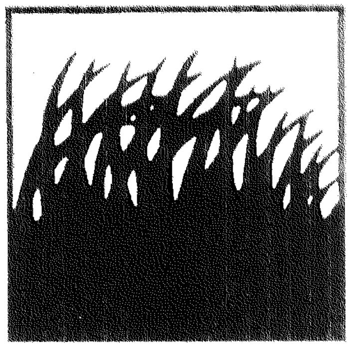

Hawaii Integrated Biofuels Research Program

Phase 6

Final Report Vol. I

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HAWAII NATURAL ENERGY INSTITUTE
School of Ocean and Earth Science and Technology
University of Hawaii at Manoa

September 1994

Hawaii Integrated Biofuels Research Program

Phase 6

Final Report 1994
Volume I

to the

National Renewable Energy Laboratory
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by

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September 1994

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HAWAII INTEGRATED BIOFUELS RESEARCH PROGRAM-PHASE 6
EXECUTIVE SUMMARY

INTRODUCTION

Roughly 90 percent of the energy used in Hawaii is supplied by imported petroleum resources. About two-thirds of the petroleum energy is consumed as liquid transportation fuels (gasoline, diesel, and jet fuels); whereas only about one-third is consumed in generating electricity. The large cost of importing oil into the state, with the major portion being used for transportation fueling, and the uncertainty of uninterrupted supplies of petroleum, make the development of non-petroleum-based transportation fuels the highest priority energy issue facing Hawaii today.

Biomass is the most flexible non-petroleum energy alternative available today — it can be burned for heating in various industrial and domestic applications or for producing steam to generate electricity; and, most significantly, it can also be converted into gaseous or liquid fuels for use in all of the above processes or to serve as transportation fuels. Hawaii is well suited to assume the role of a leader in the development, production, and utilization of transportation fuels from biomass — with no indigenous fossil fuels, there is great need for alternative fuels for Hawaii; conditions for plant growth are ideal in Hawaii, enabling high yields of biomass feedstocks; and a wealth of experience and expertise exists in the Hawaiian agricultural industry and the university community to support the development of advanced technologies for biofuels production.

OVERVIEW OF HAWAII INTEGRATED BIOFUELS RESEARCH PROGRAM

The Hawaii Integrated Biofuels Research Program, completing its sixth phase of funding by the U.S. Department of Energy (USDOE) via the National Renewable Energy Laboratory (NREL), features basic and applied research on the production of biomass and its conversion into gaseous and liquid fuels and into electricity to support the production of biofuels. The Biofuels Program, managed by the Hawaii Natural Energy Institute of the University of Hawaii, brings together investigators from various institutions of the University of Hawaii, including the School of Ocean and Earth Science and Technology, College of Engineering, and College of Tropical Agriculture and Human Resources, and from private industry, government, and non-profit research organizations. As appropriate, and to the extent possible, this research program integrates information and activities from other ongoing and planned bioenergy development efforts in the state of Hawaii. Coordination with other USDOE bioenergy research ensures that the work performed in this program has broad-based applicability to the entire U.S. Intrinsic to the program is a strong educational component to create an infrastructure of skilled personnel in biofuels systems research and development for technology transfer. For example, through the sixth phase of this program, many of the university faculty and staff, and specialists from private industry, government, and non-profit research organizations involved in this program, have taken active roles in the academic training of about thirty graduate students and post-doctoral fellows.

The objective of the Hawaii Integrated Biofuels Research Program is to create the necessary infrastructure to aid in the development of sustainable biomass-based energy systems. This objective is met by research and demonstration activities organized along four broad components: (1) Biomass Systems Integration, (2) Biomass Production, (3) Biomass Conversion, and (4) Development of Dedicated Feedstock Supply Systems (DFSS) for Closed Cycle Biomass Conversion. Brief descriptions of the research components and the specific tasks that comprise Phase 6 of this program follow. Summaries of the individual tasks, outlining the research accomplishments in the recently completed phase as well as future plans, are presented in the pages following this Executive Summary using the format prescribed by NREL.

Biomass Systems Integration

The objectives of this component are integration of the information developed in the Biomass Production and Biomass Conversion research components to match biomass crops at suitable sites, and projection of the yields and economics of producing biofuels.

Geographical Information System/Biomass Economics: Using the biomass system model developed by this team in earlier phases of this program, and the HNRIS database and geographical information system, analyses of short-rotation intensive-culture (SRIC) tropical hardwood yield and cost estimates were performed for specific plantation and bioconversion sites on the islands of Hawaii and Maui. Potential Eucalyptus plantations were modeled for the Hamakua coast, the Hilo coast, and the Ka'u region on the island of Hawaii, and for specific locations at Hawaiian Commercial and Sugar Company on Maui. Bioconversion facilities at existing sugar processing sites at Hamakua Sugar Company in Haina, Hilo Coast Processing Company at Pepeekeo, and Ka'u Agribusiness Company at Pahala were assumed in the modeling activity for the island of Hawaii. The Hawaiian Commercial and Sugar Company Paia sugar factory was used for the Maui study. A sensitivity analysis of the effect of changes in establishment cost, harvesting cost, land rent, transportation cost, and yield on total delivered cost of hardwood chips was performed. Data, assumptions, and results for the SRIC biomass yield and cost analyses of this investigation were compared with those of other investigators with favorable results.

Biomass Production

The objectives of the Biomass Production component are the identification of the fastest growing, highest yielding biomass species, and the improvement of their yields through plant breeding and field testing. The tasks in Phase 6 include:

Genetic Characterization of Tropical Hardwoods: As a logical succession to work performed in Phase 5 of the Biofuels Program on genetic variation within *Eucalyptus*, in Phase 6 the genetic variation within and among ten species of *Acacia* (including nine from Australia and one species endemic to Hawaii) were examined using allozyme polymorphism. Polymorphism at fifteen loci revealed wide variation in the allele frequencies among species. The genetic identities estimated among *Acacia* species were unusually low and need further verification using a larger sample before conclusions can be reached on the genetic relationships among different species. Nevertheless, the wide variation in genetic identities among species suggests either high divergence among species in their evolutionary lineage or polyphyletic assemblage.

Nitrogen-Fixing Tree Research: The Short-rotation Biomass Trial, employing *Eucalyptus grandis* planted alone and in combination with nitrogen-fixing species was completed. The one-year rotations produced significantly less biomass than either two- or four-year rotations. The first year of a two-year short-rotation *Leucaena* hybrid study also was completed. These two trials are planted in two distinct environments, low-elevation, and mid-elevation (~1000 meters). Yields in the lowlands after three harvests were much higher than at the mid-elevation. Two advanced *Leucaena* hybrid lines, have undergone 25% selection pressure in the last two years. The final result is a population of highly psyllid-resistant material expressing significant biomass vigor. Forty-three *Acacia koa* provenances were planted at two locations on Hawaii and Oahu. The *Acacia koa* plantings are now in their fourth year, with 119 provenances under investigation. Superior lines are already being investigated with the Hawaiian Sugar Planters' Association (HSPA) to multiply the best lines.

Biomass Conversion

The goal of the Biomass Conversion component is to identify optimal means of producing biomass-based transportation fuels. This component focuses on the analysis and testing of thermochemical processes to convert biomass into fuel gas and methanol, and on alternative pretreatments to facilitate the biochemical conversion of biomass into ethanol.

Pyrolytic Gasification of Biomass in Supercritical Water: In the previous phase of this program it was found that the gasification of glucose in supercritical water resulted in nearly complete carbon gasification efficiency at low reactant concentrations and acceptable conversions at relatively high reactant concentrations. The prior work utilized capillary tube flow reactors that could not accommodate packed beds of catalysts, which were believed to be necessary to achieve complete conversion of high biomass concentrations; nor could such reactors accommodate slurry feeds of wet biomass. To that end, a new reactor system was assembled and tested in the present phase. Glucose gasification results using the new reactor reproduce results obtained on the previous reactor reasonably well. Studies of catalytic gasification of glucose employing a newly found catalyst were initiated with very encouraging preliminary results. Complete conversions of low concentrations of water hyacinth in water and depithed bagasse liquid extracts have also been achieved with this catalyst.

Catalytic Gasification: Parametric tests varying temperature, space time (the time the gas resides in the catalyst bed), and steam:biomass ratio with catalytic tar reforming, were performed in a reconfigured bench-scale biomass gasifier/tar-cracker system to determine product gas composition and tar yield under different catalytic tar reforming conditions. Virtually complete conversion of tars into gas species was obtained and near-synthesis-quality gas was produced using a commercial tar-cracking catalyst. Energy balance computations were performed to determine the additional energy consumed in catalytic tar reforming. A pilot-scale catalytic tar reforming unit was designed and a test plan prepared for incorporating slip-steam catalytic tar-reforming trials in the biomass gasifier facility demonstration program on Maui.

Fuel Nitrogen in Biomass Gasification: Gasification of high-nitrogen-content biomass can produce excessive amounts of nitrogen-containing compounds such as nitrogenous tars, ammonia (NH_3), hydrogen cyanide (HCN), and nitrogen oxides (NO_x). These compounds can negatively impact the environment and end-use energy-conversion processes (e.g., through fouling of catalysts used in methanol synthesis and tar reforming). Formation of the aforementioned compounds during biomass gasification is not fully understood and research in this area, to date, has been minimal; therefore, an experimental investigation was initiated in Phase 6 to broaden the base of information on nitrogenous compound formation in biomass gasification. Gasification tests were performed on a bench-scale, indirectly-heated, fluidized bed gasifier to examine the effects of gasifier operating conditions (e.g., temperature, equivalence ratio, and residence time) on the formation of nitrogenous tar species, NH_3, HCN, and NO_x species, and to inventory the nitrogen from gasified biomass.

Solvolytic Pretreatment: Previous work by these investigators established that hot, compressed liquid water can dissolve all of the hemicellulose, a significant fraction of the lignin, and some cellulose from biomass without the addition of acids, bases, or solvents.

This novel treatment, termed "Aquasolv," has the potential to render the solid cellulosic residue more accessible to biological conversion techniques being developed by NREL. In Phase 6 of this program, several agricultural residues, including sugarcane leaves and bagasse, and wood chips (aspen and southern pine) were tested. Solubilization of up to 50% of biomass was obtained. Collaborative work with both public and private sector research facilities, begun in earlier phases of this program continues. The use of products of the Aquasolv process for pulp and paper applications as well as in enzymatic hydrolysis for ethanol production are being evaluated. In addition, the influence of important process variables was examined using a factorial experimental design.

Steam Pretreatment: In Phase 6, a wide range of steam-explosion conditions were tested to identify optimal conditions for using steam explosion as a pretreatment in converting biomass into ethanol. In this investigation, sugarcane bagasse was treated by steam-explosion using a 10-liter batch reactor. The experiments and equipment were redesigned to facilitate quantification of all effluent streams for each run. Unextracted samples of the exploded fiber from this task were subjected to enzymatic hydrolysis in another task of the Biofuels Program. A new discharge chamber was installed on the steam exploder, offering significant improvements over the original chamber used in the previous phase of this program. In conjunction with the ethanol application, co-product process routes were also investigated. Major support for this task is being provided by HSPA, the Governor's Agriculture Coordinating Committee, and the Office of Technology Transfer and Economic Development of the University of Hawaii.

Screening of Alternative Pretreatment Processes: Two of the more environmentally benign pretreatment options for biomass-to-ethanol conversion are being investigated in this program, steam explosion and solvolysis. Neither option, in its purest form, requires the addition of chemicals. This task was established to identify the optimal conditions for steam explosion and solvolysis as pretreatments for converting biomass into ethanol. Unextracted samples of the pretreated fiber were subjected to enzymatic hydrolysis using a test protocol provided by NREL. The hydrolyzed samples were analyzed via high performance liquid chromatography, and results were correlated according to the "reaction ordinate" of the particular sample..

Interface — Development of Dedicated Feedstock Supply Systems

The goal of the Development of DFSS component is to investigate issues regarding the cultivation, harvesting, storage, and transportation of selected energy crops to identify critical cost factors and formulate a research program that addresses those factors.

Development of DFSS: Although banagrass, a napiergrass (*Pennisetum purpureum*) cultivar, has been identified through small experimental trials conducted by HSPA as having high yield potential, experience and information for larger-scale plantings of this energy crop are lacking. To that end, a 10-acre banagrass demonstration trial was established on Molokai to obtain critical cultivation and cost information on that energy crop. Partial support for this project was provided by HSPA.

SUMMARY

The Hawaii Integrated Biofuels Research Program features basic and applied research relating to biomass resource assessments and crop production, thermochemical and biochemical conversion, and biomass systems integration. The program has made, and will continue to make, significant contributions toward developing the information required for the production of alcohol fuels and electricity from biomass feedstocks in an environmentally sound manner.

HAWAII INTEGRATED BIOFUELS RESEARCH PROGRAM-PHASE 6

TASK SUMMARIES

GIS/BIOMASS ECONOMICS
PHASE 6, TASK 1A

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The objectives of this task are to develop the decision support tools needed to assess the biomass resource potential in Hawaii; to estimate yield and delivered cost of biomass feedstocks from short-rotation intensive-culture (SRIC) plantations; to estimate yield and cost of producing electricity and alcohol fuels; and to integrate these biomass system components within an economic framework.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

Using our biomass system model developed in earlier phases of the Biofuels Program, and the HNRIS database and geographical information system, we completed analyses of SRIC tropical hardwood yields and costs for specific plantation and bioconversion sites on the islands of Hawaii and Maui. Potential Eucalyptus plantations were modeled for the Hamakua coast, the Hilo coast, and the Ka'u region on the island of Hawaii, and for specific sugarcane fields at Hawaiian Commercial and Sugar Company on Maui. Bioconversion facilities at the Hamakua Sugar Company mill in Haina, the Hilo Coast Processing Company mill at Pepeekeo, and the Ka'u Agribusiness Company mill at Pahala were assumed in the modeling activity for the island of Hawaii. The Hawaiian Commercial and Sugar Company Paia mill was used for the Maui study.

A sensitivity analysis on the effect of changes in establishment cost, harvesting cost, land rent, transportation cost, and yield on total delivered cost of hardwood chips was performed. Using the Hilo coast site for our SRIC biomass system model, the parameters having the greatest sensitivity are yield and harvesting cost; a 10% change in yield results in ~7% change in delivered cost, while a 10% change in harvesting cost causes a 4% change in delivered cost. We compared the data, assumptions, and results of our team's SRIC biomass yield and cost analysis with those of our professional collaborator, BioEnergy Development Corporation/U.S. Forest Service Institute of Pacific Islands Forestry (BDC/IPIF). As expected, predicted DBH, yield, and average delivered cost of *Eucalyptus grandis* and *E. saligna* from our team's SRIC system model were consistent with and similar to results from BDC/IPIF. Two management regimes, A and B, from BDC/IPIF were used as inputs to our SRIC system model, and the model was applied to Hilo coast plantations using weather and site information from HNRIS. For Regime A, predicted DBH and delivered cost from BDC/IPIF and our SRIC system model were 6.0 and 5.3 inches (±10%), and $54 and $59 per dry tonne (±9%), respectively. For Regime B, predicted DBH and delivered cost from BDC/IPIF and our SRIC system model estimates were 8.0 and 7.5 inches (±6%), and $45.0 and $43.7 per dry tonne (±3%), respectively.

Using our SRIC system model, we then identified and utilized a management regime optimized for planting density and rotation age (Optimized Regime 1), and compared the results with those from Regimes A and B mentioned above. Optimized Regime 1, which features a planting density of 578 trees per acre (7 m^2 growing space per tree) and a rotation age of seven years at harvest with the same amount of nitrogen fertilizer applied per tree as in Regime B (0.48 kg N per tree), results in an estimated average delivered cost for Hilo coast plantations of $39.7 per dry tonne. By increasing the nitrogen fertilizer application to 0.58 kg N per tree (Optimized Regime 2), the average delivered cost was $2 less, at $37.7 per dry tonne. BDC/IPIF Regime A represents the smallest tree size and shortest rotation age, and results in the highest delivered cost. Regime B, which produces a larger tree with a longer rotation period and lower planting density, results in a delivered cost lower than that of Regime A due to reduced harvesting and processing costs. In comparison with these two regimes, our SRIC system model suggests that a planting density intermediate to those of Regimes A and B and with a longer rotation age which produces larger trees and higher stand yield per acre, would offer the lowest delivered cost.

SIGNIFICANT ACHIEVEMENTS

Least-cost or optimized estimates of biomass (*Eucalyptus grandis*, *E. saligna*, and *Leucaena leucocephala*) feedstock yields (dry tonnes/hectare) and delivered costs ($/dry tonne) were obtained for the islands of Hawaii and Maui. Manufacturing costs of ethanol, methanol, and electricity from local biomass resources were estimated in collaboration with Dr. Richard Bain of the National Renewable Energy Laboratory. A hypothetical, integrated forest products system featuring high-value hardwood, veneer, utility lumber, and wood chips was developed, and component yields and net returns were projected for specific plantations on the island of Hawaii. A significant number of peer-reviewed publications describing our methodology and analytical results were completed in this phase of the program.

To update and refine our empirical SRIC biomass system model, we requested individual tree growth and performance data from project colleagues Dr. Robert Osgood and Nick Dudley of the Hawaiian Sugar Planters' Association (HSPA) who completed a report in November 1993 entitled "Comparative Study of Biomass Yields for Tree and Grass Crops Grown for Conversion to Energy" for the State of Hawaii Department of Business, Economic Development and Tourism. Currently, our model includes field trial data through two years of age provided by HSPA for *E. grandis*, *E. saligna*, and *L. leucocephala* from the five-year study. By including this additional mensuration data taken at three, four, and five years of age, our model would be enhanced significantly for future analyses.

PUBLICATIONS AND REPORTS

1. Phillips, V.D., W. Liu, R.A. Merriam, and D. Singh. 1993. "Biomass System Model Estimates of Short-rotation Hardwood Production in Hawaii." *Biomass and Bioenergy*, Vol. 5, No. 6, pp. 421-429.

2. Phillips, V.D., W. Liu, R.A. Merriam, and D. Singh. 1994. "Potential for Short-rotation Intensive-culture Hardwood Production in Hawaii." *Agricultural Systems*, Vol. 46, pp. 33-57.

3. Merriam, R.A., V.D. Phillips, and W. Liu. 1993. "Space-age Forestry Implications of Planting Density and Rotation Age on SRIC Management Decisions." *First Biomass Conference of the Americas*, Burlington, Vermont, August 30-September 2.

4. Phillips, V.D., R.A. Merriam, and. W. Liu. 1993. "Short-rotation Forestry for Energy Production in Hawaii." *First Biomass Conference of the Americas*, Burlington, Vermont, August 30-September 2.

5. Liang, T., A. Khan, V.D. Phillips, and W. Liu. 1994. "Hawaii Natural Resource Information System: A Tool for Biomass Production Management." *Biomass and Bioenergy* (to appear).

6. Phillips, V. D., W. Liu, W., R.A. Merriam, and R.L. Bain. 1994. "Short-rotation Forestry as an Alternative Land Use in Hawaii." *Biomass and Bioenergy* (to appear).

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

In Phase 6, we demonstrated successfully that our SRIC biomass system model can reliably estimate yield and optimized cost of producing tropical hardwood at the state, county (island), and plantation (field) levels. Applying the model, we estimated costs of ethanol, methanol, and electricity from woody feedstocks for specific locations. We used the model to develop a hypothetical, integrated forestry operation that would produce high-value hardwoods, veneer logs for plywood, utility logs for lumber, and wood chips for energy on a 20-year rotation. The decision support tools and information we have generated is useful to land owners and decision-makers evaluating the economic viability of short-rotation forestry in Hawaii, including growing biomass crops for energy purposes. This methodology is readily transferable to other areas nationally and worldwide.

GENETIC CHARACTERIZATION OF ENERGY CROPS
PHASE 6, TASK 2A

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The purpose of this task is to investigate genetic variation within and between provenances of tropical biomass energy crops using DNA and enzyme markers to identify superior germplasm for future crop improvement efforts.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

Genetic variation within and among ten species of *Acacia*, including nine from Australia and one species endemic to Hawaii, were examined using allozyme polymorphism. Polymorphism at fifteen loci revealed wide variation in the allele frequencies among species. The Nei's species pair-wise unbiased genetic identities ranged from 0.026 between *A. koa* and *A. aulacocarpa*, to 0.792 between *A. auriculiformis* and *A. mangium*, with an overall mean of 0.289. The genetic identities estimated among *Acacia* species were unusually low and need further verification using a larger sample before conclusions on the genetic relationships among different species can be made. Nevertheless, the wide variation in genetic identities among species suggests either high divergence among species in their evolutionary lineage or polyphyletic assemblage.

Height and DBH were recorded for 18 months-old provenances of *Eucalyptus spp.* out planted in the field. These trees had been analyzed previously for association between allozyme heterozygosity and biomass accumulation in the juvenile stages under greenhouse conditions. Thirty trees per provenance and two provenances each of *E. grandis*, *E. saligna*, *E. urophylla*, and *E. camaldulensis* were included in the study. The correlations between height and heterozygosity ranged from 0.306 for *E. camaldulensis* (provenance 278-6) to -0.276 for *E. urophylla* (provenance 203-3). In general, both height and DBH showed negative association with heterozygosity for *E. urophylla* and *E. grandis*, whereas *E. camaldulensis* and *E. saligna* exhibited positive associations. Similar trends were observed in the relationship with volume (height x DBH). We intend to assess this relationship at the two-year growth stage, which is approximately one-third the rotational age for *Eucalyptus spp.* in Hawaii.

We continued to develop a genetic tree improvement program for Eucalyptus in Hawaii to complement and extend the existing plan of the U.S. Forest Service, Institute of Pacific Islands Forestry, and BioEnergy Development Corporation (BDC). Our suggestion includes both clonal and seed orchard approaches.

Seven provenances each of seven species of promising Australian *Acacia spp.* were sown in the greenhouse during Spring, 1993. Germination and seedling survival were poor due to excessive rain leading to water logging and root rot caused by seed-borne fungi. We have arranged for these seed lots to be sown in the nursery facilities of BDC during Fall, 1994. This material will be out planted in provenance trials on the island of Hawaii, and the genetic variation will be assessed using allozyme markers.

Seven isozyme systems were resolved to determine genetic variation within 56 single-tree progenies of *Prosopis pallida* (mesquite or kiawe) collected at four sites on Oahu. Trees from three of the four sites exhibited the same isozyme band pattern. In the case where the pattern was not the same, the difference was observed in only one enzyme system. These results indicate that the genetic variation of *Prosopis pallida* sampled on Oahu in this study is narrow.

SIGNIFICANT ACHIEVEMENTS

At least three Australian Acacia species showed promise for Hawaiian conditions, *A. auriculiformis*, *A. mangium*, and *A. crassicarpa*. However, large-scale species and provenance testing involving diverse sites in Hawaii is required before conclusions can be drawn on the suitability of different Acacia species. Preliminary evaluation of ten Acacia species for genetic variability was also conducted.

The species of Eucalyptus differed in the relationships between allozyme heterozygosity and biomass accumulation at the 18-months growth stage. The preliminary results from data collected in the greenhouse experiment conducted previously and in the field at 18 months are of considerable importance for tree improvement. If this relationship is determined to be statistically significant, selection of genetically superior trees at an early stage of growth can take place thus saving time, space, and cost in tree breeding.

Enzyme systems showing polymorphisms were resolved to determine isozyme band patterns in *Prosopis pallida* and *Acacia koa*.

PUBLICATIONS AND REPORTS

1. Aradhya, K.M. and V.D. Phillips. 1994. "Lack of Association Between Allozyme Heterozygosity and Juvenile Traits in Eucalyptus." *New Forests* (in press).

2. Phillips, V.D. and K.M. Aradhya. 1994. "Genetic Improvement of Eucalyptus in Hawaii." Submitted to *Journal of Tropical Forest Science*.

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

During Phase 7, mensuration of out planted provenances of Eucalyptus will be completed, and growth traits will be correlated with allozyme heterozygosity to verify relationships at one-third rotational age. This evaluation should allow us to draw some conclusions on whether allozyme heterozygosity is an indicator of superior performance in the field.

Forty provenances involving seven Australian Acacia species, and several seed lots of the endemic *A. koa*, will be evaluated for genetic diversity and tested for adaptability under Hamakua and Ka'u conditions on the island of Hawaii in collaboration with BDC.

We will continue to evaluate the genetic base of existing and newly introduced tropical hardwood germplasm, and will explore the feasibility and planning of Eucalyptus and Acacia seed orchards in diverse environments in Hawaii. The out planting of randomly selected individual seedlings from the greenhouse experiment will enable us to track development and compute correlations as the trees mature. The results are expected to reveal important information on the relationship between heterozygosity and biomass which will be used for progeny selection in the early growth stage.

The limited number of *Prosopis pallida* populations sampled on Oahu during Phase 6 does not adequately represent species throughout the state of Hawaii. In Phase 7, additional populations will be analyzed, and techniques for isozyme analyses of *Acacia koa* will be refined.

NITROGEN-FIXING TREES
PHASE 6, TASK 2B

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Highest total dry matter (DM) biomass yields for tree stands in Hawaii have been approximately 25 t/ha/y. Yields have plateaued because of inferior plant material. Yields of 35 t/ha/y DM can be expected with improved tree varieties; such yields represent a 40% increase in productivity. A task for researchers is to identify top yielding biomass varieties and develop sustainable forest systems for incorporating such material. Methods that improve biomass production include hybridization and genetic advancement through selection for pest and disease resistance, improved seedling vigor, vegetative propagation of superior lines and individual trees, identification of superior varieties through field evaluation, and developing appropriate methods to capitalize on hybrid seed production. Many of these objectives were studied in Phase 6 of the Biofuels Program with favorable results.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

SET 89-1, Short-rotation Biomass Trial, employing *Eucalyptus grandis* planted alone and in combination has been completed. The best mean annual increment (MAI) from this trial was 21 t/ha/y for two-year old *Paraserianthes falcataria*. The best mixed plots produced approximately 18-19 t/ha/y from two- to four-year rotations. The one-year rotations yielded significantly less biomass ($P<0.05$) than either two- or four-year rotations. Lower than average yields for the Eucalyptus were due to high disease incidence in this species soon after the initial coppice was taken in 1990. At the plant population of this experiment (6,600 plants/ha), the maximum rotation age is approximately two to three years based on the similar MAI of both rotations (15.5 t/ha/y). The next generation of mixed forest plantings should be based on clonal material developed by the Hawaiian Sugar Planters' Association (HSPA) and the University. HSPA has several clonal Eucalyptus species developed from micropropagation, while the University has developed approximately 25 clonal Leucaena hybrids and species.

The first year of a two-year short-rotation Leucaena hybrid study has been completed. These two trials are planted in two distinct environments. One trial is located at low elevation (Waimanalo) and the other at approximately 900 m elevation (Mealani). Leucaena selections in these trials were based on findings from an earlier study (SET 91-2). The best yielding lines were K748 x K636 (highest in yield in SET 91-2) and K748 x K584. Yields in the lowlands after three harvests were much higher, with the highest yield recorded to be 26 t/ha/y DM. At Mealani only 6 t/ha/y was obtained in a single harvest. Owing to cooler temperatures, Leucaena can be harvested only two to three times per annum at higher elevations, whereas in the lowlands five to six harvests can be realized. In order to develop a reliable supply of F_1 hybrid seed, we have cloned various *L. pallida* species including K748, K804 (arboreal Pallida), and the intraspecific *L. pallida* , K806 x K748. These have been transplanted at Waimanalo, and will serve as mother plants for future cloning in seed production orchards and clonal biomass production schemes.

Two advanced hybrid lines, KX2 (*L. pallida* x *L. leucocephala*) and KX3 (*L. diversifolia* x *L. leucocephala*), have undergone 25% selection pressure in the last two years. The final result from SET 92-3 and SET 92-4 is a population of highly psyllid-resistant material that expresses good biomass vigor (see report on deliverables for Phase 6). The remaining lines will be kept in place to serve as a seed orchard. The best lines have also been cloned and will serve as mother plants to develop a seed orchard with HSPA.

Progress in other areas relating to tree production include planting 43 *Acacia koa* provenances at two locations on Hawaii and Oahu in 1994. The *Acacia koa* plantings are now in their fourth year with 119 provenances under investigation. Superior lines are already being investigated with HSPA to multiply the best lines. We are developing a sterilization technique for micropropagating out poor Leucaena selections. The expected completion date for SET 91-3, a three-year wood biomass trial in Waimanalo on *Leucaena spp.*, is September 1994. We have established a cooperative agreement with the International Center for Research in Agroforestry (ICRAF) in Kenya, Africa, for determining suitable Leucaena varieties to combat a psyllid that arrived on the continent recently.

SIGNIFICANT ACHIEVEMENTS

1. Completed analysis of SET 89-1, short-rotation biomass study. We now can recommend various mixtures and management for these types of trials.

2. Developed high yielding, psyllid-resistant Leucaena selections for biomass and livestock forage production in Hawaii. This study requires another year of analysis.

3. Developed a sterilization procedure for Leucaena micropropagation.

4. In cooperation with HSPA, developed a clonal technique for Leucaena based on rooted cuttings.

5. Developed through advanced progeny selection highly vigorous, psyllid resistant Leucaena material for use in Hawaii.

PUBLICATIONS AND REPORTS

1. Brewbaker, J.L. 1993. "Chapter 8. Tree Improvement for Agroforestry Systems." Crop Improvement for Sustainable Agricultural Systems. C. Francis and M.B. Calloway (eds.). U. of Nebraska Press. pp. 132-156.

2. Brewbaker, J.L., and C.T. Sorensson. 1994 "Domestication of the Lesser-known Species of the Genus *Leucaena*." Tropical Trees: The Potential for Domestication and Rebuilding of Forest Resources. R.R.B. Leakey and A.C. Newton (eds.). HMSO Publishing. London, England. pp. 195-204.

3. Osgood, R.V., N. Dudley, and M.T. Austin. 1993. "Commercial *Leucaena Leucocephala* 'K636' Seed Production Results from Biomass Research." Hawaiian Sugar Planters' Association Annual Report, 1993. Aiea, Hawaii. pp. 42-43.

4. Sorensson, C.T., H.M. Shelton, and M.T. Austin. 1994. "Seedling Vigour of Some *Leucaena* spp. and Their Hybrids." *Tropical Grasslands*, Vol. 28, pp. 182-190.

5. Sun, W., J.L. Brewbaker, and M.T. Austin. 1993. *Acacia koa* Genetic Improvement. Abstract in Western Forest Genetics Association Annual Meeting. Oahu, Hawaii, October 8-10.

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

We have completed all work planned for Phase 6. In Phase 7, we will continue clonal operations and develop seed production orchards with HSPA. We will also continue monitoring SET 93-2, SET 93-3, and SET 93-6 Leucaena biomass studies. We are interested in developing a mixed forest based on clonal Eucalyptus and Leucaena.

PYROLYTIC GASIFICATION
PHASE 6, TASK 3A

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In Phase 5 of the Biofuels Program, we found that the gasification of glucose in supercritical water at 600°C, 34.5 MPa, and 30 s residence time resulted in ~100% carbon gasification efficiency at low reactant concentrations and ~80% conversion at reactant concentrations as high as 0.8M glucose (14% by weight in water). The prior work utilized capillary tube flow reactors that could not accommodate a packed bed of catalysts, which we believe is necessary for achieving complete conversion of high concentration glucose. Nor could such reactors accommodate slurry feeds of wet biomass. In Phase 6, a 0.375 inch O.D. Inconel 625 reactor system was assembled. This reactor has been operating six hours per day, two days per week during the past seven months at temperatures as high as 700°C and pressures as high as 34.5 MPa without significant problems. Gasification results from this reactor reproduce earlier work reasonably well. We have initiated studies of catalytic gasification employing a newly found solid catalyst X. Catalyst X is not expensive, survives well in supercritical water, and is extremely effective. Complete conversions of high concentration glucose (22% by weight in water) to gas are obtained at weight hourly space velocities (WHSV) as high as 22.2 h^{-1}. Complete conversions of low concentration water hyacinth in water and depithed bagasse liquid extract have also been achieved. We are now modifying the feed system to study gasification of high concentration wet biomass and sewage sludge feeds. We have also initiated fundamental studies of the heterogeneous catalytic gasification chemistry. The University has retained a patent attorney and has begun preparing a patent application on the process. The identity of catalyst X will be revealed after the patent has been filed.

An economic study of this process by F.S. Frenduto of Air Products Corporation dated 17 March 1992, projected economic feasibility if complete gasification of 18% by weight biomass in water could be achieved. We have realized this goal, which defines success for our work. We invite industrial participation in the design of a pilot plant to prove this process at a larger scale.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

Three kinds of reactants were studied in the packed bed reactor in Phase 6: (1) glucose as a biomass model compound in water; (2) various whole biomass feedstocks (including water hyacinth and depithed bagasse liquid extract); and (3) hazardous and waste materials (including phenol as a model compound of liquid effluent and sewage sludge). Benzene and toluene were also considered, but were not used because of their low solubility in water.

The gas components from the gasification of glucose, hydrogen, carbon monoxide, carbon dioxide, methane, and trace amounts of higher hydrocarbons, are essentially the same with or without catalyst X. The presence of solid catalyst X results in a carbon gasification efficiency approaching 100%, with glucose concentrations as high as 1.2 M (22% by weight in water). Effectively no tar or char is detected by drying the liquid effluent of the reactor. GC-MSD injections detect trace amounts of organic acids and esters. TOC analysis is being conducted to verify the carbon gasification efficiency. The glucose gasification reaction is sensitive to reaction temperature. Complete conversion is observed at 600°C, 34.5 MPa; however, as temperature drops, the carbon gasification efficiency decreases dramatically. A reaction temperature below 580°C results in incomplete conversion. A fundamental study of the heterogeneous catalysis chemistry indicates that external mass transfer does not play a major role in the gasification of glucose.

Gasification of diluted feeds of water hyacinth and depithed bagasse liquid extract with catalyst X at 600°C, 34.5 MPa results in virtually complete conversion to gas. The gas contains hydrogen, carbon dioxide, and methane, and almost no carbon monoxide.

The destruction of phenol and sewage sludge has been carried out at the same conditions employed for glucose and whole biomass. More than 50% of the phenol is gasified at WHSV = 0.08 h^{-1}; and nearly 100% of the diluted sewage sludge is gasified at WHSV = 0.5 h^{-1}, which results in the formation of hydrogen, carbon dioxide, methane, and trace amounts of carbon monoxide and ethane. Virtually no tar or char products are detected by evaporating the liquid effluent from the reactor. TOC analysis of the water effluent from the sewage sludge experiments is being performed.

We are working with Dr. Akira Suzuki of Organo Corporation of Japan to design a feeding system which can accommodate high concentrations of whole biomass and waste materials without plugging.

SIGNIFICANT ACHIEVEMENTS

1. High concentration of glucose (22% by weight in water) evidenced complete conversion to gas at 600°C, 34.5 MPa with catalyst X. The gas contains hydrogen, carbon dioxide, carbon monoxide, methane, and trace amounts of other hydrocarbons. Catalyst X is not expensive, survives well in supercritical water, and is highly effective.

2. Diluted whole biomass feeds, including water hyacinth and depithed bagasse liquid extract, have been gasified. Almost no carbon monoxide is detected in the gas product.

3. A packed-bed catalytic reactor can effectively destroy phenol and sewage sludge in supercritical water.

PUBLICATIONS AND REPORTS

1. Yu, D., M. Aihara, and M.J. Antal. 1993. "Hydrogen Production by Steam Reforming Glucose in Supercritical Water." *Energy and Fuels*, Vol. 7, No. 5.

2. Antal, M.J., X. Xu. 1993. Extended abstract, "Hydrogen Production from Wet Biomass in Supercritical Water." Presented at *AIChE 1993 Annual Meeting*, St. Louis, Missouri.

3. Antal, M.J., X. Xu, and J. Stenberg. 1993. "Hydrogen Production from High-Moisture Content Biomass in Supercritical Water." Presented at *USDOE Hydrogen Program Review Meeting*.

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

We have completed all planned work and have achieved all stated objectives for Phase 6. In Phase 7 we will concentrate on catalytic gasification of whole biomass and destruction of hazardous and waste materials.

CATALYTIC GASIFICATION
PHASE 6, TASK 3B

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Biomass gasification is an initial step in producing methanol from biomass. The quality of the product gas, including the gas composition and the amount of tars in the product gas, strongly affects methanol synthesis, as tars can poison methanol synthesis catalysts and decrease methanol synthesis efficiency. Catalytic tar reforming converts tars into gas species, increases gas yield, and improves gas composition for methanol synthesis. Elimination of tars from the product gas also reduces the potential negative impact of tars on the environment. This task investigates catalytic reforming of biomass gasification tars via a series of parametric experiments and designs a slip-stream test system for incorporation in the pre-commercial biomass gasifier facility on Maui.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

Parametric tests, varying temperature (650–800°C), space time (the time the gas resides in catalyst bed, 0–2 s), and steam:biomass ratio (0–1.22) with catalytic tar reforming, were performed on a bench-scale biomass gasifier/tar reformer system to determine product gas composition and tar yield under different catalytic tar reforming conditions. The nickel-based catalyst used in all experiments is G-90B provided by United Catalyst, Inc. Over the range of operating conditions tested, gas yield varied from 0.98 m^3/kg biomass to 1.69 m^3/kg biomass and tar yield varied from 53.9 g/kg biomass to <1 g/kg biomass; carbon conversion varied from 81% to about 95%; and the H_2:CO ratio of the product gas varied from 0.82 to 1.85.

Following are salient findings from the above-mentioned tests:

1. Temperature and space time have significant effects on catalytic tar reforming. Higher temperature or longer spacetime aids tar conversion. For each temperature, a "Critical Space Time" exists at which point essentially all tars are reformed into gas species.

2. Temperature and space time also affect product gas composition and gas yield. Gas yield increases with increasing temperature or space time. Hydrogen and carbon monoxide increase, and carbon dioxide decreases with increasing temperature or space time. At fixed temperature, if space time exceeds a critical space time, methane and other light hydrocarbons are essentially eliminated from the product gas, and gas yield and gas composition approach equilibrium. The test results agree well with theoretical predictions.

3. Increasing steam:biomass ratio increases H_2:CO ratio but decreases the heating value of the product gas. Hydrogen and carbon dioxide increase, and carbon monoxide decreases as steam:biomass ratio increases due to the water-gas shift reaction.

4. Under the conditions tested, methane concentration and tar yield show similar trends; however, methane cracks more slowly than tars and oils during catalytic reforming. It appears possible to estimate tar yield following catalytic tar reforming by tracking methane concentration and using a correlation between methane and tars (this would simplify measurement of tars because methane is easier to measure than tars).

5. Under the conditions tested, gasification is an exothermic process, with heat release being influenced by equivalence ratio, temperature, and residence time. Catalytic tar reforming is an endothermic process. The additional energy required to sustain the process depends on reforming temperature, space time, steam:biomass ratio, steam injection temperature, and input raw gas temperature. Under the conditions tested, the additional energy consumed for catalytic tar reforming (ignoring heat loss in the reformer) is <18% of the biomass feedstock gross heating value. Increasing steam:biomass ratio reduces energy consumption but decreases the heating value of the product gas.

SIGNIFICANT ACHIEVEMENTS

The following were achieved in this phase of the task:

1. Performed parametric tests on catalytic tar reforming and identified the influence of reforming conditions on product gas and tar conversion.

2. Performed energy balance computations and determined the additional energy required for catalytic tar reforming.

3. Designed a pilot-scale catalytic tar reforming unit and established a test plan for the biomass gasifier facility on Maui.

PUBLICATIONS AND REPORTS

1. Kinoshita, C. M., Y. Wang, and J. Zhou. 1994. "Tar Formation under Different Biomass Gasification Conditions." *Journal of Analytical and Applied Pyrolysis*, Vol. 29, pp. 169-181.

2. Wang, Y., J. Zhou, and C. M. Kinoshita. 1994. "Parametric Tests on Catalytic Tar Reforming of Gasified Biomass." *Sixth National Bioenergy Conference*, Vol. 1, pp. 267-274.

3. Zhou, J. 1994. "Catalytic Tar Reforming for Gasified Biomass." *M.S. thesis*, Biosystems Engineering Department, University of Hawaii.

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

We have completed all planned work and have achieved all stated objectives, on schedule, in Phase 6. Follow-on work is planned for the next phase of the Biofuels Program.

FUEL NITROGEN IN BIOMASS GASIFICATION
PHASE 6, TASK 3C

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Gasification of biomass with high nitrogen content can produce excessive amounts of nitrogen-containing compounds such as nitrogenous tar species, ammonia (NH_3), hydrogen cyanide (HCN), and nitrogen oxides (NO_x), which can have negative impacts on the environment and on energy-conversion processes (e.g., fouling of catalysts used in methanol synthesis and tar reforming). Formation of the aforementioned compounds during biomass gasification is not fully understood and research in this area, to date, has been minimal; therefore, an experimental investigation was initiated in this phase of the Biofuels Program to broaden the base of information on nitrogenous compound formation in biomass gasification.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

Leucaena, a leading energy crop candidate with 2-3% nitrogen content, was harvested from the University of Hawaii's Agricultural Experiment Station and processed to yield approximately 100 kg (dry-basis) of feedstock. Gasification tests were performed on a bench-scale, indirectly-heated, fluidized bed gasifier to: (1) investigate the effects of gasifier operating conditions (e.g., temperature, equivalence ratio, and residence time) on the formation of nitrogenous tar species, NH_3, HCN, and NO_x species; (2) inventory the nitrogen from gasified biomass; and (3) develop a better understanding of the mechanisms responsible for nitrogenous compound formation.

Nitrogenous tar species, collected with twin-chamber dry-ice condenser traps and methanol scrubbers, were analyzed with an off-line Perkin Elmer AutoSystem gas chromatograph (GC) and flame-ionization detector. NH_3 and HCN were collected via liquid absorption techniques and analyzed with Orion Research gas sensing and ion-selective electrodes. Major gas species (e.g., CO, CO_2, H_2, and CH_4) were measured using a GC equipped with a thermal conductivity detector and NO_x species were quantified with an on-line Thermo Environmental Model 10AR chemiluminescence analyzer. Char samples also were analyzed for nitrogen content.

Concentrations of nitrogenous compounds were obtained as functions of temperature (700°C to 900°C), equivalence ratio (0.2 to 0.4), and residence time (2.3 s to 6.7 s). It was found that nitrogenous compounds are mainly sensitive to gasification temperature, and NH_3 is the dominant fixed-nitrogen (FN) species (i.e., NH_3, HCN, NO_x). In addition, HCN and NO_x, collectively, account for less than 3% of the fuel nitrogen.

Single-point temperature tests (at 700°C and 834°C) were conducted to validate results of the multiple-point tests and to obtain a more accurate fuel nitrogen balance. Good repeatability (with respect to the multiple-point test results) was achieved and a fuel nitrogen balance of approximately 80% was obtained at 700°C; however, closure decreased with increasing temperature. About 10% and 2% of the fuel nitrogen was retained in the char at 700°C and 834°C, respectively.

Additional parametric temperature tests were performed using a longer GC packed column to investigate N_2 formation, as N_2 was not measured in the initial tests. Because of air intrusion during gas sampling and analysis, N_2 concentrations higher than those needed for complete closure were obtained. However, N_2 produced from decomposition reactions involving FN species is believed to be present in the gas.

SIGNIFICANT ACHIEVEMENTS

Experimental results indicate that substantial quantities of nitrogenous compounds are produced during gasification of a high nitrogen feedstock. Salient findings of this research include the following:

1. NH_3 is the dominant FN species (accounting for as much as ~60% of the fuel nitrogen); it is strongly dependent on temperature, but less dependent on equivalence ratio and residence time; NH_3 decreases with increasing temperature and residence time.

2. HCN is not a prominent species (representing only 0.2%–2% of the fuel nitrogen); HCN increases with increasing temperature and residence time.

3. NO is the only NO_x species formed in appreciable quantities (still existing only as a trace species); NO decreases with increasing temperature, equivalence ratio, and residence time (being most sensitive to temperature).

4. Nitrogen-containing tar species, collectively, decrease with increasing temperature and equivalence ratio.

PUBLICATIONS AND REPORTS

1. Ishimura, D.M., S.M. Masutani, C.M. Kinoshita, and Y. Wang. 1994. "Investigation of Nitrogenous Compound Formation in Biomass Gasification." *Sixth National Bioenergy Conference*, Vol. 2, pp. 713-720.

2. Ishimura, D.M. 1994. "Investigation of Nitrogenous Compound Formation in Biomass Gasification." *M.S. thesis*, Mechanical Engineering Department, University of Hawaii.

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

All proposed work for Phase 6 has been completed. Phase 7 efforts will focus on follow-on testing and the development of a theoretical model.

SOLVOLYTIC PRETREATMENT
PHASE 6, TASK 3D

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The principal constituents of biomass (cellulose, hemicellulose, and lignin) are linked together by a variety of physical and chemical bonds. Separation of these components is required to obtain the highest value products possible, while still utilizing all of the biomass. The removal of lignin, for example, is necessary to recover the cellulosic fibers for various purposes. Such a fractionation is possible using only liquid water at elevated temperatures (190–220°C). The term "Aquasolv," meaning to dissolve with water, has been adopted to describe the process developed in this laboratory. This solvolysis reactor has been used to process a variety of feed materials. Agricultural residues such as sugarcane leaves and bagasse as well as wood chips (aspen and southern pine) have been investigated. Solubilization of up to 50% of biomass is possible. Collaborative work with both public and private sector research facilities is ongoing. The use of products of the Aquasolv process for pulp and paper applications as well as enzymatic hydrolysis for ethanol production are being evaluated. In addition, the influence of important process variables was determined using a factorial experimental design. Detailed chemical analysis of the solid and liquid products was also performed.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

A factorial experimental design was completed to determine the effect of important process parameters on the yield of lignocellulosic residue. For this work, sugarcane bagasse was used as the feed material. Reaction temperature, time, and operating cycle were varied on two levels; 190 and 220°C, 45 and 120 s, batch or continuous. During a batch cycle, the flow of hot water is stopped upon filling the reactor. In a continuous cycle, flow is maintained throughout the reaction time. The distribution of the major components of biomass (cellulose, hemicellulose, and lignin) among the solid and liquid products was also investigated. It was found that changing the reaction temperature had the largest effect on yield, followed by reaction time; the operating cycle had no effect. The yield, then, was independent of the amount of water used, but was sensitive to temperature. Hemicellulose and lignin were preferentially solubilized. Solubilization of cellulose, however, was minimal (<10%). Complete solubilization of the hemicellulose and two-thirds of the lignin was achieved under the most severe conditions (220°C, 120 s). An archival publication has been prepared based on this work and results obtained in Phase 5 of the Biofuels Program.

The potential use of this inherently simple fractionation process for chemical-free pulping is being evaluated. Samples of lignocellulosic residue were produced from wood (aspen and southern pine), hesperaloe, and sugarcane components (bagasse and leaves) for testing as pulps. Physical and optical properties are now being determined in collaboration with the USDA Forest Service, Arbokem, and Kamyr.

In addition, enzymatic hydrolysis of lignocellulosic residue from sugarcane bagasse and aspen is being studied by Dr. Lee Lynd of Dartmouth College. Preliminary results indicate that the Aquasolv Process is a good pretreatment for ethanol production. Similar work is also being done by Dr. William Kaar of HNEI. Fermentation of the liquid products will also be investigated by Dr. Lynd. To this end, efforts are being made to increase the concentration of the liquid product. By reducing the quantity of water used, the extract concentration has been increased from 2 g/l to 18 g/l.

SIGNIFICANT ACHIEVEMENTS

1. The effect of important process parameters on the yield of lignocellulosic residue has been determined by conducting a factorial experimental design. The yield was independent of the amount of water used, but sensitive to its temperature. The distribution of major biomass components between the solid and liquid products was also established. Solubilization of cellulose was minimal (<10 %). Complete solubilization of the hemicellulose and two-thirds of the lignin was achieved under the most severe conditions (220°C, 120 s).

2. Collaborations with several research facilities capable of evaluating the use of the products of the Aquasolv Process in pulp and paper, and ethanol production have been formed.

PUBLICATIONS AND REPORTS

1. Allen, S.G., L.C. Kam, A. Zemann, and M.J. Antal. 1994. Extended abstract, "The Aquasolv Process: Process Characterization and Product Applications." Presented at *207th ACS National Meeting*, San Diego, California, March 13-17.

2. Allen, S.G., L.C. Kam, A.J. Zemann, and M.J. Antal. 1994. "Macroscale Fracionation of Sugarcane with Hot Compressed Liquid Water by the Aquasolv Process." Submitted to *Industrial and Engineering Chemistry Research.*

3. Allen, S.G., M.J. Spencer, M.J. Antal, N. Ross-Sutherland, and A.J. Baker. 1994. "Chemical-free Pulping Via the Aquasolv Process." Presented at *AIChE 1994 Annual Meeting*, San Francisco, California, November 13-18.

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

The objectives for Phase 6 have been met. In Phase 7, collaborative work on product applications, particularly enzymatic hydrolysis will continue. Industrial involvement in this work is being sought.

STEAM PRETREATMENT
PHASE 6, TASK 3E

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Steam explosion has been reported in the literature to be an effective means of rendering lignocellulosic biomass material more easily digestible by cellulosic enzymes, a requirement in most of the currently favored biomass-to-ethanol conversion technologies. A wide range of steam explosion conditions, using saturated steam from 150 to 650 psig, has been tested. This study sought to identify the optimal condition for using steam explosion as a pretreatment to convert biomass into ethanol. In this research, run-of-mill Hawaiian sugarcane bagasse was treated by steam-explosion in a 10-liter batch reactor. The experiments and equipment were designed such that all effluent streams were quantitatively collected for each run. The conditions that were tested totaled 95 in number, and spanned (saturated) steam pressures of 159 to 500 psig and run times of 0.5 to 44 minutes. The resulting pretreated bagasse samples were evaluated for total sugar recovery. Major support for this task was provided by the Hawaiian Sugar Planters' Association, the Governor's Agriculture Coordinating Committee, and the Office of Technology Transfer and Economic Development of the University of Hawaii.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

A new discharge chamber was installed on the steam exploder, offering significant improvements over the original chamber. The new chamber has a 50 cm opening, permitting total access to the interior. Furthermore, the chamber was outfitted with a cooling water jacket which not only cools the discharged biomass very quickly but also minimizes operator discomfort during the process of removing material from the chamber. A larger (one-half inch) tube heat exchanger cooling coil, through which the chamber is vented, was also installed; the larger tube greatly reduces venting time.

The 95 experimental runs all utilized whole sugarcane bagasse collected on one occasion at Oahu Sugar Company. The bagasse had a moisture content of 50.4%. One kilogram charges of bagasse were used for each run. Post-explosion mass recoveries ranged from 78–99% of feedstock mass.

Each sample of exploded bagasse was water extracted in duplicate. The water extract was analyzed for furfural and monosaccharides using high performance liquid chromatography. Furfural contents (xylan equivalent) ranged from 0.3% to 4.9% of feedstock mass, and were highest for high severity and/or low temperature samples; very little monosaccharide was detected in the water extracts. Unextracted samples of the exploded fiber were subjected to enzymatic hydrolysis using a standard procedure (this work is reported under Task 3G, "Screening of Alternative Pretreatment Processes").

The processing conditions that were used in the study were converted to "reaction ordinates" according to the relation published by Overend and Chornet; many samples with similar reaction ordinates had dissimilar chemical characteristics.

At the request of Dr. Dan Hsu of the National Renewable Energy Laboratory (NREL), we exploded chopped switchgrass, corn stover, yellow poplar sawdust, and shredded newspaper, in test matrices comprised of twenty different temperatures and reaction times. The exploded samples were forwarded to the Department of Chemical Engineering, Auburn University, for ethanol conversion evaluations.

SIGNIFICANT ACHIEVEMENTS

1. A new discharge chamber was installed which permits easier and more complete mass recovery.

2. An extensive time/temperature matrix of 95 samples of steam exploded sugarcane bagasse was completed. The samples were analyzed for mass recovery, sugar recovery, degradation products, and efficacy of hydrolysis using a cellulase enzyme preparation.

3. Chopped switchgrass, corn stover, yellow poplar sawdust, and shredded newspaper were steam exploded for ethanol conversion evaluations by NREL.

PUBLICATIONS AND REPORTS

1. Kaar, W., C. Gutierrez, and C. Kinoshita. 1994. "Steam Explosion of Sugarcane Bagasse as a Pretreatment for Conversion to Ethanol." Submitted to *Biomass and Bioenergy.*

2. Kinoshita, C.M., W.E. Kaar, and L.A. Jakeway. 1994. "Testing and Technoeconomic Evaluation of Steam Explosion of Hawaiian Biomass Feedstocks," HNEI report to Office of Technology Transfer and Economic Development, University of Hawaii.

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

We have completed all planned work and have achieved all stated objectives for Phase 6. In Phase 7, we hope to investigate catalyzed steam explosion to improve digestion while limiting degradation.

SCREENING OF ALTERNATIVE PRETREATMENT PROCESSES PHASE 6, TASK 3G

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Most of the recent economic studies concerning biomass-to-ethanol conversion have determined that chemical pretreatment, followed by enzymatic hydrolysis, is the most promising approach. Two of the more environmentally benign pretreatment technologies are steam explosion and solvolysis; neither, in its purest form, requires the addition of chemicals. It was the objective of this study to identify the optimal conditions, if any, for using steam explosion as a pretreatment for converting bagasse into ethanol and to compare those results with a limited number of solvolysis treated samples. In this research, run-of-mill Hawaiian sugarcane bagasse was treated by steam-explosion using a 10-liter batch reactor. The experiments and equipment were designed such that all effluent streams were quantitatively collected for each run. The conditions that were used totaled 95 in number, and spanned (saturated) steam pressures of 159 to 500 psig and run times of 0.5 to 44 minutes. The resulting pretreated bagasse samples were evaluated for total sugar recovery. Major support for this task was provided by the Hawaiian Sugar Planters' Association, the Governor's Agriculture Coordinating Committee, and the Office of Technology Transfer and Economic Development of the University of Hawaii.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

Unextracted samples of the exploded fiber were subjected to enzymatic hydrolysis using Chemical Analysis and Testing Standard Procedure No. 008 provided by the National Renewable Energy Laboratory (NREL). The enzyme mixture (Environmental Biotechnologies) was also provide by NREL.

The hydrolyzed samples were analyzed by HPLC and results were correlated according to the "reaction ordinate" of the particular sample. For the steam explosion experiments, both glucose and xylose conversions, as well as a theoretical "ethanol potential," were determined for each sample; all of these quantities relate back to the chemical composition of the original feedstock and incorporated corrections for mass recovery. For the solvolysis samples, only glucose and xylose conversions, as a percentage of pretreated mass, were calculated.

It was discovered that glucose conversion was favored at the higher treatment severities; whereas xylose recovery was favored at low severities. Because of this inherent trade-off, the ethanol potentials for the steam explosion samples of sugarcane bagasse were relatively insensitive to pretreatment conditions. Should a feedstock having a different chemical composition be examined, the results might be significantly different.

SIGNIFICANT ACHIEVEMENTS

1. A complete time/temperature matrix of 95 samples of steam exploded sugarcane bagasse has been tested. The samples were analyzed for efficacy of hydrolysis using a cellulase enzyme preparation.

2. A limited number of solvolysis treated samples were subjected to the enzyme hydrolysis protocol. Results suggest that solvolysis pretreatment closely parallels steam explosion when the time and temperature of pretreatment are similar.

PUBLICATIONS AND REPORTS

1. Kaar, W., C. Gutierrez, and C. Kinoshita. 1994. "Steam Explosion of Sugarcane Bagasse as a Pretreatment for Conversion to Ethanol." Submitted to *Biomass and Bioenergy.*

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

Enzymatic hydrolysis of the water extracted fiber samples continues. In Phase 7, we hope to apply our screening process to catalyzed steam exploded biomass in pursuit of improving digestion while limiting degradation.

DEVELOPMENT OF DFSS
PHASE 6, TASK 4A

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A hypothetical study conducted by these investigators in Phase 6 of the Biofuels Program concerning the potential for growing energy crops on the island of Molokai suggested that banagrass, a napiergrass (*Pennisetum purpureum*) cultivar, could be produced and delivered to a conversion facility for about $56 per ton (dry basis). Although banagrass has been identified through small experimental trials conducted by the Hawaiian Sugar Planters' Association (HSPA) as having high yield potential, experience and information for larger-scale plantings of this energy crop are lacking. To that end, a 10-acre banagrass demonstration trial was established on Molokai. The objective of this task is to investigate issues regarding the cultivation, harvesting, storage, and transporting of banagrass to identify critical cost factors and formulate a research program which addresses those factors. Partial support for this project was provided by HSPA.

GENERAL TECHNICAL OR SCIENTIFIC PROGRESS

Banagrass is vegetatively propagated; therefore, the first step in establishing a demonstration trial is the production of vegetative seedpieces. A 0.7-acre block of banagrass, located adjacent to the 10-acre biomass site, was ratooned and irrigated in September, 1993. Unexpectedly, the banagrass did not flower and produced higher quality seed than originally anticipated.

Following the removal of brush, grass, and trees, the 10-acre demonstration field was ripped twice and disk-plowed twice to form a seedbed suitable for planting. Two distinct field conditions were encountered: (1) areas previously planted in trees and (2) areas having a dense cover of buffel grass. Both areas were sprayed with a preplant application of Roundup, applied via a tractor-mounted boom.

Seed was cut from the 0.7-acre banagrass block at 7 months age, and planted on April 11–14, 1994. The density of seed applied was determined to be 0.125 pound per running foot (in rows nominally spaced 5 feet apart). The amount of seed applied was estimated to be 0.73 ton per acre, assuming one-third overlap of seedpieces. Seed was distributed by hand owing to the lack of a suitable mechanical planter on Molokai. About 0.4 acre of seed was required to plant 10 acres.

Drip irrigation tubing was placed on the soil surface adjacent to each row of banagrass seed following planting (for logistical reasons, the drip tubing had to be laid on the soil surface instead of injected beneath the surface as originally planned; replacement tubing will be injected after the field is harvested at approximately eight months of age). The field was divided into four irrigation blocks, each receiving water six hours per day (with two blocks irrigated simultaneously). The irrigation system applies ~0.35 inch of water per day which exceeds pan evaporation.

A preemergent application of atrazine and Lasso herbicides was applied to the field using a tractor-mounted boom, each at rates of 2.0 lb/ac.

The field was replanted to fill in gaps and to complete the stand (the heavy presence of gaps in the banagrass stand was anticipated based on previous experience with banagrass). About 0.3 acre of replant seed was required.

Additional weed control following the replant operation was accomplished by mowing between the banagrass rows, and spot treating the clumps of buffel grass with Roundup.

Fertilizer is applied through the drip-irrigation system. Rates of fertilizer to be applied through the end of October 1994 are: Nitrogen, 200 lb/ac; K_2O, 200 lb/ac; and P_2O_5, 100 lb/ac. The banagrass crop has a rich green color and does not appear to be deficient in water or nutrients.

Complete canopy cover occurred three months after planting. Harvest of the plant crop is scheduled for December 1994; a portion of the harvested crop will be sent to Maui for use in the biomass gasifier facility in Paia. After harvesting, the field will be ratooned and new irrigation lines will be injected in the field to serve the ratoon crop.

Samples of whole banagrass were collected from the field at four months of age and forwarded to collaborators T.R. Miles, Consulting Design Engineers, and the Pacific International Center for High Technology Research, to be analyzed for thermochemical and constitutive properties.

SIGNIFICANT ACHIEVEMENTS

1. Produced and harvested ~7 tons of banagrass seed for banagrass demonstration.

2. Installed automated drip-irrigation system, including irrigation controller, and main and submain lines for demonstration site.

3. Prepared field and planted seed in 10-acre site; gap-planted field.

4. Maintained crop through six months of age.

5. Collected and prepared samples of whole banagrass for analysis by collaborators.

PUBLICATIONS AND REPORTS

A report for this task will be issued after the first crop is harvested.

SUMMARY ASSESSMENT AND FORECAST FOR COMPLETION

We have completed all planned work and have achieved all stated objectives in Phase 6. Harvest of the plant crop is scheduled for Phase 7 of this program. After harvesting, the field will be ratooned and new irrigation lines will be injected in the field.