential vegetable-based engine oil additives to improve performance and reduce engine emissions. Research activities will be conducted at bench-scale, inside NABL laboratory facilities.

Additional efforts planned for this project year include: completing existing research on fuel savings of railroad track lubricants, outreach activities supporting technical certification standards and continued growth in the acceptance of biobased lubricants, efforts toward larger NABL participation in certified standardized testing requirements.

Summary of Work to Date - Accomplishments (FY05-current): This project's overall objective is to firmly establish the National Agriculture-Based Lubricants (NABL) Center. NABL will be the premier source of fundamental biolubricants research, credible, independent biolubricants and biofuels testing, biodegradability and toxicity research, and general support for stakeholders in the bioproducts industry.

In years one through three, this project has leveraged the existing knowledge base and test equipment of the University's ABIL Research Program by facilitating the program's transition into NABL - a *National* Agriculture Based Lubricants Center. Significant program milestones have been accomplished, including several fundamental biolubricants research studies, as well as the acquisition of biolubricants-specific laboratory equipment and technical proficiencies appropriate to the requirements of such a facility.

The University's ABIL Research Program had been a leader in the development of Iowa's biobased products industry for over 15 years, and now, in the project's fourth year, in addition to completing several bio-products research projects, the NABL Center is working to fill the bio-products industry's need for expert support to assure renewable lubricants meet performance specifications; quality, certification and labeling requirements; and applicable regulatory measures.

Schedule
Project Initiation Date: July 1, 2003
Planned Completion Date: November 30, 2007

Agricultural Residue Processing

Advanced Biorefining of Distiller's Grain and Corn Stover Blends: Pre-Commercialization of a Biomass-Derived Process Technology

Bob Wooley, Abengoa Bioenergy

Principal Investigator:	Patrick Mulvihill	Funding Partners:	Novozymes North America, Inc.
HQ Technology Manager:	Valerie Sarisky-Reed		
PMC Project Officer:	Gene Petersen	Sub-contractors:	NREL, SunOpta, Auburn Univ.

Goals and Objectives: The overall objective of this project is to consolidate novel technologies into one conversion process that will be tested through Abengoa Bioenergy Corporation's pilot and demonstration facilities in 2004 - 2007 by (1) converting Distiller's Grains (DG) and Corn Stover (CS) blends to increase the ethanol output while increasing or retaining the present protein value of the residue; (2) improving the overall economics of industrial dry mill biorefining significantly; and, (3) increasing plant energy efficiency, thereby significantly reducing oil use per ethanol gallon produced, and construct a first-of-a-kind integrated biomass ethanol pilot facility.

This project will demonstrate at bench and pilot scale a viable pretreatment process for DG and CS to convert residual starch, cellulose and hemicellulose to ethanol and high-protein feed. The project will identify the optimal operating parameters for DG and CS conversion and the optimal DG/CS residue blends required to meet the nutritional values for these blends as animal feed. It will determine the most cost-effective enzyme complex for increased carbohydrate hydrolysis for the process and in parallel develop a yeast biocatalyst capable of fermenting the six and five carbon sugars present in the mixed feedstock blends. The bench and small pilot scale phases of the project will be performed at the NREL and NZNA facilities. Final integration of the large-scale pilot facilities will occur at the York, Nebraska plant, a 50 million gallon per year dry mill plant.

Project Description: The project has been conducted in two parts: Residual Starch and Co-Products (RSCP) and Biomass. The RSCP pilot plant was completed at York, NE in 2003 and more than 200 trials have been conducted to optimize the dry-grind to EtOH process. Work continues of evaluation of the most promising yield improvements and enhancements of co-product values.

The Biomass PP (BMPP) has been constructed and is contiguous to the RSCP PP. The BMPP is currently in start up mode and is expected to be fully operational by the end of August, 2007. As much bench scale work as possible was conducted by our academic and industrial partners in advance of the BMPP completion. The biomass process involves fractionation and includes development of a C-5 fermenting organism for utilization of the majority of hydrolyzed sugars released form the biomass. Data will be acquired through 2008 for design and economic justification of a demonstration scale facility.

Summary of Work to Date - Accomplishments (FY05-current): Several improvements to the dry-grind process were identified that gave improved yield in the RSCP testing. Some of these improvements are currently being introduced to our commercial facility to validate the extent of economic and quality gains. Some others require pilot scale production of sufficient quantities of material to evaluate their commercial value. Introducing the changes to the commercial plant and measuring the results will require several more months.

The BMPP is on track to start up soon and validate the technical performances seen at the bench scale and allow confirmation of the capital and operating costs envisioned. The C5 fermentation will be conducted in 2008 when the organism development is completed.

Biomass Bench scale work:

- Established optimal process parameters for fractionation of corn stover. The impact of key process parameters on conversion yields were determined for cellulose hydrolysis and ethanol fermentation of pretreated corn stover. Achieved >90% cellulose conversion yields at high substrate solids content >20% total solids).

- Adapted several hexose and xylose-fermenting yeasts strains to corn stover pre-hydrolysate. The development of a recombinant xylose-fermenting yeast strain (by NatureWorks) was delayed due to termination of project funding December 2006). Work has resumed since July 01, 2007. In collaboration with NREL, NIR models were developed for rapid analysis of chemical composition of corn stover feedstock and washed pretreated corn stover. We are now collaborating with Idaho National Lab (INL) and Auburn University to develop a NIR model for wheat straw.
- Extensive tests were performed by Novozymes and Dyadic to formulate effective enzyme cocktails for Abengoa cellulosic substrates. High solid substrate hydrolysis and fermentation were optimized using bench scale bioreactors.

Biomass Pilot plant process development:
Numerous pilot plant fractionation tests were performed at vendor facilities before we selected equipment for our York biomass pilot plant. ABNT developed engineering design, piping and equipment specifications and hired a general contractor to build the pilot plant. The plant is currently about 40% through the commissioning phase. Fractionated materials are being produced for development of biocatalysts (enzymes and xylose-fermenting yeasts).

Schedule
Project Initiation Date: January 2, 2003
Planned Completion Date: December 31, 2008

Making Industrial Bio-refining Happen!

Pirkko Suominen, NatureWorks, LLC

Principal Investigator:	Pirkko Suominen	Funding Partners:	Genencor; Iogen;
HQ Technology Manager:	Neil Rossmeissl		Abengoa Bioenergy
PMC Project Officer:	Gene Petersen	Sub-contractors:	N/A

Goals and Objectives: The overall technical objective of this project is to develop and validate process technology that will cost effectively produce sugars, fuels such as ethanol and chemicals such as lactic acid from lignocellulosic biomass. The project organized in two main tasks: Task 1 – Biomass hydrolysis process technology and Task 2 – High productivity, high yield biocatalyst for hydrolyzate at low pH.

The objective of Task 1 is to develop and validate a robust, cost effective and scaleable system for sugar production from biomass. Development work will be conducted by Abengoa Bioenergy in two phases, bench-scale work and pilot operations. Objective of the bench scale work is to establish the dilute acid pretreatment parameters which provide the set targets for soluble xylose yields from chosen biomass substrate and target cellulose digestibility using set enzyme loading measured as FPU/g. Under their separate DOE co-funded project, Abengoa Bioenergy will install a biomass pilot plant at its York, NE facility. In this project data from integrated pilot plant operations will be collected, analyzed and evaluated using an economic model.

The objective of Task 2 is to develop platform biocatalyst with high productivity and high yield on sugars in hydrolyzate at low pH and high temperature. Performance at a temperature of 40 $_{o}$C and pH5 in hydrolyzate offers substantial economic benefits by lowering capital cost by at least 20 % and operating costs by more than 10% compared to existing technology. Task 2 has three main specific goals. 1) Develop a novel, robust platform biocatalyst suitable for fermentation of biomass sugars at low pH and high temperature. 2) Develop a biocatalyst converting Abengoa's hydrolyzate sugars to ethanol with set target yield and rate and provide that biocatalyst to Abengoa for scale-up and piloting. 3) Develop a biocatalyst capable of producing lactic acid with set target yield, rate and titer in a low cost process, scale this up to commercial scale at NatureWorks Blair, NE facility.

Project Description: Task 1 will focus on hydrolysis technology using wheat straw at bench scale. Preliminary Aspen model will be developed, data from integrated pilot plant will be used to further develop the model and the process economics of various process options will be evaluated. (Abengoa BIoenergy)

Task 2. The approach utilized to achieve goals is not conventional in that obtaining a host with good fundamental performance under the desired conditions has been the key focus rather than selecting a biocatalyst with a large set of tools available. Thus one of the tasks is to develop tools for there robust hosts, and then engineer them to meet target metrics for both ethanol and lactic production in process relevant conditions for each. The two major pieces of biocatalyst development include improving the productivity and yield of the biocatalyst in low pH and high temperature environments and moving functionally enhanced biocatalysts into pilot demonstrations. Lactic acid production in yeast has been utilized to improve the performance of the biocatalyst in acidic hydrolyzate environments with great success. For xylose fermentation NatureWorks has developed novel fermentation technology based on xylose isomerase enzymes originating from anaerobic microbes. The lactic acid biocatalyst will be scaled up to commercial scale at NatureWorks' facility in Blair, NE. The ethanol biocatalyst will be transferred to Abengoa Bioenergy for piloting.

Summary of Work to Date - Accomplishments (FY05-current): There has been no work or funding towards Task 1 since the last review meeting. New SOW was agreed upon and work started 7/1/2007

Task 2. <u>Platform biocatalyst</u>. Since November '05 work has focused on CB1 biocatalyst. Genetic engineering techniques were developed for this host (first in the world). We now have basic engineering tools, including single-use and recyclable markers, vectors, promoters, gene replacement and overexpression techniques, and protocols in routine use. First pass annotated genome sequence was completed this month. It will facilitate all strain improvements efforts for both ethanol and lactic acid. It will also speed up efforts to improve xylose utilization rate and organic acid and hydrolyzate tolerance.

Xylose utilization. We continued to improve our novel xylose fermentation technology (patent pending). Key success factor was use of xylose isomerase pathway from anaerobic microbes. In this project xylose utilization rate was significantly improved, which also was reflected as faster ethanol production rate. The strain that was developed in this project reach 104% of June ’06 milestone rate target and 99% June ’06 milestone yield target before this part of the project was paused early 2006 due to lack of funds. Although this strain has excellent performance metrics on pure sugars, it has limitations with hydrolyzate tolerance. Methods and protocols were developed to address this. The hydrolyzate tolerant strain that was developed started sugar utilization and ethanol production in the presence of hydrolyzate at about 6 hours while the parent took 72 hours before any sugar was utilized. This part of the project was re-started in July 07. NatureWorks’ biocatalyst development is in-line with Abengoa’s pilot schedule, and the first strain meeting rate and yield targets for piloting will be transferred to Abengoa by the end of 2007.

Lactic acid biocatalyst. Genetic engineering, novel chemostat evolution and classical mutagenesis combined with innovative selection techniques have been used in combination to steadily improve biocatalyst performance. Genome wide tools have been utilized to elucidate bottlenecks in fermentation rate and yield at low pH. To test these hypothesis several genes have been modified, and modifications leading to improvements have been combined in one single strain. In a typical quarter over 50 new strains have been generated using various methods. Only few most interesting or most improved strains have been forwarded to quantitative characterization in bioreactors. A benchmarking protocol in bioreactors has been used to compare strain performance to targets (lactic acid production rate, yield and titer). Project team has met every milestone target and demonstrated steady progress towards end of project targets. Since the Nov ’05 review meeting all three measures have improved. Lactic acid production rate at low pH has been the focus improvement metric and it has improved most, from about 38% to 63% of final target. The improvements have been a concerted team effort by the molecular biologists improving the strains and the fermentation scientists and physiologists developing improved fermentation protocols for these strains.

As scheduled, low pH lactic biocatalyst reach good enough performance for scale up. Since this yeast has been genetically modified to produce lactic acid instead of the typical yeast fermentation product ethanol, an evaluation process by EPA is required. NatureWorks followed the required steps and after evaluation EPA granted a TME (temporary manufacturing exemption) to NatureWorks for manufacturing lactic acid using the developed yeast in Blair facility. The same model can now be used for yeasts engineered to ferment xylose/sugars from hydrolyzates to ethanol. Seed protocol for the lactic acid producing yeast was successfully developed. Several successful plant scale lactic acid fermentation trials were conducted using the approved yeast. Further trials are scheduled using the same and further improved strains. NatureWorks is in-line to start commercial production in 2008.

Cost and Schedule

Project Initiation Date: September 30, 2003
Planned Completion Date: May 31, 2009

City of Gridley Biofuels Project

Tom Sanford, City of Gridley

Principal Investigator:	Tom Sanford/Dennis Schuetzle	Funding Partners:	N/A
HQ Technology Manager:	Neil Rossmeissl	Sub-contractors:	TSS Consultants (Rancho Cordova, CA); Harris, Sanford and Hamman (Gridley, CA); Renewable Energy Institute International (REII) (McClellan, CA)
PMC Project Officer:	John Scahill		

Goals and Objectives: Since the late 1990's, the City of Gridley, CA, has been exploring ways in which to solve a local waste problem by finding a productive use for rice harvest waste. Through a preliminary contract administered through the DOE's National Renewable Energy Laboratory, the City performed pilot work on converting rice straw, rice hulls and other agriculture waste products to ethanol by means of thermochemical processes employed at 5-10 ton/day pilot plants in Mississippi and Denver.
The primary objective of the Gridley Ethanol Project is to identify technologies that can effectively and economically co-produce bioethanol and bioenergy from rice harvest waste to:

- Help preserve the Community's agriculture economy in Butte County and adjacent counties.
- Support continued rice farming in the Sacramento Valley by providing a practical straw disposal alternative to burning.
- Create jobs, a new tax base and economic development in the Sacramento Valley.
- Comply with the environmental legislative mandates to phase out most of the open field rice straw burning.

The Phase I development efforts included: Assessments of candidate conversion technologies; marketing assessments; material handling and process systems assessment; preliminary environmental assessments; development of financial projections, risk issues, and recommendations for Phase II.
The proposed Phase II activities will include the following Tasks:

<u>Task 1</u>
Evaluate the performance of a commercial scale (300 dtpd @ 8,500 BTU/lb biomass energy content) Thermochemical Conversion System (TCS)
Validate that the syngas from the TCS will be suitable for the co-production of bioalcohols and electricity using next-generation catalyst and unit processes.

<u>Task 2</u>
Develop a 1.0 dtpd Fuel Production System (FPS) Process Development Unit (PDU).
Integrate the FPS-PDU with the commercial scale TCS.
Validate the performance of the FPS-PDU over long-term, continuous operation.

<u>Task 3</u>
Develop plans and obtain funding for testing and validating a 1/5-1/10th scale Integrated Biofuels and Energy Production (IBEPS) using different waste biomass feedstocks

<u>Task 4</u>
Develop plans for a commercial plant that utilizes 325 dtpd of rice harvest waste that has been augmented with other local agricultural waste products

<u>Task 5</u>
Provide project management in support of Tasks 1-4

Project Description: The City of Gridley is located in the heart of California's rice growing area and its economy is uniquely dependent on rice production and markets. In addition, Gridley operates a municipal utility, with responsibility for delivering electrical power to the community. The Gridley community, including local rice growers, initiated the Gridley Ethanol Project to solve a major rice straw disposal problem and help maintain the economic viability in Butte County and the greater Sacramento Valley.

Gridley has been exploring ways in which to solve a local waste problem by finding a productive use for rice straw and rice hulls. Under a contract administered through DOE's NREL facilities, pilot work has been performed on converting rice straw to ethanol by means of thermochemical conversion utilizing pyrolysis, steam reforming and gasification at pilot plants in Mississippi (PGT) and Colorado (BCT). The capability of these systems is being evaluated using a 5E model to: Assess technology effectiveness (E1); energy efficiency (E2); environmental impact (E3); economic viability (E4), and; socio-political evaluations (E5). Data is being gathered and evaluated for the processes described above for the pilot and production plants. Preliminary 5E assessments have been completed for all candidate systems including a financial model for co-generation of electricity, heat and ethanol for the proposed commercial plant. In addition, the potential commercial uses for the ash are being developed with NSTDA.

Summary of Work to Date - Accomplishments (FY05-current): A draft interim report for Phase I of the DOE Gridley Biofuels Project has been completed which provides results on 1) feedstock collection, transport and processing; 2) pilot plant studies, laboratory simulations and systems modeling; 3) environmental assessments; 4) economic and marketing assessments; and 5) socio-political evaluations for conversion technologies that have the potential of economically and effectively converting rice harvest waste and other agricultural wastes to bioethanol and bioelectricity.

Approximately four years of laboratory, pilot and modeling studies were carried out to assess and validate the potential capabilities of a pyrolysis/steam reforming, thermochemical conversion technology and associated syngas to bioalcohol catalyst conversion processes. Experimental data was collected from two separate 5-10 ton/day pilot systems to assess the capabilities of the pyrolysis/steam reforming conversion process. The syngas generated from these pilot systems was converted to bioalcohols using catalyst formulations similar to those originally developed by Dow Chemical Co. in the mid-1980s. Detailed results from those studies are provided in this report. It was found that the pyrolysis/steam reforming process converts renewable biomass (e.g. wood, rice harvest waste) and fossil (e.g. coal) biomass to syngas with a net conversion efficiency of 72-76%. In addition, more than 99.5% of the volatile and elemental carbon in the biomass was converted to syngas.

The composition and energy content of the syngas is primarily dependent upon the operating conditions (temperature, residence time) and the ratio of water to carbon containing compounds in the steam reforming process. Thermochemical models were developed to help explain the experimental results. The energy content of the syngas was found to vary from 350-475 BTU/SCF. This syngas can be used to effectively produce electricity using currently available, high-energy efficiency, reciprocating engine/generators.
The Dow type catalyst formulations converted an average of 18% of the carbon monoxide in the syngas to primarily methanol and ethanol products with traces of propanol and butanol. The degraded catalysts also produced some benzene and higher molecular weight hydrocarbons in addition to alcohols. The ratio of methanol to ethanol varied from 1.0-1.5 for fresh catalysts, but degraded to greater than 5.0 for catalysts after more than about 100 hrs of operation. More robust catalyst and improved syngas purification processes will be required to increase catalyst lifetimes to 2,000 hrs or longer. Specifications for syngas purity are provided as a benchmark to help insure catalyst durability.

A review and assessment of catalyst technologies, developed since the late 1980's for the conversion of syngas to ethanol was completed. It was concluded that the catalyst technologies developed to date are inefficient and lack selectivity for the conversion of syngas to ethanol.

As a result, a research and development effort was initiated in early 2006 and funded by the Renewable Energy Institute International (REII), Pacific Renewable Fuels and other collaborators to develop more efficient and selective catalysts. As a result, a new family of novel catalysts has been developed (patents pending).

Integrated unit processes and process control strategies were developed (patents pending) for these new catalysts to efficiently co-produce bioalcohol (average 80% ethanol, 15-20% methanol and <2% C3-C5 alcohol composition) and bioelectricity from syngas with an average net energy efficiency of 50%.

Distillation and adsorption processes can be easily employed at the production site to produce dry, fuel-quality ethanol from this mixed alcohol product. However, these processes add additional capital and O&M costs, decrease energy efficiencies, and they may increase air emissions and wastewater effluents. Since there is already a substantial body of experimental and modeling data from the automotive industry, engine manufacturers, academic organizations and regulatory agencies on ethanol and methanol fuels, we recommend an approach that has the objective of gaining acceptance for this mixed bioalcohol fuel as a fuel oxygenate additive.

It was estimated from experimental data, thermochemical and engineering modeling, and the results of our 5E assessments that the pyrolysis/steam reforming process has the capability of converting 300 DTPD of waste biomass (e.g. reference wood feedstock material at 8,500 BTU/lb) to 8,550,000 gallons/year of bioalcohol (average 80% ethanol, 15-20% methanol and <2% C3-C5 alcohol composition), 7.45 MW (net) of electricity and 1,090,477 Therms/year (net) of process steam (@240 oF) at an average bioalcohol cost of $1.36/gallon. These yields represent a net average energy efficiency of 50% for bioalcohol and electricity and 62% if a co-located host can use all of the process steam. These yields represent the highest net energy conversion efficiency for any biomass to fuels and energy process developed to date.

It was estimated that the capital, and operational and maintenance (O&M) costs for a 450 ton/day plant (350 tons/day rice straw; 50 tons/day rice hulls and 50 tons/day wood as received) located in the Northern Sacramento Valley (Gridley/Yuba City/Colusa) area will be $53.1 M and $10.7 M, respectively, at 2007 Northern California economics. This plant will generate enough energy to sustain its operation with a net co-generation of 7.45 MW of electricity and 8,550,000 gallons of bioalcohol/year. The production costs for electricity and bioalcohol are estimated to be $0.080/KWH and $1.36/gallon, respectively. The estimated Return on Investment (ROI) for this plant is 41%, assuming a wholesale price of $1.95/gallon for the bioalcohol (without incentives). If incentives of $0.50/gallon are added, the ROI increases to 81%. It is recommended that the income from the sale of the bioalcohol be used to provide an attractive ROI to the plant financiers and operators as well as subsidize the production of bioelectricity, which will reduce the electricity production cost to about $0.045/kWh.

Our emissions models, based upon measured emissions from individual unit processes, predict that the total air emissions and waste water effluents from such a plant will be less than that from a natural gas-fired power plant operating at an equivalent energy output.

Since rice straw and rice hulls contain 15-17% of inorganic material, 68-77 tons of ash per day will be generated from a 450-ton per day (biomass as received) production plant. Therefore, an R&D effort was carried out between REII and Thailand’s National Science and Technology Administration (NSTDA) to assess potential commercial uses for this ash. It was found that this non-toxic ash can be used as an additive to increase the strength and durability of cement and asphalt; for the production of high-quality mullite ceramics; and the production of filtering media for water purification.

A Request for Proposal was distribute to BCT (currently Range Fuels), ThermoChem, Thermo Conversions, Nova Fuels and COHREN in December 2006. Thermo Conversions and Nova Fuels were the only organizations that responded to this RFP.

Although nearly 4 years of laboratory, pilot and modeling studies have been carried out to assess and validate the potential capabilities of these discrete processes, it was found that there still remain several barriers before commercial success can be achieved. During 2003-2006, experimental data was collected from 5-10 ton/day syngas pilot systems to assess the capabilities of the pyrolysis/steam reforming conversion process. The syngas generated from these pilot systems was converted to bioalcohols using catalyst formulations similar to those originally developed by Dow Chemical Co. in the mid-1980s. It was found that the pyrolysis/steam reforming process converts renewable biomass (e.g. wood, rice harvest waste) and fossil (e.g. coal) biomass to syngas with a net conversion efficiency of 72-76%. In addition, more than 99.5% of the volatile and elemental carbon in the biomass was converted to syngas.

More specifically, this Integrated Biofuels and Energy Production System (IBEPS) uses an advanced Thermochemical Conversion System (TCS) employing a pyrolysis/steam reforming process (combined with an innovative catalytic-based Fuels Production System (FPS) for the efficient and economical co-production of bioalcohol and electricity. The TCS is being commercialized by Thermo Conversions, LLC (TC), and the FPS is being commercialized by Pacific Renewable Fuels (PRF).

Other Refinery-Related Projects

Biorefinery and Hydrogen Fuel Cell Research

Cyrus, Georgia Environmental Facilities Authority

Principal Investigator:	K.C. Das	Funding Partners:	State of Georgia
HQ Technology Manager:	N/A	Sub-contractors:	The University of Georgia
PMC Project Officer:	Kevin Craig		

Goals and Objectives: The overall project goals include [1] Developing pyrolysis-BioOil processing systems; [2] Laboratory development for fuels and chemicals; [3] Production, characterization and uses for pyrolysis-Char; [4] Developing Atomic layer epitaxy for fuel cell technology; [5] Developing fermentation based conversion of biomass to fuels and products; [6] Developing biomass production technologies (e.g. algae biomass production, forestry residue harvesting technology); [7] Developing and testing catalysts for biomass conversion to products; [8] Technology transfer and education and [9] Project Management and Reporting.

Project Description: This project involves research, development, and technology transfer of biorefinery technology (thermochemical and sugar platforms) and advanced technology for fuel cells. Georgia is a leading producer of biomass from forest, agriculture and other industries. Biorefining provides opportunities for economic development, particularly in rural areas. Outcomes from this project will include new technology for production of fuels and products from biomass; developments in biomass production, harvesting, pretreatments and related logistics; and technology and education of a workforce familiar with biorefining. Research performed by GEFA/UGA includes production of BioOil in batch and auger fed continuous reactors. The BioOils are transformed through blending and refining processes to prepare green diesel. A system to further evaluate this process is being developed to produce high heating value, low polarity green diesel (refined bio-oil) suitable for blending with petroleum and biodiesel. An extraction pretreatment step is being investigated to evaluate the economic potential to produce waxes, hemicellulose, extractives and fatty acids from pinewood.

Pyrolysis Char is being produced under different conditions (different environments such as steam, nitrogen, carbon dioxide, etc, and different temperatures and biomass) and characterized for surface properties. Application for chars includes soil amendment, carbon sequestration agent, catalyst etc. Crops and biomass that are more suited for the southeast US for ethanol production (e.g. sweet potatoes and grain sorghum) is being evaluated. Substrates, enzymes and microorganisms are being screened at the bench-scale for its effectiveness for ethanol production. Biomass production, harvesting, storage, and logistic modeling studies are being conducted. Including traditional woody biomass and grasses of the southeast US and biomass such as algae that will be developed in conjunction with waste treatment operations. Catalytic processes allow the possibility to develop a variety of new products while reducing inputs required for conversion. We are evaluating homogeneous and heterogeneous catalysts in pyrolysis applications to increase gas and/or BioOil generation. In addition we will focus on developing catalysts for transesterification and for syngas conversion to hydrogen (and other products).

We are developing methods for deposition of catalytic metals with atomic layer control. The focus will be on controlling the atomic level proximity of metals such as Pt, Ru, Rh, Os, and Pd to create improved catalysts. This process will result in layering of these metals with atomic control. In addition, templates will be used to create nano-clusters of these materials that will result in further control over size, structure, and proximity of these metals, as well as increasing the surface area.

Technology transfer and education goals include training workshops and conferences to be held under the auspices of the University of Georgia. These may include topics in bioenergy, biodiesel production, etc. Target audience includes industry personnel, government, and entrepreneurs. The other educational goal includes training of graduate students and undergraduate students in biorefinery principles and technology details.

Summary of Work to Date - Accomplishments (FY05-current):

1) *Pyrolysis of Georgia biomass to value added products*:
Bench scale pyrolysis equipment (batch and continuous) have been setup and several Georgia biomass including poultry litter, poultry processing waste, forestry residues, pine chips and pellets, and peanut hulls are being pyrolyzed to develop the processing technology. The products of this pretreatment are being evaluated as energy feedstocks and for bioproducts, e.g. the use of char as ammonia absorbent in the poultry industry.

   Status: Process development ongoing. Char has been evaluated for adsorption capacity. Field trials to follow.

   Key accomplishment: A key goal of demonstrating hydrogen production from peanut hulls at a 1 ton/d (biomass throughput) scale has been completed. Process operation data for over 500 hours have been collected.

2) Diesel-like fuel from wood - *BioOil fuel blend development and engine testing*
A bench scale pyrolyzer was developed and BioOil was generated in quantities over 15 L. The purpose of this work was to characterize the BioOil and use it towards engine testing. Pyrolyzing pine pellets in the lab scale continuous pyrolyzer developed BioOil. Blends of BioOil with other solvents/fuels have been prepared and are being characterized. One 30-minute run of a BioOil blend was conducted successfully in a diesel engine.

   Status: BioOil blend analysis and testing ongoing. Engine performance to be evaluated next.

   Key accomplishment: A patent application has been submitted for this product.

3) Biodiesel feedstocks and processing
Transesterfication of oils and fats to produce biodiesel
This work evaluates new sources of oils and fats that could be substrates for producing biodiesel. The work is partially funded by the Peanut Board. Once developed, the biodiesel will be tested for properties and behavior in engine testing.

   Status: Basic properties study ongoing – next step will include fuel testing.

4) Fuel testing and engine testing capability – *BioOi/Char characterization laboratory setup*
Fundamental research capability in testing the properties of BioOil and Char has been advanced at the University of Georgia. Analytical equipment added to our capability include: Agilent Micro GC, Karl-Fisher titrator, Viscometer, Bomb calorimeter, Liquid chromatograph (HPLC), Thermogravimetric analyzer (TGA), Differential scanning calorimeter (DSC).

   Status: Approximately half of the intended analytical equipment have been purchased and are in the process of being installed and calibrated. Capabilities in standard methods of analysis are being developed presently.

5) Char based carbon sequestration fertilizer - *Field-testing of Char use in Agriculture*
Two chars (peanut hull and pine chip) were produced in Athens and applied to a field site to evaluate the benefits of using char in agriculture. Data to be collected will include nutrient benefits, water holding and irrigation benefits, and carbon sequestration benefits.

   Status: Char applied to irrigated cornfields – planting and initial analysis complete.

   Key accomplishment: Two years of data on char use in soils have been collected. This is the only field scale data of this kind in the US. Several similar sites exist in other countries such as Brazil, Indonesia, Japan, etc.

6) Ethanol from wood, crops, and byproducts research - *Evaluation of commercial yeast strains that are used to produce ethanol*
We have obtained commercial yeast strains for producing ethanol from the three major companies in this industry and are in the process of evaluating them. Our initial studies suggest that some strains are significantly better than others in converting glucose to ethanol. In the next four months we will complete this study and know which strain has the best productivity (g/Lh of ethanol produced from glucose) and which strain can accumulate the highest concentration of ethanol.

7) *Producing ethanol from rendered bakery wastes*
We have received a grant from Reconserve Inc., Flowery Branch, Georgia to evaluate the use of their rendered bakery wastes for the production of ethanol. We are beginning our analysis by comparing the production of hydrolysates from rendered bakery wastes versus corn meal as a control. In the next three months, the process for producing rendered bakery waste hydrolysates and converting it to ethanol will be optimized.

8) *A*tomic layer epitaxy
Initial testing of various combinations of metals to be used in epitaxy studies have been completed. Additional testing and method developments are ongoing.

Schedule
Project Initiation Date: July 1, 2005
Planned Completion Date: June 30, 2008

Infrastructure Platform

Introduction

The Infrastructure Platform is a new platform within the Biomass Program. It was implemented in FY 2007 in response to growing concerns about how current infrastructure capacity could handle a growing supply of biofuels.

In order to achieve large-scale market adoption of biofuels, significant infrastructure challenges, including distribution, storage, materials compatibility, fuel dispensing and vehicle end use, must be addressed. In terms of the overall biofuels supply chain, the infrastructure platform focuses on the distribution of fuels from the biorefinery to use in vehicles. Feedstock logistics, including transport of feedstocks to the biorefinery, is covered under the Biomass Program's Feedstocks Platform. Work conducted under the infrastructure platform is broken down by fuel type, with current projects focused primarily on ethanol.

Given the fact that the E85 market has been slow to develop, DOE, in close collaboration with EPA and DOT, is evaluating the performance, materials and emissions impacts of E15 and E20. Beginning in FY 2007, the infrastructure platform began testing of intermediate ethanol blends on legacy vehicles and small engines, and this continues to be the platform's area of focus in terms of funding. If intermediate blends prove to be acceptable based on a variety of different environmental, performance and other criteria and are approved by EPA, these intermediate blends could be used nationwide in all types of vehicles, thereby reducing the need for substantial near-term increases in E85 fueling stations and flexible-fuel vehicles (FFVs). Adequate infrastructure will need to be in place to handle increased ethanol blends.

Platform Performance Goal

To develop a systematic approach to build an adaptable cost-effective infrastructure system that will ensure widespread biofuels use for transportation applications.

Objectives

- Reduce the cost of transportation and distribution of biofuels to levels that are cost-competitive with gasoline transportation and distribution (approximately $0.15/gallon) by 2022.
- Facilitate the development of nationwide capability to transport and distribute up to 35 billion gallons of biofuels by 2017.

FY 2007 Accomplishments

FY 2007 marked the beginning of the Infrastructure Platform within the Biomass Program. The platform will have a formal budget beginning in FY 2007. Its accomplishments since its inception are as follows:

- Began testing intermediate blends of ethanol (i.e., E15 and E20) on small engines and vehicles in collaboration with the Department of Energy's Vehicle Technologies Program. Testing considers emissions, catalyst durability, drivability, and materials compatibility in legacy fleet vehicles, as well as full useful life emissions and durability testing on small engines. A report with preliminary results of testing on small engines was provided to the Environmental Protection Agency in October 2007.
- Began formal collaboration with industry at the Infrastructure Planning Workshop in October 2007.

Budget

The Infrastructure Platform will not have its own budget line item until FY 2009. However, expenditures in this area in FY 2007 were $0.75 million and in FY 2008 were about $8 million.

2008 Plans

- Continue testing of intermediate ethanol blends on vehicles and small engines. The Biomass Program and Vehicle Technologies Program are expanding their current test plan of small engines to include marine, motorcycles and snowmobiles. A progress report with results from testing of small engines and some vehicles is expected in summer 2008.
- Continue conducting an infrastructure mapping exercise to outline various scenarios for achieving the volumes required by the Renewable Fuel Standard (RFS). The mapping exercise will consider the implications of various acceptable ethanol blend levels, location of FFVs and fueling stations, and pipeline development, among other factors that will ultimately affect achievement of the RFS.
- Conduct a Pipeline Feasibility Study in coordination with the Department of Transportation to scope out the feasibility of constructing pipelines dedicated to the transportation of ethanol.

Joan Glickman, Technology Manager – Infrastructure
Department of Energy
Office of the Biomass Program, EE-2E
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Additional Project Summaries

Biodiesel and Fuels Demonstration

Mississippi State University Sustainable Energy Research Center

Bill Batchelor, Mississippi State University

Project Summary: Overall, the project is progressing on schedule. There have been no major setbacks or schedule delays. Variances were reported under the biodiesel, ethanol, biomass utilization, distributed generation, chemicals and feedstocks portions of this project. Minor delays were reported due to obstacles encountered in research methods and new software packages. The environmental sustainability portion of the project is progressing ahead of schedule. This project's spending is on schedule with the originally proposed budget.

The purpose of this project is to conduct research needed to develop and support an economically and environmentally sustainable renewable energy industry in Mississippi. Research in this project has been organized into three research platforms: Fuels, Value-Added Chemicals, and Power. The Fuels platform consists of multidisciplinary teams focused on developing improvements in production and use of biodiesel, ethanol, bio-oil, and gasoline from syngas. Each of these fuels can be developed from biomass produced in MS. The biodiesel group is conducting research to develop biodiesel from lipids derived from biomass grown in MS. They will develop extraction techniques, test physical properties, and evaluate the use of these new formulations. The ethanol group is focusing on the development of more efficient microbes to convert organic carbon compounds from biomass to ethanol, as well as microbes that can convert synthesis gas to ethanol. The bio-oil group is developing more efficient pyrolysis techniques to develop bio-oil. They are conducting research on the use of bio-oil, including blending with diesel fuel and development of high valued chemicals.

The gasoline group is studying the catalytic conversion of bio-derived synthesis gas to methanol and gasoline. The Value-Added Chemicals and Products group is conducting research to derive high valued compounds from waste products resulting from the generation of renewable energy. The Power group is conducting research in developing and improving power generation from biomass. The syngas team is conducting research to understand linkages between syngas feedstock properties and resulting gas composition. The utilization group is developing methods and tools to gain improved understanding of combustion processes for biomass fuels.

Oxydiesel Demonstration in California and Nevada

Thomas Sopko, O2Diesel Inc.

Project Summary: The current e-diesel project with O2Diesel Inc. is titled, "Ethanol-Diesel Test Program." Using congressionally mandated funds, the objective of this program is to conduct a thorough evaluation of e-diesel use in on- and off-road vehicles and equipment while operating in regular service. This work effort builds on previous e-diesel activities and focuses on testing that addresses safety and regulatory requirements for development of this fuel technology. Current activities include CARB/EPA Diesel Engine Control Strategy (DECS) verifications as well as soil and water (multimedia) studies. Progress to date includes tests on two engines, three fuel blends, and five different after-treatment devices as part of the DECS. Test plans are being finalized for the multimedia study.

E diesel Test & Research Project
Nathan Fields, National Corn Growers Association

Project Summary: The recipient stopped the project due to unfavorable results. All three of the John Deere diesel engines (8.1L, 6.8L, and 12.5L) experienced premature fuel system failure during the 2,000 hr durability tests. As a result of a status meeting between the recipient and John Deere on May 11, 2006 the project was discontinued due to the failures encountered. The scope is currently being revised. (Note that the discussions regarding the revision of scope are underway and are therefore not to be disclosed unless NCGA specifically agrees. As of July 2, 2007, the Congressional sponsor's concurrence with the revised scope has been received and NCGA has been asked to expedite submitting the remaining information needed to formalize the scope revision.)

John Deere & Company became part of the program as the result of E diesel testing done on one of their combines in central Illinois. After over 800 hours of use on a 10% E diesel blend (using the GE Betz additive package), the engine was removed and dismantled by Deere engineering staff. No indications of failure or unusual wear were found. Subsequent meetings between Deere, Illinois DCEO, and Illinois Corn Growers led to the development of this program, which is very similar to the testing that would be performed by John Deere in bringing a new engine to the market.

Of course, the overall objective of the program is to commercialize E diesel fuel as a cleaner-burning substitute for conventional #2 diesel fuel. This testing program, if successful, could lead to John Deere extending warranty coverage to the fuel for use in its engines. It is also conceivable that John Deere could use E diesel to substitute for #1 diesel as "factory-fill "in some of its equipment and or machinery.

The John Deere E diesel Test & Research Program is separated into three distinct phases: Phase 1 – Laboratory Studies, Phase 2 – Laboratory Studies, and Phase 3 – Field Tests and Evaluations. Phase 1 consists of regulated and unregulated emission test and a 2,000-hour durability test with engine emission degradation tests performed at 500-hour intervals. Phase 2 will consist of two additional 2,000-hour durability tests, plus numerous other tests on both bare engines and in vehicles including wind tunnel, component compatibility (fuel system and engine gaskets and sealants, plus plastic, rubber, elastomeric and metallic part compatibilities with E diesel fuel), E diesel fuel standards development, fuel pump-ability, and hot/cold starting characteristics at ambient temperatures ranging from +120° F to -20°F. Testing will either be performed at Deere's Product Engineering Center (PEC) in Waterloo, Iowa, or farmed out to major testing laboratories (such as SwRI), depending on laboratory availability and testing schedules. This will be coordinated through John Deere & Company.

National Biodiesel Infrastructure Development Initiative

Tom Verry, National Biodiesel Board

Project Summary: Deliverable A.1.DL.1, Northville Industries Services' (NIS') final report "B5 Soy Test Data and Report," was completed and approved this quarter. Under task A.3.ML.1 Jefferson Biofuels LLC has completed its site plans and permitting requirements for its Kansas City biodiesel blending terminal. EF1 - NEPA paperwork is being reviewed by the Golden Field Office. Jefferson Biofuels LLC is in the process of completing the permitting requirements needed for its Jefferson City terminal; this task is taking longer than anticipated but is expected to be completed within the next quarter. Under task C.1 this quarter there were three BQ-9000 training sessions held with nearly 80 in attendance. NBB submitted justification to Golden Field Office to eliminate the Fuel Test Survey under task C.2. NBB is proposing funds from this task go to a newly proposed task D, USPS Biodiesel Demonstration, to be executed by NREL. NBB is waiting for Golden's official approval of this modification. Spending is slightly behind schedule but expected to get back on track once NEPA and sub-contractor restrictions are lifted. The DOE amount and cost share amount from last quarter has also been updated for last quarter based on corrections submitted by the recipient. Cost share was decreased due to a calculation error the first quarter. NBB overestimated its cost-share by including food and a non-allowable event (Canadian event).

The NBB will partner with petroleum products merchant wholesalers to perform pipeline run(s) with an expected result of understanding how biodiesel behaves in the pipeline, particularly if it is fungible, and why or why not. Limited testing has been done to date on biodiesel movements through pipelines. None of it is publicly available information. This project will be the first demonstration of soydiesel in a pipeline. This demonstration will raise awareness and dispel speculation about the concerns of moving low-level blends of biodiesel on the pipe. This project will have an outreach and education component directed at petroleum marketers on the proper procedure to blend, ship, and store ASTM D6751 quality biodiesel. This project will also establish an emergency implementation plan should fuel quality situations occur in the future, as did in Minnesota last winter. Further, this grant will result in the installation of a biodiesel meter-blending terminals at each of two existing petroleum terminals.

National Biofuel Energy Laboratory

Kelly Jezierski, NextEnergy

Project Summary: Overall the project is slightly behind schedule and will likely need a no cost time extension. Spending is also slightly behind. Cost share is substantially lower than it should be, it is currently at about 6% of funds spent to date. Task A is almost complete and has culminated with the dynamometer group testing various custom fuels, results are currently being reviewed. The major accomplishment for Task B was the initiation of the fuel additives for cold flow impact evaluation. This task is slightly behind schedule, the team has reached out to a couple of companies for additional help to effectively evaluate more additives. The review of biodiesel blends has continued in Task D. Lastly, initial parameters for the biofuels and biofuel blends database have been identified.

Little is known about the impact of the unavoidable compositional variability of biodiesel (and even conventional diesel) on diesel emissions. The alkyl ester makeup of biodiesel varies very widely world-wide, as does the hydrocarbon makeup of petroleum diesel. Not enough is known about the impact of these variations on fuel characteristics (e.g., cetane number, stability and cold weather performance) and engine performance (e.g., emissions, power output, cold-weather driveability, wear of fuel system and engine parts). In particular, very little is known of the impact of biodiesel on the production of certain emissions, such as formaldehyde, that are currently not regulated but are expected to be regulated in the future. It is the purpose of this program to resolve these issues.

Associated Products, Combined Heat and Power, and Other Technologies

Canola-based Automotive Oil R&D

Ira Pierce, The Green Oil Company

Project Summary: This research and development project will construct sufficient metrics on the sciences of Canola Oil, (Task 1); and on decision making towards adoption (Task 2) specifically directed at industries that are potential large-scale users of bio-based automotive products. This study is an early stage effort designed to develop practical knowledge required to achieve these stated objectives.

At a later date, we may consider using the decision making model on farmers, as well. They will have to elect to plant Canola on their lands, with their decision making based on criteria that are similar in many ways to those for users.

The overall objective of the government and the bioproducts industry is to replace petroleum lubricants and fuels with rapidly biodegradable, petroleum-free, environmentally safe products. To do so, industry must produce bioproducts of the highest quality, in large volumes and at competitive prices. Accomplishing that objective requires confident investors and integration of the entire “farm to refinery” operation.

Phillips Biomass Combined Heat and Power Facility

Carl Nelson, Green Institute

Project Summary: As noted in the previous quarter, Green Institute is seeking a workplan change from DOE to focus more on research activities with the remaining funding. A six-month no cost extension has been granted while the DNFA relative to this scope change circulates for signature. While awaiting approval of the scope change, Green Institute has focused their efforts on reporting on the development of urban biomass utilization for the Twin Cities region. The report has been completed.

The project objectives are to develop a biomass combined heat and power plant in the Phillips neighborhood of South Minneapolis and support the work of the Phillips Community Energy Cooperative in delivering energy efficiency services to low-income residents.

EERC Center for Biomass Utilization 2005

Dr. Bruce Folkedahl, University of North Dakota Energy & Environmental Resource Center (EERC)

Project Summary: Management and Strategic Studies and Biodiesel Education and Outreach tasks included organizing sessions, workshops and speakers at various biomass and biofuel related conferences.

Biomass Gasification and Distributed Power Production construction activities were delayed pending NEPA approval, construction and procurement activities are scheduled to continue in the next quarter.

Novel High-Cetane Oxygenates from Waste Glycerol from Biodiesel Plants efforts produced four candidates for cetane and cold-flow filter-plugging tests and one candidate to be used as a gasoline octane enhancer.

Process Integration for Economical Hydrogen Production from Ethanol efforts continued with varying parameters in pilot-scale testing to optimize product streams.

Biojet Fuel Cold-Flow Improvement submitted two samples of biojet fuel for evaluation at the UND lab, initial results show acid concentrations to be higher than specification and actions are being taken to resolve the problem.

Urea Fertilizer Production from ethanol Coproduct Carbon Dioxide process optimization continued with catalyst stability tests and reaction condition optimization as well as evaluating and compensating for a new possible reaction mechanism.

Chemical Feedstocks from Lignocellulosic Pyrolysis efforts continued on performing economic analysis of using bio-oil-extracted polymers in Enhanced Oil Recovery treatments, domestic data is difficult to find to perform this analysis and this activity has been delayed.

Utilization of Cuphea Oils for Biodiesel Production, Landfill Methane for Microturbine Power, Ethanol Processing for Hydrogen Production - System Integration, Biomass III Energy and Products Workshop, Biomass Gasification and Distributed Power Production, and Economically Optimized Biodiesel Production from Low-Value Feedstocks all entered the final write-up phase, the overall project is scheduled for closeout June 2007.

The goal of the EERC CBU Program is to develop economically and environmentally sound technologies to promote efficient biopower or bioenergy, transportation biofuels, and bioproducts such as marketable chemicals and hydrogen. An overreaching goal of the EERC CBU is to develop technologies that will expand the use of biomass in practical and economic ways within the framework of sustainable development and environmental protection. The EERC CBU is in its fifth year of operation.

Anaerobic Digestion

Research on Anaerobic Digestion: Optimization and Scalability of Anaerobic Digestion of Mixed High Strength Food Processing Wastes for Renewable Biogas Energy

Floyd Schanbacher, The Ohio State University Research Foundation

Project Summary: This project consists of three main tasks: 1) Implementation of Research-scale Anaerobic Digester System, 2) Research and Operating Costs for Anaerobic Digestion of Biomass to Energy, and 3) Project Management and Reporting.

Task 1 **-** Design and Construction of Research-scale Anaerobic Digesters proceeded mostly on schedule. The digesters were fabricated and the installation area was prepared for their arrival. Due to performance limitations of the on-board biogas analyzer, subsequent related tasks are delayed and adjustments were made to the affected neighboring equipment. A suitable replacement analyzer has been identified and the task should be able to proceed as expected.

Task 2 **-** Research and Facility Operation activities included continued work on optimizing design and operation of the anaerobic digestion systems including bringing new lab-scale anaerobic digestors online, enhancing the microbiology and metabolism of anaerobic digestion through microbial genomic and metabolomic analysis of a variety of anaerobic bacterial species contained in a comprehensive molecular library, and appointing two graduate students to survey the food processing industry based biomass available in the state of Ohio with potential for use in biogas production including location, energy potential, and suitability for anaerobic digestion.

Outreach efforts included sponsoring a workshop titled "Waste to Energy Workshop for the Ohio Livestock & Food Processing Industries" in conjunction with the Ohio Department of Development and the Combined Heat and Power Association. To date, 20% of the project funds have been spent with 75% coming from cost share.

This project has two main objectives: 1) design, acquisition, and installation of research-scale anaerobic digestion systems (two) optimized for operation with high-strength non-lignin biomass wastes common to Ohio's agricultural and food processing industries, and 2) operating costs for support of research and development essential to our program for conversion of high-strength biomass wastes to renewable energy via anaerobic digestion.

This program includes facilities and interdisciplinary capacity for anaerobic digestion research at laboratory bench-scale (0.5-8 liter), drum-scale (45 gal), large (sub-pilot) research-scale (1,600 gal), and semi-commercial pilot-scale (8,000) scales using high-strength or mixed biomass types as feedstocks. This funding will be used to acquire the research-scale (2 x 1600 gal ea) anaerobic digestion systems for testing and optimizing the energy yield from high-strength food processing biomass wastes in concert with our lab- and drum-scale digesters.

New York Biomass / Methane Gas Fuel Cell Power Project

Dr. Caine Finnerty, NanoDynamics, Inc

Project Summary: This project is on schedule, however spending is slightly behind the spend plan. The following information should be treated as proprietary. During the past quarter several notable achievements occurred. 1) A single cell power of 17.25 W was achieved. It is project that next quarter 20 W will be achieved, a project milestone. 2) A cell stack was tested using simulated reformate fuel and a max power of 64.73 W was achieved. 3) Workable prototypes of B and C were fabricated. 4) Optimization of prototype A is complete over a hundred cells have been fabricated for testing. Optimization for prototypes B and C is still underway.

NanoDynamics has recently made a series of significant advances in the development of tubular anode supported ceramic solid oxide fuel cells that have resulted in cell power densities of as high as 2 Watt per square centimeter with measured electrochemical efficiencies greater than 55% and fuel utilization over 90% while the cell is operating at rated load. NanoDynamics has also demonstrated the ability to perform direct reforming of propane and methane fuel in tubular fuel cells with a 1000 hour endurance test revealing little or no deterioration of the cell structure. Such high power density in combination with high fuel utilization and high electrochemical efficiency provides the possibility of developing efficient compact (and therefore lower cost) fuel cell systems. NanoDynamics has filed a patent on an innovative cell manufacturing process that will allow the extension of the cell technology employed in their microtubular fuel cells larger stationary applications. This cell casting technology offers the potential to scale-up the benefits all ready demonstrated for portable applications to systems sizes of 10 kilowatts or greater. Employing these larger format cells and experience gained from the development of hydrocarbon reforming technologies, it will be possible to develop fuel cell systems that operate from biomass produced gases to generate both electricity and heat (C.H.P).

This project will develop a novel solid oxide fuel cell casting technology and innovative catalyst design. Fuel cells and “short” fuel cell stacks (up to five cells) including gas distribution manifolding will be designed, built and tested to evaluate the feasibility of scaling-up this novel cell manufacturing technique to multi kilowatt applications. The fuel cell’s anode material composition and structure will be optimized to improve the performance of the fuel cell in biomass gas applications. The results of this project will provide the basis for construction of solid oxide fuel cell systems in the future capable of producing significant power efficiently from biomass gas.

Solid Waste Authority Pyramid Resource Center

Tim Berlekamp, SWACO

Project Summary: Through proprietary technology, SWACO's landfill gas will be cleaned to produce fuels for the production of electricity through either micro-turbines or fuel cells, compressed natural gas for fueling SWACO's duel fuel transfer fleet, which will run on bio-diesel and CNG, make methanol for the production of bio-diesel, hydrogen and direct methanol fuel cells as well as creating food grade CO_2. By utilizing the created energies and by-products for commercial purposes, this project will demonstrate the viability of using landfill gas as an alternative energy resource. SWACO will monitor the efficiency, economics, and performance of the commercial uses for a period of twenty-four months.

Communications, Outreach, and Partnerships Part I

Biobased Products

Mark Williams, Growth Dimensions for Belvidere and Boone County Inc.

Project Summary: Under task A, a bio-lubricant/grease company continues to explore the development of a new biobased product division; the Rockford Airport (Freedom Field) Biomass to Hydrogen demonstration project continued with information gathering and concept stage development; and BioVantage, a biodiesel product commercialization and production company has entered the investment and marketing strategy stage. Under Task B, the Third RFP solicitation was advertised March 1, 2007 with an end date of March 31, 2007. The proposal for a biodiesel product commercialization and production company was reviewed and determined to move to DOE review. Proposal was submitted to DOE for review March 29, 2007. Subsequent review by DOE determined that the project will require a NEPA review. Growth Dimensions has determined that it is necessary to eliminate the Task 3 - Design Services Task, because the Growth Dimensions is in the process of negotiating on the acquisition of an existing facility for the use and has decided it would be more prudent to The decision has been made to eliminate Task C, design of an Ag-Tech commercialization center, and instead focus the funding on support of Task A. In the next quarter the revised scope and budget will be submitted reflecting these changes. Due to complications with Task C and the subsequent revision of the scope, project spending continues to be behind schedule. A no-cost extension will be requested in the 3rd quarter, 2007.

The objectives of this project are three-fold: (1) biomass product development and commercialization support services; (2) development and management of a competitive capital award program; and (3) preliminary design and engineering studies of the proposed Ag-Tech Commercialization Center.

Alternative Energy Enterprise Program (Strategic Biomass Initiative)

Sumesh Arora, Mississippi Technology Alliance

Project Summary: Under task A, modifications to the ban floor in the east and west feeding alleys were completed. Due to poor health and personal issues on the part of one of the sub-contractors, the project is slightly behind schedule, but is expected to be on track during the third quarter. Three additional sub-grants were awarded during the last quarter. A no-cost extension was requested through December, 2008, in order to complete oversight and support of projects supported under this award.

The overall objective of this project referred to by MTA as the Strategic Biomass Initiative (SBI) is to foster viable commercial enterprises in Mississippi based on the state's natural biomass resources and to further develop near-term biomass technologies through university based applied and research and development (AR&D). This project will examine barriers to commercialization of biomass technologies and identify AR&D as well as commercial demonstration opportunities which can overcome these barriers. The project will also consider the need for post-commecialization AR&D as needed by the existing biomass technology based companies in Mississippi and help develop industry-unversity partnerships to overcome the challenges faced by the industry.

Kentucky Rural Energy Supply Program

Cam Metcalf, Kentucky Pollution Prevention Center

Project Summary: The project is on schedule. Cost share is currently low, 10% instead of the required 25% or about $150,000 low.

- The project's quarterly meeting was held and was attended by House Representative Tanya Pullin and a representative for Senator Jim Bunning's office.
- Sub-award 1, "Development of an Ethanol Pilot Scale Facility to Evaluate the Effect of Collection, Storage, and Pretreatment of Corn Stover": Lower moisture content corn stover was baled and a compositional analysis was performed. It was found that there was a slight decrease in glucan content which was explained by the ensiling process.
- Sub-award 2, "Development of an Integrated Solar Heat Pipe System for Improving Building Energy Efficiency": A preliminary set of simulations has been performed to compare the performance of a baseline solar heat pipe system to water wall, concrete wall and direct gain systems in Louisville, KY, Madison, WI, Rock Springs, WY and Albuquerque, NM. Results are not in yet.
- Sub-award 3, "Differentiating Microbial Pathway and Membrane Adaptations for Enhanced Performance in Extreme Environments": The saponification and methylation procedures to form fatty acid methyl esters from C. thermocellum whole cells was revised from the standard protocol to a new method that increases yield by up to three times.
- Sub-award 4, "Novel Catalytic Approaches for Bio-Oil Upgrading": The catalyst type was changed from a basic cracking catalyst to a reforming catalyst. The project is moving forward with promising results, increasing % carbon and decreasing % oxygen in the oil by ~40% for both.
- Sub-award 5, "Photo-catalysts for Solar Energy and Hydrogen Production": The electrochemical system is fully operational as of the end of the quarter. The first series of topography images of the nanowires have been obtained. Initial experiments with the EC system have shown that a surface of gold coated mica onto which the nanowires can be deposited may not withstand the experimental conditions.
- Sub-award 6, "Production of Biomass Briquettes as an Alternative Fuel Source": The briquetter has been installed and is operational; however they have not been able to find a binder that works.
- Sub-award 7, "Weather Responsive Ventilation for Residential Energy Efficiency and Indoor Air Quality": Early results from the superposition study indicate that flow continuity cannot be measured in real time. To overcome the problem, a post-processing program was written which iterates the internal pressure coefficient to achieve continuity. The technique appears reliable and acts as an error checking procedure as convergence will not occur if sensors readings are inaccurate (e.g. rain water in the pressure taps).

The Kentucky Rural Energy Supply Program was established in 2005 by a federal direct appropriation to benefit the citizens of the Commonwealth by creating a unified statewide consortium to promote renewable energy and energy efficiency (REEE) in Kentucky. The Kentucky Rural Energy Consortium (KREC) was formed and seeks to advance comprehensive research on biomass and bioenergy of importance to Kentucky agriculture, rural communities, and related industries. The research goals for the consortium include dramatically reducing the U.S. dependency on foreign oil and creating an economically viable bioenergy industry in the Commonwealth.

Regional Biomass Program- Council of Northeastern Governors (CONEG)

Frederic Kuzel, Council of Great Lakes Governors

Project Summary: In the last quarter the review committees for the two Bioheat projects recommended changes to each of the projects in order to enhance the deliverables and make the projects more efficient. This necessitated additional discussion and negation with the selected contractors and has delayed the actual signing of the agreements. The Bioheat Laws and Regulations contract will be signed next quarter and the Bioheat Consumer Education project will be signed next quarter. CONEG representatives attended several congressional briefings on energy and biofuels and provided written summaries. A presentation was given on cellulose ethanol to the Eastern Lands Council and Western Land Managers Conference in DC. The Bioheat notebook is still waiting for additional research data from states. It may be necessary to distribute a partial notebook and follow-up with supplements later as reports become available. The CONEG staff hosted several conference calls and meetings with the Partnership Principal Committee and attended numerous conferences and workshops related to biofuel and cellulosic ethanol outreach and education. Spending continues to be slightly behind schedule.

The Northeast Regional Biomass Program (NRBP), a public-private, cooperative initiative funded by the DOE, is one of five federally supported programs that seeks to increase the production and use of biomass energy resources. It brings together eleven Northeastern states, the federal government, regional and national organizations, and key industrial concerns in the Northeast. The eleven states are Connecticut, Delaware, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, and Vermont. Through a combination of research and demonstration projects, outreach and education, and assessment and partnership-building, the NRBP seeks to enhance the development and use of biomass resources and technologies appropriate to the Northeast.

Regional Biomass Program-Council of Great Lakes Governors (CGLG)

Frederic Kuzel, Council of Great Lakes Governors

Project Summary: CGLG continues to monitor the state sub-grant projects through quarterly technical reports, conference calls, and email communication. Representatives from all Great Lakes states participated on conference calls of the Great Lakes Biomass Emissions Resource Group in January and February. The purpose of this group is to address common issues related to emissions from biomass energy processes. The group developed a letter to be sent to biomass combustion equipment manufacturers alerting them to the various permitting and emissions requirements in the states. The GLBSRP continues to manage the Antares project to measure success of the National Biomass Partnership. During this quarter, Antares completed the revised final reports for the Southeast and Great Lakes regions. During this quarter, Antares completed the revised final reports for the Western region, completing the reports for all five of the regions. The GLBSRP initiated the first planning conference call for the Conference on Renewable Energy from Organics Recycling, which is presented annually by BioCycle magazine. Under task E a year long drivability test continues and a winter cold start drivability test was conducted at sub-freezing temperatures using E0, E20, and E40 fuel. Spending is slightly behind schedule but CGLG continues to make progress.

The purpose of this earmark is to facilitate the increased use of bioenergy and biobased products in accordance with state and regional goals and DOE's plans and strategies. This project is intended to increase the use of biomass technologies, biomass fuels and biobased products through extensive outreach and education. The project is designed to expand and strengthen the existing networks that have been put in place over the past twenty years, benefit from the years of technical experience of its regional managers and state representatives, and to take advantage of the access provided by four regional governors' organizations to bring biomass development issues to the highest levels of state government.

Regional Biomass Program (Southeastern Biomass State & Regional Partnerships Project)

Frederic Kuzel, Council of Great Lakes Governors

Project Summary: The purpose of this project is to facilitate the increased use of bioenergy and biobased products in accordance with state and regional goals that support DOE's plans and strategies. Funding for activities during FY06 will be supported with FY05 funding.

Regional Biomass Program- Western Governors Association (WGA)

Frederic Kuzel, Council of Great Lakes Governors

Project Summary: In the last quarter, WGA continued to conduct conference calls, briefings, and agency meetings and attended several bioenergy conferences. One new state subgrant was awarded. WGA staff continued to conduct quarterly calls to track biomass related recommendations such as proposed tax incentives, possible actions the utility industry could take, and implementation plans. Timeframes and funding plans were discussed with each awardee. Additional feasibility studies have been completed and a conference was held to discuss utilization of beetle damaged trees in Colorado. WGA is slightly behind schedule with their spending but continues to make progress.

The purpose of this earmark is to facilitate the increased use of bioenergy and biobased products in accordance with state and regional goals and DOE's plans and strategies. This project is intended to increase the use of biomass technologies, biomass fuels and biobased products through extensive outreach and education. The project is designed to: expand and strengthen the existing networks that have been put in place over the past twenty years, benefit from the years of technical experience of its regional managers and state representatives, and take advantage of the access provided by four regional governors' organizations to bring biomass development issues to the highest levels of state government.

Not Reviewed

Development of Biofuels Using Ionic Transfer Membranes

UNLV

Project Summary: UNLV and subcontractor Ceramatec began work on installing equipment and evaluating various properties of NaSICON-type membranes working towards a new method of producing sodium methoxide. Training of staff is proceeding as planned and care is being taken to minimize the quantities of waste produced in the lab. Progress was made on all tasks as schedule with a few minor variances that they should be able to recover from in the next quarter. Financially they are slightly behind (18% instead of 20%) on cost share but have used approximately 25% of their budget so costs should equalize in the following quarters.

Sodium methoxide is an effective catalyst for the transesterification of vegetable oils, animal fats and recycled greases one application of which is biodiesel production. These basic catalysts are useful in processing biomass or plant based oils in general. For example, approximately 0.7 kg sodium methoxide per barrel of biodiesel is required, typically used as a 5-6 wt% sodium methoxide in methanol solution. One method produces high-purity sodium methoxide from sodium metal, an expensive raw material that also requires complex infrastructure for safe handling of sodium. Another makes sodium methoxide from Na/Hg amalgam, but the product contains trace mercury. Improved methods for producing these basic catalysts more inexpensively could benefit the oils processing industry and possibly other chemical processes requiring a basic catalyst.

The University of Nevada, Las Vegas and an industrial partner propose to investigate an electrochemical process to produce high-purity sodium methoxide from low-cost aqueous sodium hydroxide using a sodium-selective NaSICON-type membrane, providing a lower-cost yet high-purity product with no hazardous contaminants and reduced waste stream. Since the membrane is thought to be permeable to sodium only, lower-cost impure sodium hydroxide streams can be utilized. This scalable process will reduce the cost of biodiesel manufacture, and allow on-site production of the catalyst, thereby further reducing transportation costs, avoiding inventory and shelf-life costs, and reducing safety hazards. Ultimately a “one-step process” or “zero inventory option” is envisaged by integrating the on-site sodium methoxide generation with the downstream biodiesel process.

Asphalt Roofing Shingles into Energy Project, Xenia (OH)

Owens Corning

Project Summary: The project met with GO to discuss a re-scope because the cement demonstration is not proceeding as planned. Progress was made on other tasks such as: pilot scale testing of shingles fed into a pre-calciner was performed, emission analysis is pending; working with Rosby Resource Recycling to inform contractors of the opportunity to recycle shingle tear-offs; a relationship is now in place with a CFB to perform a shingle demonstration once details are worked out; work continues on developing a method to remove inorganic material (granules) from the shingles for re-use in shingle manufacturing; Phase II of the asbestos thermo-degradation study lab work was completed, field work was completed at the University of Cardiff. FL Smidth pyroprocess and emissions tests were once again postponed due to pilot testing lab availability.

The demonstration project will allow Owens Corning and a cement kiln or possible extension into a Circulating Fluidized Bed (CFB) boiler, to study the feasibility of utilizing post consumer residential asphalt shingles as an alternative raw material and an alternative fuel. The project's goals include demonstrating the feasibility of: (1) Implementing a system that moves Ohio towards long-term pollution prevention, waste reduction and recycling sustainability; (2) Creating a program and the supporting infrastructure for recapturing the natural resources of a large, consistent waste stream; and (3) Developing a demand for value-added recyclable material sufficient to create competitive market prices. The ultimate objective of the project is to demonstrate the potential value of diverting post-consumer residential asphalt shingles from landfills into a system that will sort, process and deliver materials into alternative raw material and alternative fuel applications. Additionally, slip streams (that can be created during the recycling of shingles to enhance their fuel related properties), will be evaluated for their feasibility as a raw material input into the asphalt shingle manufacturing process.

City of Stamford Waste to Energy Project

City of Stamford Water Pollution Control Authority

Project Summary: Under Task A the SWPCA and Pullman and Comely have signed their agreement to draft the subcontractor contracts. Those contracts are in draft form and are being review by SWPCA staff for accuracy and insurance and other requirements. Under Task B, some work has been started on this review although the official contracts have not been signed. A literature search is in progress. Under Task C, the SWPCA laboratory has gotten price quotations for instruments and analysis for this portion of the project. In addition, the laboratory has continued to do total and volatile solids determinations and pH on samples of dewatered biomass that will be used in the project. The SWPCA is ready to recommend and instrument and sampling system. Additionally the SWPCA has collected all ASTM and EPA approved analytical methods for the solids characterization. Spending has not yet begun but is expected to start in the next quarter with the signing of the sub-contracts.

The goal of Stamford's Waste-to-Energy project is to determine the technology needed to convert pellets of dried wastewater residual into a renewable fuel which can in turn be used to generate power. Department of Energy Funds matched with funds from the Stamford WPCA will be used to meet the objectives of the project set forth below and throughout this document.

The objectives for this project are:

- Evaluate and assess technology for thermal conversion of biomass and electrical generation.
- Perform sampling, bench-scale testing, vendor testing, and laboratory analysis to determine the most acceptable gasification alternatives.
- Prepare a detailed-alternatives analysis of selected technologies.
- Develop a preliminary design for interfaces, structures, generators (turbines), and equipment necessary to the generation process.
- Conduct economic analysis based on preliminary design.
- Prepare constructability reviews, cost estimate, and implementation schedules for construction of the full-scale demonstration facility.
- Develop final design of a generation facility including interfaces, structures, generators (turbines), and equipment necessary to the generation process.
- Produce plans and specifications for the construction of the facility. It is estimated that there will be approximately 250 design drawings and 900 pages of detailed project specification.

Madison County Landfill Gas Utilization Project

County of Madison, New York

Project Summary: A no cost time extension was granted to the project through 3/31/2008. Activities included development and internal review of an RFP. A RFP scoring document, Madison County energy cost analysis, and finalizing and release of RFP have all been delayed until next quarter. Other personnel commitments attributed to the delay. The project hopes to make up time compressing the time for review and screening of proposals.

Madison County proposes to develop a Landfill Gas (LFG) Utilization Project to recover the energy value of landfill gas produced on the site of the existing County-owned and operated landfill. This project will build on previous efforts to utilize an existing supply of landfill gas. This Madison County proposes to develop a Landfill Gas (LFG) Utilization Project to recover the energy value of landfill gas produced on the site of the existing County-owned and operated landfill. This project will identify available technologies for landfill gas utilization and select and implement the best long-term use of the fuel for implementation based on maximum recoverable fuel. Emerging technologies with a high probability of commercial success will be considered.

The landfill presently collects and flares approximately 236.5 million cubic feet of medium energy value LFG (550 Btu per standard cubic foot) per year with an existing LFG collection system. The existing system consists of piping, valves, and an 8-foot by 20-foot blower skid. The blower skid houses valves, piping, condensate collectors, safety and control devices and two 600 standard foot per minute (scfm) blowers. In June 1998, as part of a landfill closure project, the County installed these components of a methane gas collection system for environmental control and with the intention of making the LFG available for generating electricity.

Most operational LFG generation projects are larger than that which could be supported by the amount of gas easily available from the Madison County landfill. However, industry professionals and other successful projects around the state support the conviction that the amount of gas that could be recovered from the landfill exceeds the initial, default estimates.

From the outset of efforts to capture the LFG energy, an electricity generation project was favored due to high electricity prices in New York State. However, pre-deregulation conditions in New York made transmission of the electricity uneconomical. Recently, another electricity generation project was investigated in cooperation with the New York Power Authority. Cost proposals received in 2005 for that project determined that it was too expensive as designed by the Authority. It is believed that many elements of the project were over-designed.

Recently energy prices have risen. Long-term forecasts predict ever increasing costs for energy. This evolutionary change in the market dictates reassessment of uses for the landfill gas. Several entities have expressed interest in developing this landfill as a source of energy.

The County will undertake a preliminary, separately funded effort to identify physical and operational improvements in landfill-site gas management and to increase gas availability. Department of Energy funds will be used undertake a follow-on project. Types of projects that will be considered for implementation may include combined heat and power, power generation, pipeline or direct burn projects. Competitive processes will be used to identify candidate projects.

Ohio State University 4-H "Green" Building Project (OH)

The Ohio State University Research Foundation

Project Summary: This project will be completed by the time of the Peer Review. The only field work remaining on this project is under Task B. Work to be completed in the next quarter includes: exterior site work; continuing work on the building enclosure; installing heat pumps and associated piping; and beginning finishes in all phases of the building. Spending for this project is on schedule.

Ohio 4-H, a component of OSU Extension will build a 4-H Center located on The Ohio State University campus in Columbus, OH. DOE's funding is for: geothermal well drilling; installation of the geothermal loop for the building's heating and cooling system. The project covers only these aspects of the construction. Once these activities are completed, DOE’s involvement ends. That is, DOE will not be responsible for or involved with the other activities related to completing construction.