Final Technical Report

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Contents

Executive Summary

The overall objectives of this project were to provide enhanced educational resources for the general public, educational and development opportunities for University faculty in the Southeast region, and enhance research knowledge concerning biomass preprocessing and deconstruction. All of these efforts combine to create a research and education program that enhances the biomass-based industries of the United States.

This work was broken into five primary objective areas:

- Task A - Technical research in the area of biomass preprocessing, analysis, and evaluation.
- Tasks B&C - Technical research in the areas of Fluidized Beds for the Chemical Modification of Lignocellulosic Biomass and Biomass Deconstruction and Evaluation.
- Task D - Analyses for the non-scientific community to provides a comprehensive analysis of the current state of biomass supply, demand, technologies, markets and policies; identify a set of feasible alternative paths for biomass industry development and quantify the impacts associated with alternative path.
- Task E - Efforts to build research capacity and develop partnerships through faculty fellowships with DOE national labs

The research and education programs conducted through this grant have led to three primary results. They include:

- A better knowledge base related to and understanding of biomass deconstruction, through both mechanical size reduction and chemical processing
- A better source of information related to biomass, bioenergy, and bioproducts for researchers and general public users through the BioWeb system.
- Stronger research ties between land-grant universities and DOE National Labs through the faculty fellowship program.

In addition to the scientific knowledge and resources developed, funding through this program produced a minimum of eleven (11) scientific publications and contributed to the research behind at least one patent.

Project task accomplishments are detailed in the following task reports.

Project Task Area A - Biomass Deconstruction and Evaluation

Dr. Alvin Womac, University of Tennessee

Executive Summary

Biomass particle size impacts handling, storage, conversion, and dust control systems. A classifying knife mill (2-ft wide rotor) was tested for coarse/ medium size reduction of biomass, including switchgrass, wheat straw, and corn stover. Biomass selections were prioritized based on gasification potential and current cellulosic ethanol industry developments: Tennessee Biofuels Initiative – switchgrass; Iogen plant (Idaho) – wheat straw; Iowa and Oklahoma plants – corn stover. The knifemill was operated at a range of classifying screen sizes (0.5 to 2 inches), a range of feeding rates (1 to 9 kg/min), and a range of operational speeds (250 to 500 rpm, with 500 rpm being the manufacturer maximum). Tests were conducted with energy-monitored mechanical drive. Post-test particle sizes were determined using American Society of Agricultural and Biological standardized forage sieve analysis, and image analysis of particles contained on each standard sieve opening. This approach was developed because biomass stems are not spherical-shaped, hence traditional calculations using upper and lower sieve opening sizes to determine representative sizes are not valid, based on our validation tests. A Geometric Mean Diameter (actually Dimension) (GMD) was calculated following the ASABE S424.11 for both particle length and width. Particle length data are reported herein. Analysis of variance and mean separation of results indicated that different knifemill screen sizes, as hypothesized, generated different particles ($P<0.001$) within switchgrass, wheat straw, and corn stover. Example data are: Mean GMD for particle through 2-inch knifemill screen were 14.8, 14.08, and 17.0 mm for switchgrass, wheat straw and corn stover, respectively. Uniformity of particle sizes, as indicated by the standard deviation typically ranged from about 2.5 to 5 mm, with wheat straw producing the widest range in sizes. Variance in sizes among biomass increased as screen size opening decreased in size. Mean GMD for particle through 1-inch knifemill screen were 10.55, 7.33, and 7.82 mm for switchgrass, wheat straw and corn stover, respectively. Also, lower speed generated larger particles in the switchgrass ($P<.05$), but showed no difference in generate different particles in the wheat straw and corn stover cases (P=0.17

and P=0.11 respectively). These differences are attributed to observations that switchgrass did not shatter as easily as corn stover and wheat straw. Implications are that size reduction applications sensitive to dust may adjust biomass selection and size reduction process to minimize small particle generation. Interestingly, none of the three materials showed particle size difference due to feeding rate (P=0.09, P=0.14, P=0.11 for the switchgrass, wheat straw, and corn stover respectively). These data aid the selection of size reduction processes, and operating parameters, in creating a biomass product specification for biorefinery applications.

Size reduction mechanical energy was directly measured for switchgrass (*Panicum virgatum* L.), wheat straw (*Triticum aestivum* L.), and corn stover (*Zea mays* L.) in an instrumented hammer mill. Direct energy inputs were determined for hammer mill operating speeds from 2000 to 3600 rpm for 3.2 mm integral classifying screen and mass input rate of 2.5 kg/min with 90º- and 30º-hammers. Overall accuracy of specific energy measurement was calculated as ±0.072 MJ/Mg. Particle size distributions created by hammer mill were determined for mill operating factors using ISO sieve sizes from 4.75 to 0.02 mm in conjunction with Ro-Tap® sieve analyzer. Then, a wide range of analytical descriptors were examined to mathematically represent the range of particle sizes in the distributions. A total specific energy (MJ/Mg) was defined as size reduction energy to operate mill and imparted to biomass. Effective specific energy was defined as the energy imparted biomass. Total specific energy for switchgrass, wheat straw, and corn stover grinding increased by 37, 30, and 45% from 114.4, 125.1, and 103.7 MJ/Mg, respectively, with an increase in hammer mill speed from 2000 to 3600 rpm for 90º-hammers. The corresponding total specific energy per unit size reduction was 14.9, 19.7, and 13.5 MJ/Mg-mm, respectively. Effective specific energy of 90º-hammers decreased marginally for switchgrass and considerably for wheat straw and it increased for corn stover with an increase in speed from 2000 to 3600 rpm. However, effective specific energy increased with speed to a certain extent and then decreased for 30º-hammers. Rosin-Rammler equation fitted the size distribution data with $R^2 > 0.995$. Mass relative span was greater than 1, which indicated a wide distribution of particle sizes. Hammer milling of switchgrass, wheat straw, and corn stover with 3.2 mm screen resulted in ‘well-graded fine-skewed mesokurtic’ particles. Uniformity coefficient was <4.0 for wheat straw, which indicated uniform mix of particles, and it was about 4.0 for switchgrass and corn stover, which indicated a moderate assortment of particles. Size-related parameters, namely, geometric mean diameter, Rosin-Rammler size parameter, median diameter, and effective size had strong correlation among themselves and good negative correlation with speed. Distribution-related parameters, namely, Rosin-Rammler distribution parameter, mass relative span, inclusive graphic skewness, graphic kurtosis, uniformity index, uniformity coefficient, coefficient of gradation and distribution geometric standard deviation had strong correlation among themselves and a weak correlation with mill speed. Results of this extensive analysis of specific energy and particle sizes can be applied to selection of hammer mill operating factors to produce a particular size of switchgrass, wheat straw, and corn stover grind, and will serve as a guide for relations among the energy and various analytic descriptors of biomass particle distributions.

Project Activity Summary

Biomass selections were prioritized based on gasification potential and current cellulosic ethanol industry developments: Tennessee Biofuels Initiative – switchgrass; Iogen plant (Idaho) – wheat straw; Iowa and Oklahoma plants – corn stover.

Size reduction energy was validated by re-checking instrument calibrations, sampling, and conversions; comparison of results with published values for similar materials; and by examining trends in the measured data over operating parameters. Initially, collected torque and speed voltage data were converted to normal units using instrument specifications and calibration curve, respectively. The converted data were filtered using a 2^{nd}-order Butterworth band-pass filter. Sensor sampling frequency was determined by sampling each channel from 1 to 24 kHz, and then examining the power spectra, and then applying Nyquist sampling theorem to ensure sampling at least 2x the highest frequency that had appreciable power. Most of the torque and speed frequencies were in the order of 10 and 2 Hz, respectively, for all power spectra between 1 and 24 kHz sampling rates. A sampling rate of 1 kHz was determined. In addition to continuous computer monitoring of a speed sensor, independent measures of speeds were taken with a handheld laser tachometer (± 0.05% accuracy). Overall accuracy of power was calculated to be ±0.003 kW. Total specific energy was determined in kWh/Mg (and MJ/Mg) from the mass feed rate data and power. Effective specific energy was determined by subtracting idle energy from total energy. SAS Non-Linear Regression (NLIN) and Generalized Linear Model (GLM) procedures were used for regression fits and analyses. Total specific energy consumption was regressed as a function of screen size, mass feed rate, and rotor speed in second order polynomial equations. Total specific energy equations were optimized for finding optimum operating parameters of knife mill by determining the function minima values of energy using Non-Linear Programming (NLP) and by maximization of coefficient of determination values. An energy utilization ratio was calculated as the ratio of effective specific energy to total specific energy. It should be emphasized that direct measures of mechanical input energy into size reduction were highly unique for these experiments – most published values were based on inferred values using indirect means. Published values were typically based on fuel use in an internal combustion engine without compensation for engine efficiency (typically 30 to 50 %), or electrical energy use that did not compensate for electric motor efficiency and power factor. Other difficulties in comparisons with published values were a lack of corresponding published particle sizes. Expected trends were found in some published comparisons, such as increased energy with decreased particle size. Also, results of other knife and hammer mill tests with screen sizes similar to our sizes produced values with similar orders of magnitude. Our particle sizes classifications were determined with thickened, horizontal-excited forage sieves (Amer. Soc. Agr.& Biol Engineers forage standard sieves) that reduced sieve spearing by biomass particles having high dimensional aspect ratios (ie long and thin stems). Thus, measures are indeed classifications. For validation, dozens of sieved samples were manually measured, and were subjected to calibrated imagery analyses. Those results indicated that coarse reduction of grasses had particle lengths ~5x the geometric mean dimensions (GMD, determined from sieve opening dimensions) and particle widths ~ 0.3x GMD. Validating particle area of porous biomass with direct measures is more elusive, primarily because B.E.T. methods using a gas to coat outer surface areas also disperses gas product into the porous regions of the biomass. Hence, surface area measures were comparable among different degrees of size reduction. So, area validation is being closely tied to refined measures of particle size and shape.

Size reduction of dry biomass (<20% moisture wet basis, w.b.) through size reduction equipment equipped with classifying screens had much greater mass throughput than the same biomass in wet condition (~50% moisture) through the same mills under same operating conditions. Wet condition of an energy crop (switchgrass) and an agricultural residue (corn stover) were most prone to reduced mass throughput due to blockage of the classifying screen – due to buildup of fibrous rind. Mass throughput is an important variable for capacity and energy. Instrumented test runs of knife mill size reduction indicated total specific energy ranging from 10 to 40 kW-h per metric ton, for low-moisture switchgrass and classifying screen opening from 1.9 to 5 cm. Increased-rotational speeds significantly increased size reduction energy. This increase may be due to increased losses due to adding inertia to the biomass, increased frictional losses between classifying screen and biomass, and parasitic power losses of the equipment. An understanding of the actual energy and the effects of operating parameters aids in determining the tradeoffs in particle size specification for downstream processes.

Finest particle size reduction was completed using a staged approach by passing knife mill-classified biomass through a hammer-mill classifying process. Particle size validations after classification were performed with a high number of very fine sieves with openings ranging in size from 20 to 4,750 microns. Typical geometric mean particle sizes were ~1200 microns produced with a mill classifying screen of 3,175 microns. Similar trends were observed with the coarser knife mill particle and classifying screen sizes. Total specific energy to produce these small biomass particles with the hammer mill had an order of magnitude of 55 kW-h per metric ton. Increased hammer mill speed from 2000 to 3600 rpm increased energy consumption by an approximate factor of 1.7. This trend of increased energy was also very prominent with the knife mill. Again, it appears that the increased energy with increasing speed is due to a combination of (1) adding inertia to the biomass, (2) increased frictional losses between classifying screen and biomass, and (3) parasitic power losses of the equipment in bearings and power transmission. Interestingly enough, these energy losses overshadowed the differences in ultimate failure stress of different biomass selections (corn stover, wheat straw, and switchgrass, to name a few). An understanding of the actual energy and the effects of operating parameters aids in determining the tradeoffs in particle size specification for downstream processes.

Validation of particle sizes and areas were conducted by sieving, image analysis, observation of particle shapes, and calculation techniques. Direct measures of particle sizes with laser diffraction, such as those based on Fraunhaufer theory of spherical particles, were deemed not appropriate since coarse biomass particles were not spherical. Also, direct measures of particle area did not correlate well with particle size distributions. One example was the B.E.T. method using a gas to coat sample surface areas that also evidently coated internal porous regions of the biomass. All sieve methods were not appropriate either. Sieving with vertical-excitation, screen-type ASTM sieves gave completely different results compared to horizontal-excitation, punched-aluminum ASABE sieves. ASTM particle spectrum results for switchgrass, corn stover, and wheat straw were much finer than ASABE results, and this was attributed to spearing of sieves with particles of high length-to-width aspect ratios. Image analysis of same particle sizes indicated that geometric mean sizes determined by sieves under-estimated length values, and over-estimated width values, as verified with manual measures of particle dimensions. However, use of image analysis of biomass particles in two dimensions provided an improved basis for validation, and compensation of offsets in sieve values. Estimates for third-dimensions were based on smallest of the two other dimensions. This allowed for calculation of surface volume and area based on external measures. Thus, it was determined that outer particle area can be calculated based on observation of particle shape, size, and partition mass for samples partitioned using ASABE sieves and image analysis. Validation was performed by comparing calculated surface areas before and after size reduction. Wrong assumptions of particle shape were often disclosed by observing opposite-than-expected trends in surface area before and after size reduction (after-grind surface area should be greater than before-grind surface area). Another observation was that particle area should increase for decreased particle sizes. Hence, surface area measures were validated using refined measures of particle size, shape, mass partition, and observation of trends versus indicators of particle distributions.

Publications Produced

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Project Task Areas B and C - Fluidized Beds for the Chemical Modification of Lignocellulosic Biomass

Dr. David Harper, University of Tennessee
Dr. Duane Bruns, University of Tennessee

Executive Summary

The main goal of this project was to find an efficient method for chemically modifying biomass to improve its utility and profitability in the marketplace. To this end, the project was very successful. At the onset of the project, fluidized beds were targeted as a means to modify biomass chemically. This did not prove successful. However, fluidizing biomass did prove effective for sorting, conditioning, and drying. This will be an integral part of the front-end of any biomass handling facility. Instead, the fluid-bed reactor was redesigned to provide blueprint for constructing a small-scale biomass pyrolysis plant. This plan can be implemented and modified to produce a liquid fuel from biomass with a very small capital investment via the thermochemical route. The modification part of the project was continued utilizing novel wet chemical methods. These proved successful in modifying a potential high value product of a cellulosic biorefinery. This product can be used in reinforcing plastics, flexible transparent films, and biomedical applications. In addition, methods were developed for process monitoring and incorporating modified cellulosics into products that will further reduce costs once implemented.

Introduction

Essential to improving the economics of biofuels is to develop new chemicals and materials from cellulosic sources. Petroleum refineries operate under the same concept by providing fuel as well as many chemical byproducts that are the raw materials for many goods. Thus, there is a necessity to development new biomass processing methods to promote the use of renewable feedstocks. Eventually, the feedstock will replace the use of some hydrocarbon resources, reduce the related green house and environmental issues, and reduce dependence on imports. Utilizing biomass as a feedstock can be energy intensive. Biomass has a very low bulk density, which is increased through size reduction. After reducing the size, the material must be dried and sorted for use in different products. One can take advantage of the size reduction by fluidizing it in a fast moving gas stream. The fluidized material can then be dried in a fluidized bed and sorted by a series of cyclones. The reduced size, increased surface area, and efficient mass transfer afforded by the fluidized environment allows for the potential modification of the physical and chemical nature of the biomass.

Project Goals and Objectives

The goal of this project was to develop a highly efficient process for drying, sorting, and modifying biomass for use as renewable material in durable goods. In addition, this project has the objective to evaluate and utilize the modified biomass in prototype materials to assess its performance characteristics. Ideally, the reactor design for a prototype process will be flexible enough to run a wide range of conditions and reactive gases to provide several modification options. The reactor design would is to produce reactions at the solid/gas interface in order to minimize use of solvents, the amount liquid waste, and the amount residual unreacted material in the finished product while simultaneously maximizing efficiency by recycling the reactive gases. This process was to be compared to more traditional methods of modification for effectiveness and efficiency.

Project Results

<u>Fluidization of Biomass</u>

A prototype train of equipment was developed to condition and separate biomass that is in a particulate form. It contains in order: 5-cm spouted bed with a 30-degree inclusive cone with a single inlet, 10-cm cyclone and 2.5-cm cyclone. The cyclones were fabricated with the design dimensions given in Perry's Chemical Engineering Handbook. The spouted fluidized bed separates particles by elutriation (drag force) and each cyclone exerts a centrifugal force on the particles along with a drag force. Demonstration of particle classification was completed. Roughly 100 grams have been classified by slowly ramping the fluidization gas flow rate up 2 slpm and then holding the flow rate constant until very few additional particles are being elutriated from the spouted bed. The particles are classified into 6 cuts. They are ready for size distribution analysis and wet chemistry studies to evaluate the effect of particle size on amount of acetylation. Presently, this is done manually taking about 5 hours to separate a 30-gram charge of particles.

Electrostatics are important in the fluidization of particles from both safety and operational aspects. For safety electrostatic discharge must be avoided in explosive atmospheres, this is a concern for all sizes of particles. Operationally, static makes the particles stick or clump together which becomes more important as the particles get smaller where Van der Waals forces dominate. For classifying our wood flours electrostatic and gravitational forces are important. Electrostatics is one reason that screen cuts fail in classifying wood flours as small particles remain in all cuts. We have found that fluidizing with air from 40 to 50% relative humidity can largely mitigate electrostatics. This amount of relative humidity is the best for all sizes of particles that we have fluidized. Spouted beds with cone angles of 30, 45 and 60 degree inclusive were evaluated. The 30-degree cone was clearly the best. Small amplitude vibrations are also known to help with fluidization of small particles. This has been tried with a small engraver with positive results. Loading the bed with other heavier particles has also led to enhanced fluidization. Limited trials with a variety of size, density and weight fraction of added particles have been made. If such particles are magnetic, separation from the residual (largest) particles in the bed could be easily accomplished. Pulsation of the fluidized gas utilizing a rotating ball valve showed major effects on fluidization and elimination of dead zones. Thus, this concept has been evaluated over an experimental matrix that included fluidizing gas flow rate, gas split between the constant flowing and pulsating stream, and pulse frequency. Operating conditions were identified that provided acceptable operation of the spouted bed with a particle depth up to 6 inches from the gas inlet.

Gas Phase Modification of Biomass

One of the main objectives of this project was to accomplish gas phase modification of biomass. Several attempts were made to achieve some level of modification with fixed bed reactor designs. The first attempts were made with closed fixed bed reactors (Figure 1). The bed temperature was maintained at 160°C to allow for the flow of gas through the reactor without condensation of the acetic anhydride on the biomass. After several attempts with this configuration, a significant amount of condensation was still observed on the biomass. The first reactor was made from quartz and glass. The second model was made of stainless steel and was a completely closed system. Ultimately, a high enough gas flow with enough acetic anhydride was never achieved to be able to get a detectable amount of biomass conversion without condensation. Modification of up to 10% gain in mass was detected in several runs, but these were determined to be caused by the condensation of the gas in the high pressure environment in the reactor.

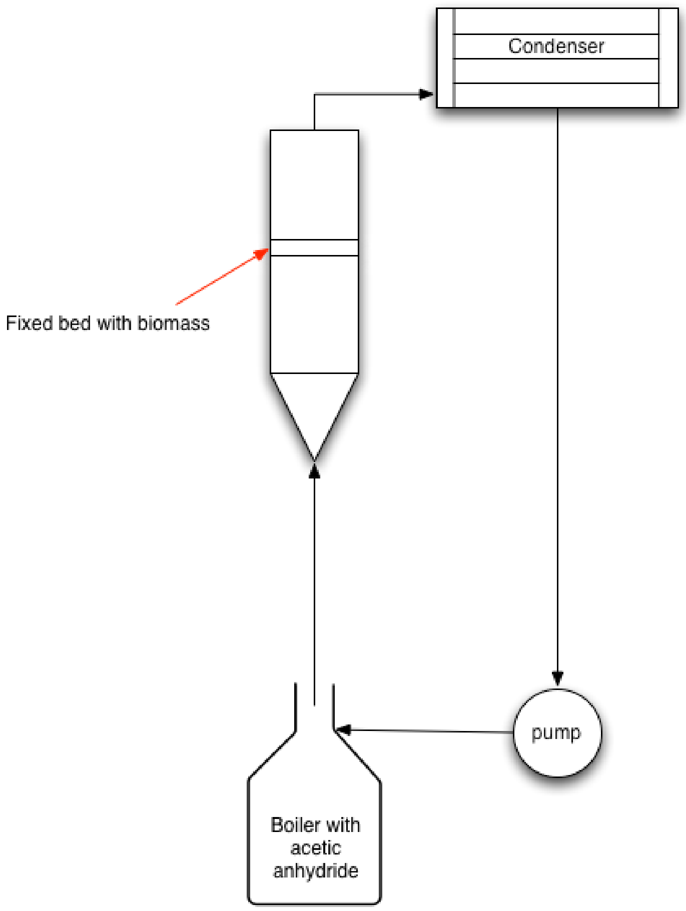


Figure 1. Fixed bed reactor with recirculating gas flow.

This phase of the project was abandoned after multiple attempts to achieve a result. Focus shifted to modification of the fluid bed for pyrolysis. Further chemical modification to produce modified biomass was carried out under wet conditions as discussed in more detail following.

Design of Fluidized Bed Reactor for Fast Pyrolysis

A report detailing the building of a fluid bed reactor for the fast pyrolysis of biomass was produced (Appendix A). The work details the process flow, material and labor costs, and energy balance. The reactor design was for a plant that would convert one ton of dry biomass a day into pyrolysis oil. This was targeted as a pilot scale operation. For this process, the pyrolysis oil will have 20 times the energy content compared to the process heat needed to produce the liquid. This assumes energy content of 80,000 BTUs/gal of pyrolysis oil.

Modification and Monitoring of Biomass Modification

The ability to modify and monitor the modification process via near infrared (NIR) instrumentation and multivariate statistical models was established. The NIR technology was used to help optimize and quickly evaluate biomass conversion in the biomass reactor. However, the method was never applied to that application due to gas reactor's inefficiency. The technology is applicable to industrial application of NIR technology to biomass modification. The details of the study and analysis are contained in Appendix B.

Two primary methods were used to modify biomass in this project, acetic anhydride and vinyl acetate modification. Some of the spectroscopic evidence suggests that these modification methods preferential modify the various wood polymers at different rates. Mechanistically you still arrive at the same reaction product in the end, acetylated wood hydroxyls (Figures 2 and 3).

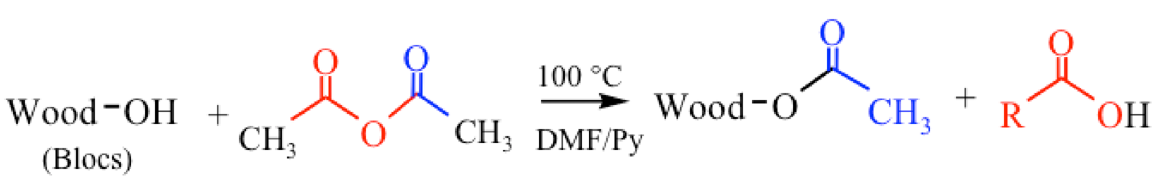


Figure 2: Modification of biomass with acetic anhydride.

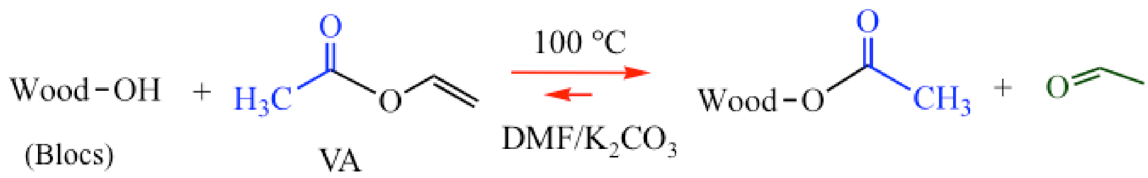


Figure 3: Modification of biomass with vinyl acetate.

Infrared spectroscopy found slight differences in the chemistry of the two modification methods when using principal component analysis (see Appendix B for methodology) (Figure 4). These differences are believed to be indicative of a preferential modification for acetic anhydride to modify lignin preferentially and vinyl acetate to modify polysaccharides. Further evidence of these differences in reaction pathway is observed in the mechanical response of the wood polymers through solid rheology. As the modification levels increases with acetic anhydride modification, the storage modulus decreases (Figure 5a). Also, there is a change in the transition temperature of lignin, between 50-100°C, to lower temperatures compared to the control with increasing modification. The same behavior is not evident in the vinyl acetate modified wood (Figure 6b). However, the storage modulus, which is associated more closely with cellulose structure, does demonstrate more dependence on the modification level with vinyl acetate modification. At higher weight gain levels differences in modification levels for any of the wood polymers between the two reaction pathways are indistinguishable. A need still exists to define the kinetics of each of these two reaction pathways.

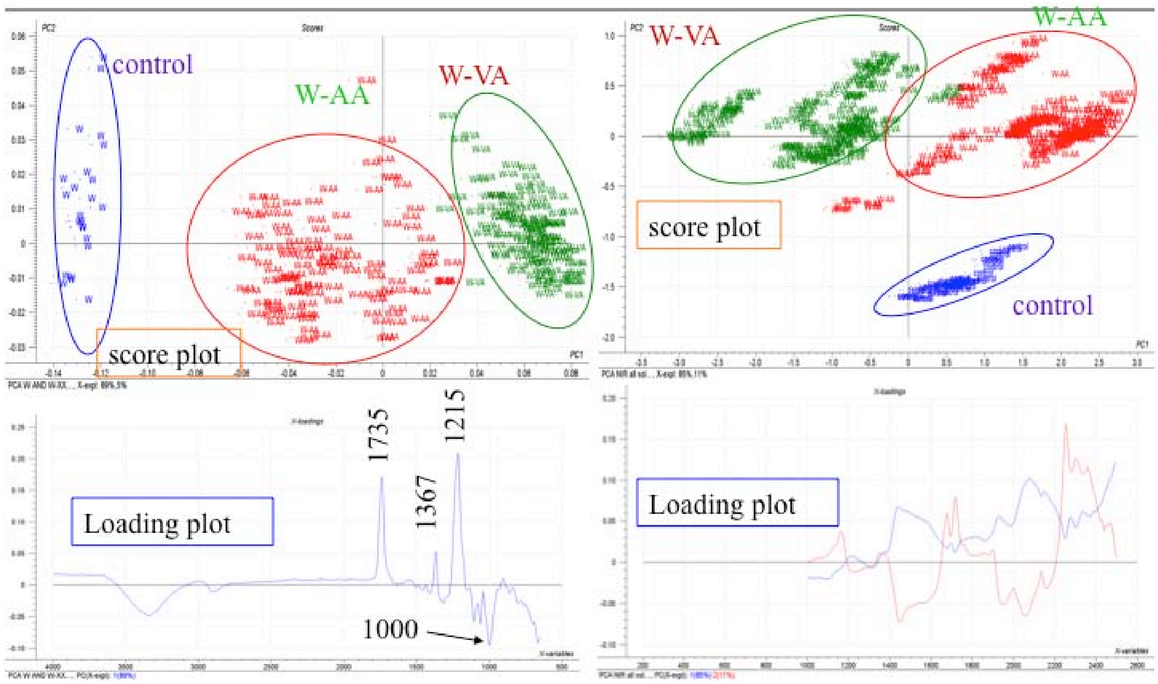


Figure 4: PCA score and loading plots for 13% weight gain for vinylacetate (VA) and acetic anhydride (AA) modification of wood.

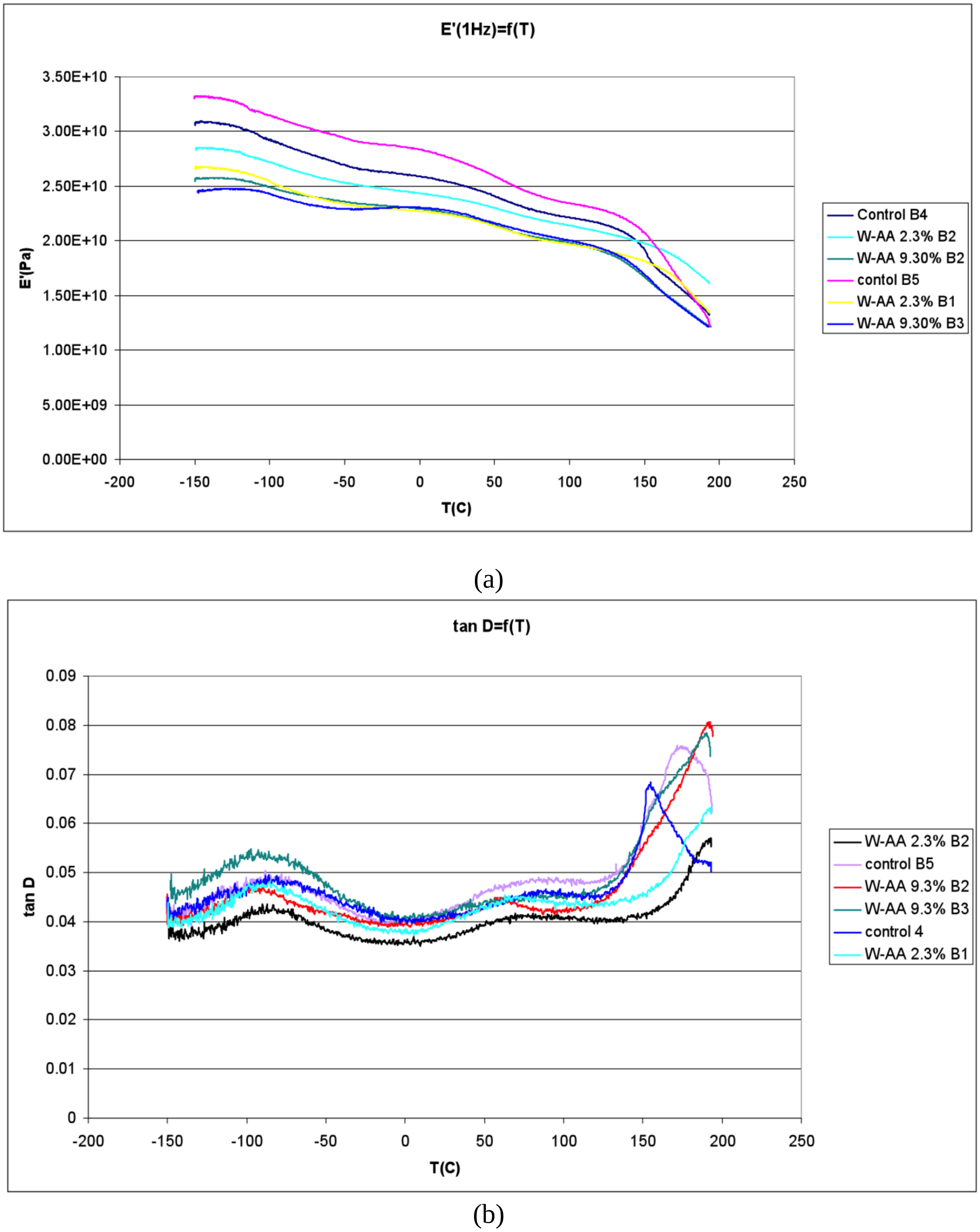
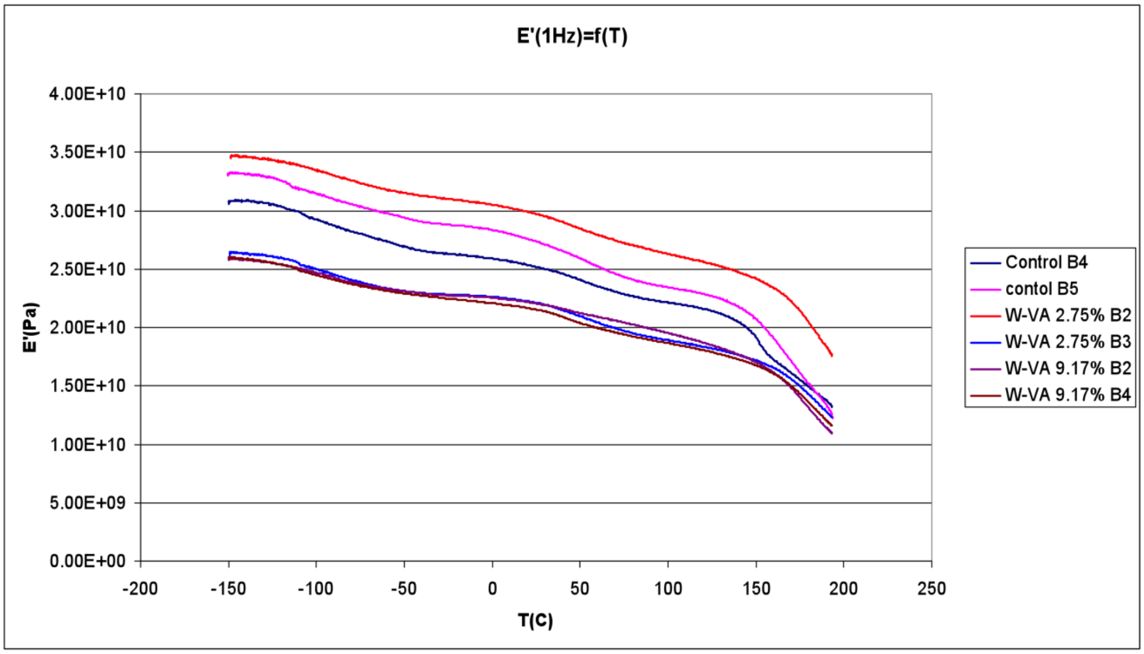
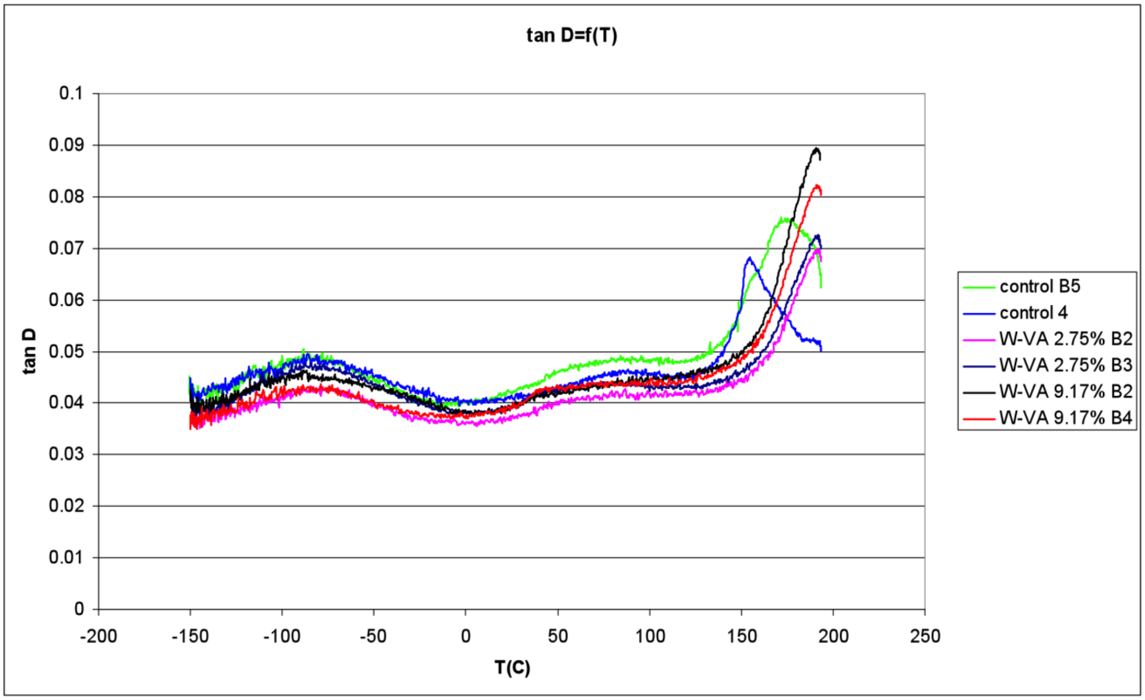


Figure 5: (a) the storage modulus for AA modified wood and (b) the loss tangent for AA modified wood.



(a)



(b)

Figure 6: (a) the storage modulus and (b) loss tangent for VA modified wood.

Modified Nanomaterials

Cellulose, the main structural component in a plant cell wall, is the most abundant renewable resource on Earth. Cellulose is also the main feedstock being considered in second-generation biorefineries for the production of liquid fuels. Much of this material will not be completely converted into sugars because of its crystalline nature. What will remain after the saccharification process are micro or nano fibers that are highly crystalline.

These fibers have the potential for utilization in a large numbers of applications and provide a valuable revenue stream for biorefineries. The modulus of nanocellulosic crystals has been estimated to be in the range of 105 – 137 GPa.[1] One of the biggest problems with using the fibers as a possible reinforcing fiber is their propensity to agglomerate and not disperse in many matrices. In order to solve this problem, we used several modification methods to enhance the dispersion of these fibers in nonpolar matrices and weakly polar solvents.[2] Many of the same characterization techniques discovered earlier in the project were applied to these fibers for the different modification methods.[3] The details of these studies can be found in Appendices C and D.

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Project Outputs

Refereed Manuscripts

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P. Tingaut, N. S. Çetin, N. Özmen, N. Henry, D. P. Harper, M. Dadmun, G. Sèbe. 2009. The acetylation of cellulose nanowhiskers with vinyl acetate under moderate conditions. *Macromolecular Bioscience*. 9(10): 997-1003. 10.1002/mabi.200900073. *Uploaded to DOE reporting system separately.*

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Presentations

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LaToyia Thompson, Chris Wheat, and Tina Stewart, Chemical Engineering Senior Research Project, "Billion Ton Report with Poplar Trees as Surrogate Biomass and Spouted Fluidized Beds, Subtitle: Equilibrium Moisture Content (EMC)", Knoxville and Oak Ridge AIChE Section, Student Awards Banquet, April 26, 2007.

N. Çetin, N. Özmen, P. Tingaut, D. P. Harper. 2009. Chemical modification of cellulose whiskers with acetic anhydride. The Tenth International Conference on Woodfiber-Plastic Composites. Madison, WI.

New Collaborations

An international linkage between the University of Bordeaux I and The University of Tennessee Institute of Agriculture was established because of this project.

A collaborative relationship was established between the faculties at the Kahramanmaras Sutcu Imam University in Kahramanmaras, Turkey.

New Technologies/Techniques

Through project funding, we were able to establish the ability to sort and condition particle to a specified moisture content using a fluidized bed with a series of cyclones.

A pyrolysis pilot plant design was produced from data collected during fluidization experiments (*Uploaded to DOE reporting system separately).*

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The ability to manufacture nanocrystalline cellulosic particles was established using acid hydrolysis.

New methods of modifying nanocrystalline cellulose was discovered. This allowed for these materials to disperse and be suspended in weakly polar media.

Project Task Area D – Analyses for the Non-Scientific Communities

Dr. Kelly Tiller, University of Tennessee
Dr. Jim Doolittle, South Dakota State University
Dr. Tim Rials, University of Tennessee
Dr. Sam Jackson, University of Tennessee

Executive Summary

Significant research and resources have focused on a variety of issues related to renewable bio-based energy (fuels and power) and products (chemicals and materials). A number of efforts—both government and academic, public and private—have developed roadmaps for various aspects of further developing a biomass industry to promote the development and use of renewable bio-based energy and products. Potential benefits include reduced dependence on foreign oil, increased dependence on domestic sustainable renewable resources, reductions in harmful pollutants and greenhouse gases, and agricultural sector and rural development benefits. Despite the vast biomass knowledge and research base, key missing components are a common thread that weaves various aspects of biomass research together in a coherent picture, translation of academic research findings into a format that can be understood and interpreted by policy makers and the public, and a comprehensive quantitative analysis of the potential impacts associated with a highly developed and successfully integrated biomass industry. Diverse stakeholders—from academic researchers to policy makers to the general public—need to know where we are today, what the feasible alternatives are for moving forward, and what the impacts may be.

The finished BioWeb product can be found at http://bioweb.sungrant.org.

This research has engaged some of the country's most knowledgeable and highly respected biomass researchers to

(1) provide a comprehensive analysis of the current state of biomass supply, demand, technologies, markets, and policies;

(2) identify a set of feasible alternative paths (based on a predetermined set of criteria) for biomass industry development; and

(3) quantify the impacts (economic, environmental, ag sector, trade, rural development, among others) associated with the set of feasible alternative paths selected.

Task Summary

As described in more detail below, the activities of this project was coordinated and conducted jointly with South Dakota State University, co-recipients of the DOE biomass special appropriation. The summary of tasks that follows includes the full scope of the joint project effort.

- Established a small steering committee to coordinate and monitor the project.
- Commissioned 111 separate topical area research papers/content sections.
- Began the development and publications process for a series of policy briefing papers.

Project Description

The Sun Grant BioWeb is a public, educational website that provides current information about biomass resources for bioenergy and bioproducts. This site is designed to helps a user understand: What biomass is, where it is, and how much is available, The ways it can be converted to biofuels, biopower, and bioproducts, The current state of biomass technology, research, production, and use, and Biomass economics and policy.

BioWeb is an online resource for information and data on bioenergy and bioproducts created from biomass. This electronic resource allows data to be dynamically compiled into practical and relevant content on a particular topic of interest. The content is available at varying levels of complexity for use by a diverse range of audiences. This project has engaged some of the country's top experts to provide a comprehensive analysis of the current state of biomass, alternative paths for biomass development, and economic and policy considerations. BioWeb also describes regional differences and opportunities related to biomass.

Information found on this site is useful for scientific researchers, policy makers, large- and small-scale industry, agricultural producers, and anyone who wants to learn more about biomass and its uses.

BioWeb represents a joint effort of the five U.S. regional Sun Grant Centers of Excellence (University of Tennessee, South Dakota State University, Oregon State University, Oklahoma State University, and Cornell University). BioWeb contributors represent a broad spectrum of expertise in the biomass arena, including universities, national laboratories, federal agencies, state governments, and private industry.

BioWeb is not new research or unvetted ideas. Rather, it is a first-of-its-kind organization and packaging of existing work, reviewed by academic professionals for accuracy. This resource complements existing research and educational efforts. BioWeb fills a niche that can benefit all agencies, organizations, and individuals contributing to the advancement of a feasible and valuable biobased industry for America.

Content Development Methodology

To develop and organize content, BioWeb is built on a content management system (CMS) utilizing a dedicated web server. This system allows data and content to be digitally managed with ease. The CMS is centrally managed by the BioWeb IT Support Staff (1, Figure 7). Research Section Coordinators identify top industry, government, and academic experts to author content related to specific bioenergy and bioproduct fields (2-3). Content reviewers are selected in a similar process. Both authors and reviewers are recognized authorities in their respective fields.

Section Coordinators also serve as primary editors for the five major focus areas (Feedstocks, Biofuels, Biopower, Bioproducts, and Biorefineries). Under their direction, content is entered into the CMS. All content of BioWeb is reviewed by independent authorities who have expertise and familiarity with the assigned subject matter (4). Reviewers are responsible for ensuring that content meets with BioWeb's standards of accuracy, relevancy, and quality. The CMS stores all content and editorial comments. It also provides a mechanism for conducting and tracking the review process. Once content is approved for publication, a technical writing team further edits the content and formats it for presentation in three different levels of detail. The three levels are: At-A-Glance (an overview summary), General (a more detailed but condensed version of the content), and Technical (the full academic text). Once the content is authored for all detail levels, the CMS creates individual webpages, constructs site navigation, and makes the content

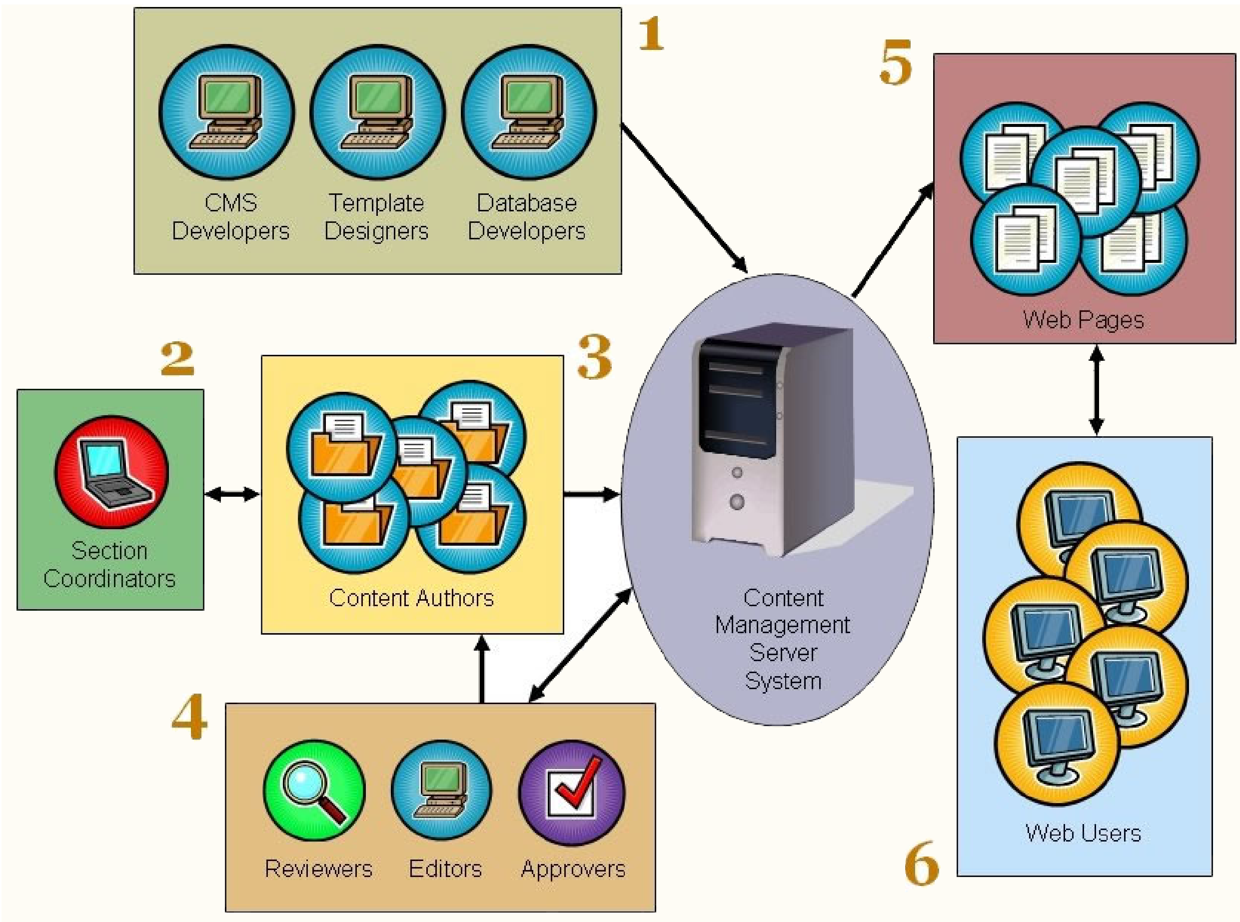

Figure 7 - BioWeb Review and Publication Process

available to web users (5-6). Users may access content through searches, a table of contents, or prepared navigation channels.

Content Summary

As noted, over 111 separate content sections were authored, reviewed, edited, and posted as content on the BioWeb site. The list of content areas is included as Appendix A.

Project Management

The BioWeb project was led by Co-Directors James Doolittle, South Dakota State University and Kelly Tiller, University of Tennessee. The project steering committee included William Boggess, Western Sun Grant Center; Ray Huhnke, South Central Sun Grant Center; Terry Nipp, Sun Grant Association; Timothy Rials, Southeastern Sun Grant Center; Norm Scott, Northeastern Sun Grant Center; and Richard Shane, North Central Sun Grant Center.

The project implementation team included BioWeb Editor Marie Walsh (University of Tennessee), Project Coordinator Sam Jackson (Southeastern Sun Grant Center), editors Joelle Brink and Evelyn Winther (University of Tennessee), programmer Sachiko Hurst (Southeastern Sun Grant Center), as well as section coordinators Marie Walsh, University of Tennessee (Feedstocks); Wally Tyner, Purdue University (Biofuels); Burt English, University of Tennessee (Biopower); Steve Kelley, NC State University (Bioproducts), and Marie Walsh, University of Tennessee (Biorefineries).

Information regarding specific authors and reviewers can be found on the BioWeb site at http://bioweb.sungrant.org.

Impacts

Since launch in April 2007, the BioWeb site has had 29,771 unique users who have viewed over 119,000 pages. Visitors hailed from 161 different countries, with the top five sources of visitors being the United States, Canada, United Kingdom, India, and Germany. The top content selection by users was ethanol conversion technologies, specifically cellulosic sources of ethanol.

Project Task Area E – Faculty Fellowship Program

Dr. Tim Rials, University of Tennessee
Dr. Thomas Klindt, University of Tennessee
Dr. Sam Jackson, University of Tennessee

Executive Summary

Supported by the DOE funding in this project, the Tennessee Agricultural Experiment Station (TAES) developed a program by which faculty at land-grant universities in the southeastern US could take a leadership role in the Nation's research effort around biofuels and bio-based materials. The scope and complexity of this research challenge demands renewed emphasis on establishing collaborative research and formal partnerships with external organizations such as The Department of Energy's National Laboratories. To facilitate this, a fellowship program was made available to provide support for research experience at Oak Ridge National Laboratory or the National Renewable Energy Laboratory.

Project Activity Description

TAES announced the availability of funds the fellowship program in 2006. TAES is solicited applications for financial assistance for collaborations addressing research, development, and demonstration of biomass based products, bioenergy, biofuels, biopower, and related processes. This funding opportunity was intended to promote greater innovation and development related to biomass, and to establish working relationships with national laboratories conducting research for greater use of biomass-based products, feedstock production, and processing and conversion.

The fellowship will supported all travel and living expenses for research experience ranging from 2-4 weeks (alternative time spans were subject to negotiation) at ORNL and NREL. The applicant was responsible for identifying potential collaborators to participate in a project of mutual interest and benefit. Also, all details of the travel and research partnership were arranged by the applicant. Importantly, research costs were covered and not be incurred by the sponsoring laboratory. This program also would not consider salary requests for individuals supported through external funds. Also, it was expected that the DOE collaborator would visit the participating university's campus for further interaction with faculty, and to present a seminar on recent research activities and opportunities.

To be eligible for a fellowship, the applicant had to be faculty, research associates, and/or postdoctoral researchers actively involved in biomass-related research at southeastern Land-Grant Universities.

Fellowship applications were accepted through 2006 and 2007. Applicants submitted an application form, a letter of support from the partnering National Laboratory, and any other supporting documentation necessary.

The program helped build relationships with national lab partners through cooperative work focused on projects designed to advance the development of the bio-based economy. In many cases, the research generated data for publication in peer-reviewed journals. Also, it is expected that the DOE collaborator will visit the participating university's campus for further interaction with faculty, and to present a seminar on recent research activities and opportunities.

Through the course of the program, five fellowships were awarded to faculty at three institutions with partners at both national labs. The results were better than expected. Strong research relationships were established that have lasted well beyond the initial term of the program. Important research goals were achieved, including some patentable and publishable work.

Awarded Fellowships

PI: Nicole Labbe, University of Tennessee

Research Partner: Luc Moens, National Renewable Energy Laboratory

Title: Biomass cell wall deconstruction by ionic liquids

Abstract: In biomass conversion, pretreatment has been viewed as one of the most expensive processing costs. In the cellulosic biomass-to-fermentable sugars conversion it can cost as high as 30c/gallon of ethanol produced. However, pretreatment is an indispensable step. It is required to alter the biomass macroscopic and microscopic size and structure as well as its submicroscopic chemical composition and structure so the cell wall deconstruction can be achieved more rapidly and with greater yield. For example in biomass-to fermentable sugars conversion, pretreatment makes cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars. The goal is to break the lignin seal and disrupt the crystalline structure of cellulose. Also, pretreatment has great potential for improvement of efficiency and lowering cost through research and development.

Early works have reported the power of ionic liquid as a solvent to dissolve cellulose. Research at the National Renewable Energy Laboratory emphasizes the development of new technologies for conversion of biomass, employing novel separation technologies. Dr. Moens is exploring the use of new solvent systems based on ionic liquids as reaction media to catalytically convert carbohydrates and lignin into useful chemicals. This fellowship will give me the opportunity to work with Dr. Moens and learn from his expertise to design new ionic liquids with desirable properties. This work will investigate the use of ionic liquids in the fermentation process, to increase accessibility for the degradation process. In addition to use ionic liquids in the pretreatment step in the cellulosic biomass-to-fermentable sugars conversion, ionic liquid can also be used in the second step, as a solvent for the enzyme-catalysed reactions. Ionic liquids have elicited an immense degree of recent interest as neotric solvents for enzyme-catalyzed reactions. A number of enzymes have been shown to retain high levels of catalytic activity in ionic liquids, with small variations in the chemical composition of the solvent.

PI: Y.H. Percival Zhang, Virginia Tech

Research Partner: Dr. Jonathan Mielenz, Oak Ridge National Laboratory

Title: Novel High-Yield Hydrogen Production from Polysaccharides Artificial Enzymatic Pathway

Abstract: Abundant, clean, and carbon-neutral hydrogen is widely believed to be a promising future energy carrier; high energy efficiency can be achieved via fuel cells. There is an increasing interest in using energy-rich biomass as a feedstock for the production of renewable fuels such as hydrogen, but so far all methods for doing so have been plagued with low energy yields, severe reaction conditions, and complex processing requirements, e.g., direct gasification of polysaccharides; direct glucose chemical catalysis; anaerobic fermentations; and ethanol fermentation followed by ethanol reforming. Furthermore, the lack of high-density hydrogen storage technologies and the relevant infrastructure for hydrogen storage and distribution prohibits realization of the hydrogen economy.

Recently, we invented a new technology for producing hydrogen from sugars (starch and cellulose). The idea is to utilize energy stored in sugars to break water and release energy in the form of hydrogen by a number of enzymatic reactions. This work was based on my previous work published in PNAS 2005 and ORNL's work published in Nature 2000. The provisional patent has been filed jointly by Virginia Tech and Oak Ridge National Laboratory in May 2006.

Publications Produced from this research: High-Yield Hydrogen Production from Starch and Water by a Synthetic Enzymatic Pathway

Dr. Zhang and his colleagues have also applied for a patent on this technology.

PI: Philip Ye, University of Tennessee

Research Partners: Drs. Zhiyu Hu and Thomas Thundat, Oak Ridge National Laboratory

Title: Autothermal Conversion of Glycerol to Hydrogen Under Nano-crystals

Abstract: The objectives of this project are to develop an autothermal conversion process of raw glycerol to high yield of hydrogen under nano-catalysis and to study the reaction kinetics. We will research catalysis mechanism at nano-scale in the autothermal glycerol conversion and present a proof-of-concept of autothermal conversion of glycerol to hydrogen using nano-catalysis. Detailed reaction kinetics measurements and analyses will be conducted through extensive experimental work in order to prove the concept and accumulate data for larger funding opportunities.

Recently, using nanocatalytic particles we achieved autothermal conversion of (glycerol + water) that generates high yield of hydrogen with high selectivity and nearly complete conversion rate external heat input. Our preliminary tests show that this autothermal process had been achieved at a temperature as low as 60% of what is found in normal ethanol reforming to hydrogen process, significantly lowing energy input in hydrogen production. This heat-integrated catalytic process could also be a less energy-intensive alternative to current methods of converting carbohydrates into fuel-grade ethanol.

PI: Adrianna Kirkman, North Carolina State University

Research Partner: Steve Phillips, National Renewable Energy Laboratory

Title: Process modeling for integration of biofuel production in existing pulping facilities

Abstract: The sustainable and cost-effective conversion of biomass to biofuels or bioenergy requires the complete and careful utilization of the biomass feedstocks. A key element in the development of these conversion processes includes integration of process heat and energy, including biomass drying. Many of these heat and energy integration questions can be answered with modeling software.

Process modeling is an efficient and cost-effect method to highlighting the technical and economic challenges for developing new technologies. Process modeling is particularly valuable for evaluation of new processes or for the integration of new processes into existing facilities. In this case process modeling can be used to evaluate the economic potential for integrating biofuels and bioenergy technology into and existing pulp and paper mill. The process modeling will highlight the economic potential in terms of capital savings, and the technical challenges. In particular, process modeling can be used to highlight the benefits of overcoming technical barriers. This type of analysis can then be used to focus research and develop activities on the technical barriers that will have the greatest impact.

NCSU, in conjunction with a group of 9 industrial partners has been developing a process model for the production of bioethanol in a pulp and paper mill that has been closed. This modeling work has been focused on the reuse of the capital equipment, e.g., biomass boilers, batch or continuous digesters, bleach towers, wastewater treatment plants and biomass feed handling systems, and the mass and energy balances for the different unit operations, e.g., pretreatment, enzymatic hydrolysis, fermentation, distillation and power production.

This process model has been developed using WINGEMS, a process modeling program that is well-accepted by the pulp and paper industry. While WINGEMS has well develop modules for the production of pulp, for heat and water integration and recycle, and for the chemical recovery cycle, it does not have modules that effectively model enzyme hydrolysis, fermentation or distillation. Conversely NREL has developed two very detailed process models for the production bioethanol; one using enzyme hydrolysis, fermentation and distillation (Biochemical Processing), and the second using biomass gasification followed by the catalytic conversion of syngas to ethanol (Thermochemical Processing). These process models were developed using ASPEN processing modeling software. While these ASPEN models are well-developed they cannot be easily integrated into a WINGEMS model, and vice versa.

The goal of this work will be to begin the process of integrating the information contained in the WINGEMS and ASPEN process models to develop a single process model that can accurately model the biochemical or thermochemical conversion of biomass to ethanol. Although, at this point it is not clear how this integration should be done. This collaboration will allow Dr. Adrianna Kirkman, an expert in WINGEMS and the technical lead on the process modeling work that has been done at NCSU, to work with the NREL staff for three weeks and develop a plan for the integration of these two modeling approaches.

PI: Joshua Yuan, University of Tennessee

Research Partner: Mark Davis, National Renewable Energy Laboratory

Title: Evaluating the phenotype of the mutants produced from lignin modification research

Abstract: Technology breakthroughs to overcome several key barriers for cellulosic ethanol production are important to meet the national target for petroleum independence. As defined by DOE, these key components includes 1) feedstocks with higher amount and more accessible cellulose, 2) technologies for efficient deconstruction of feedstocks for sugar, and 3) improved procedures for sugar fermentation to ethanol. We have been funded by Southeast Sun Grant Center on two efforts to reach these goals from the perspectives of lignin down-regulation and in planta expression of cellulosome. One of the major limiting factors for efficient conversion of lignocellulose into sugar for ethanol production is the interference of biomass processing by lignin. Previous research has proved that altering lignin content and composition by genetic modification of its biosynthesis can improve both cellulose production and the efficiency of saccharification. However, limited research has been carried out to study the effects of lignin modification in monocot species, from which several bioenergy feedstocks will be developed. We proposed a comparative genomics guided approach to study the effects of reducing lignin production in both rice and switchgrass. Besides the lignin down-regulation, we were also funded to improve cellulose digestion on-the-plant directly by expressing cellulosomes in low lignin feedstocks.

The proposed research could both increase our fundamental knowledge about the cell wall structure and biosynthesis and lead to direct economic impact on producing low lignin bioenergy feedstock. Previous research has indicated that the pretreatment step can be omitted if the lignin content in the feedstock is low enough. Our research therefore has the potential to enable the biomass processing without the often acidic pretreatment step, which will greatly increase the efficiency of saccharification. The proposed research for this fellowship will be complimentary to the existing research funded by Southeast Sun Grant for lignin modification in rice and switchgrass. The overall research will be able to demonstrate the ability to control the amount of lignin present in a key biorefinery feedstock switchgrass and allow us to further understand the role of lignin in Type II cell wall structure with rice as a model plant. Moreover, it will also allows us to control or modify the functional group profile of the lignin, leading to a switchgrass feedstock with potentially higher cellulose composition and easier conversion into sugar, which will translate into great positive economic and environmental impacts.

Precise analysis biomass processing efficiency is required for the success of our Sun Grant funded lignin modification research. NREL has developed a series of standard protocols for carbohydrate and lignin analysis in biomass, and these protocols will be applied for analyzing the lignin biosynthesis mutants in rice, Arabidopsis and switchgrass. Through this fellowship, we will carry out important collaborative research with NREL to evaluate the phenotype of the mutants produced from Sun Grant funded lignin modification research. The carbohydrate and lignin content and composition analysis will provide the most important data to understand the effects of lignin modification on biomass processing and to guide the further genetic modification work. The proposed research in the NREL visit thus will provide important data and lead to long-term collaborations that will contribute the success of our Sun Grant funded research in comparative genomics-guided lignin modification in switchgrass.

Appendix A- BioWeb Topical Area Outline

(Each point represents content currently available in the BioWeb system)

1. Biomass Resources
    a. Land Base
    b. Agricultural Resources
        i. Existing Crops
            1. Corn
            2. Grain Sorghum
            3. Soybeans
            4. Sugar Crops
                a. Sugarcane
                b. Sugarbeets
            5. Miscellaneous Other Crops
        ii. New Crops
            1. Oilseeds
                a. Industrial Rapeseed
                b. Canola
                c. Castor
                d. Crambe
                e. Cuphea
                f. Lesquerella
                g. Meadowfoam
                h. Epoxy Crops
                i. Camelina
                j. Jojoba
            2. Rubbers and Resins
                a. Guayule
                b. Grindelia
            3. Non-Wood Fiber Crops
                a. Kenaf
                b. Hesperaloe
            4. Herbaceous (Grass) Crops
                a. Switchgrass
                b. Miscanthus
                c. Miscellaneous Other Grasses
                d. Mixed Grass Systems
            5. Short Rotation Woody Crops
                a. Hybrid Poplar
                b. Willow
                c. Miscellaneous Other Short Rotation Trees
            6. Microalgae
        iii. Crop Residues
            1. Corn Stover
            2. Wheat Straw

            3. Miscellaneous Grain Crop Straws
            4. Oilseed Crop Straws
            5. Orchard and Vineyard Prunings
            6. Grass Seed Residues
        iv. Animal Manure
            1. Beef
            2. Dairy
            3. Swine
            4. Poultry
            5. Other Livestock
        v. Processing and Food Wastes
            1. Cotton Gin Trash
            2. Waste Grease and Fats
            3. Whey
            4. Food Industry Wastes
    c. Forest Resources
        i. Logging Residues
        ii. Other Removals
        iii. Fuelwood
        iv. Fuel Treatment Resources
        v. Changes in Pine Plantation Management
        vi. Mill Residues
            1. Primary Mill Residues
            2. Secondary Mill Residues
            3. Black Liquor
    d. Urban Biomass Resources
        i. Municipal Solid Waste
        ii. Construction, Renovation, and Demolition Wastes
        iii. Landfill Gas
        iv. Refuse Derived Fuel
        v. Biosolids
        vi. Miscellaneous Other Urban Wood Wastes

2. Biopower
    a. Technologies
        i. Combustion
            1. Co-firing
            2. Direct-Firing
        ii. Gasification
        iii. Pyrolysis
            1. [page: Pyrolysis Reactions]
            2. [page: Pyrolysis of Biomass Resources]
            3. [page: Biomass Pyrolysis Reactors]
        iv. Anaerobic Digestion
        v. Distributed Generation

3. Biofuels
    a. Technologies
        i. Ethanol Production
            1. Ethanol Dry Grind Process
            2. Ethanol Wet Grind Process
            3. Ethanol from Sucrose
            4. Ethanol from Cellulose Resources
        ii. Biodiesel Production
        iii. Biofuels from Syngas
            1. Ethanol from Syngas
            2. Hydrogen from Syngas
4. Bioproducts
    a. Bioproducts from Syngas
        i. Hydrogen
        ii. Ammonia
        iii. Methanol
        iv. Methanol Derivatives
        v. Mixed Higher Alcohols
        vi. Fischer-Tropsch Synthesis
        vii. Oxosynthesis
        viii. Isosynthesis
5. Environmental
    a. Life Cycle Analysis
        i. Corn Grain to Ethanol
        ii. Corn Stover to Ethanol
        iii. Switchgrass to Ethanol
        iv. Soybeans to Biodiesel
        v. Integrated Biorefinery
6. Policy
    a. Federal Biofuels Policy
    b. State Biofuels Policy
    c. International Biofuels Policy
    d. Biofuels Policy Mechanisms
    e. Federal Biopower Policy
    f. State Biopower Policy
    g. Agricultural Policy
    h. Conservation Reserve Program