

# 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<sup>1</sup> technology plant model<sup>2</sup> 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

---

<sup>1</sup> 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.

<sup>2</sup> 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 hydroxypropionic 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  
Department of Energy  
Office of the Biomass Program, EE-2E  
1000 Independence Avenue, SW. Washington, DC 20585-0121

## Project Summaries

---

Corn Wet/Dry Mill Improvements .....	117
Sugar-based Ethanol Biorefinery: Ethanol, Succinic Acid and By-Product Production. ....	117
Improved Biorefinery for the Production of Ethanol, Chemicals, Animal Feed and Biomaterials from Sugar Cane.....	120
Integrated Corn-Based Bio-Refinery (ICBR) .....	122
Separation of Corn Fiber and Conversion to Fuels and Chemicals Phase II: Pilot-Scale Operation	125
New Sustainable Chemistry for Adhesives, Elastomers and Foams .....	130
Oil Mills Improvement.....	132
National Agricultural-Based Industrial Lubricants Center Project .....	132
Agricultural Residue Processing .....	134
Advanced Biorefining of Distiller's Grain and Corn Stover Blends: Pre-Commercialization of a Biomass-Derived Process Technology .....	134
City of Gridley Biofuels Project.....	138
Other Refinery-Related Projects .....	142
Biorefinery and Hydrogen Fuel Cell Research.....	142

---

### 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,
PMC Project Officer:	Gene Petersen		Lansing, Michigan

**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,
PMC Project Officer:	Gene Petersen		Michigan State University

**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 construction 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 hydrolysis 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 27<sup>th</sup> and 28<sup>th</sup>, 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-
<b>Sample weight, g</b>	<b>0.710</b>	<b>0.699</b>	<b>0.699</b>	<b>0.720</b>
<b>Saponified Oil weight, g</b>	<b>0.501</b>	<b>0.105</b>	<b>0.202</b>	<b>0.520</b>
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
<b>Total Sterol Concentration, Wt % of Saponified Oil</b>	<b>16.63</b>	<b>13.30</b>	<b>5.81</b>	<b>18.82</b>

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 (2<sup>nd</sup> 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	Sub-contractors:	NREL, SunOpta, Auburn Univ.
PMC Project Officer:	Gene Petersen		

**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 from 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 °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 these 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. Platform biocatalyst. 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:

### Task 1

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.

### Task 2

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.

### Task 3

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

### Task 4

Develop plans for a commercial plant that utilizes 325 dtpd of rice harvest waste that has been augmented with other local agricultural waste products

### Task 5

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 distributed 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

*Transesterification 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 – *BioOil/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 Reconsolve 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) Atomic 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