

## **GSCSSA Progress Report 2006**

**Title: A New Look at On-farm Production of Bio-based Products from Grass Seed Straw**  
*(Report of work done on year 2 goals, supported by funds allocated for FY 2005)*

### **OBJECTIVES**

*Objective 1. Develop suitable on-farm straw-to-sugar processing schemes. Year 1: Feedstocks characterization.*

*Objective 2. Develop an on-farm scale gasification reactor that produces high quality syngas.*

### **INVESTIGATORS**

Michael Penner, OSU-Food Science (Straw pre-treatments and fermentation).

Jeffrey Steiner, USDA-ARS (Straw quality-anti-quality characterization and agronomy)

### **COOPERATORS**

Scott Macadam, Western Research Institute, Laramie, WY (Gasification reactor testing)

### **ABSTRACT OF 2005-2006 PROGRESS**

The compositional data base for PNW grass species was greatly expanded with the intent of demonstrating the range of properties available for genetic improvements in commercial grass seed straws. The expanded database, shared with USDA-ARS collaborators, also allowed their evaluation of the application of NIR technology to a broad spectrum of PNW grasses. Extraction processes, and their underlying chemical basis, are now being evaluated in a systematic way. Initial experiments focused on water versus sequential water/solvent extractions, acid and base loads required (buffer capacity) for pH-based extractions, mineral content solubilities, and the use of enzymes for enhanced extraction of both organics and inorganics. The compositional data is essentially complete. The methods have been developed for advanced extraction studies, although analytical approaches will continue to be a focus as new experimental questions are addressed.

### **JUSTIFICATION**

The project is directed at developing economically viable grass straw utilization schemes. The target products include biopower, biofuels, biomaterials, and biochemicals. Current activity related to this project suggests that near-term on-farm electricity and/or ethanol production will be based on gasification technologies. Hence, the focus has been to obtain data that will support the development of technological advances in this area. To maximize profits, these operations must capture the relatively high value components from the grass straw feedstocks, particularly soil amendments, industrially relevant non-carbohydrate extractives, and five-carbon sugars prior to gasification. This past year's work, as well as current work, is directed at coupling feedstock composition and bio-based extractions to pre-gasification technologies.

### **PROGRESS**

*Objective 1. Develop suitable on-farm straw-to-sugar processing schemes. Year 2 Feedstock characterization, Extraction processes*

Feedstock characterization: The aim of the compositional work has been to generate a database containing the pertinent information on the composition of representative commercial grass seed straws in the context of the broad range of structural component compositions that

exist for Pacific Northwest-relevant grasses. The thirty nine non-commercial grasses included in the study were chosen based on near infrared reflectance (NIR) data indicating that these samples were representative of the broad compositional range that may be expected. The three commercial grass straws used for this portion of the study were Kentucky Bluegrass (KB), Perennial Ryegrass (PR), and Tall Fescue (TF). Wheat straw (WS) was also included since this is a “standard” feedstock against which the bioproducts industry may use for comparative purposes. A portion of the data obtained from these analyses is summarized in Table 1. It is to be noted that the total glycan content of the commercial grass straws is toward the upper range of that expected for the entire group of grasses analyzed. Total glycan is particularly relevant because it reflects the amount of fermentable sugars available in the feedstock. The fact that there are several non-commercial species containing higher amounts of structural glycans is important, because it indicates the potential of increasing the glycan content of the commercial grasses through breeding programs. This is particularly true of the tall fescue, which had the lowest total glycan values of the commercial grass seed straws tested. The ratio of the two major monosaccharides that make up the vast majority of the glycan fraction was found to be remarkably constant between species (glucan ~ 60%, xylan ~35%). We have demonstrated that the standard analytical procedures used to measure biomass glycans actually remove carbohydrate from the feedstock prior to the actual measurement of the glycan itself. Thus, the values discussed above are reported as “structural glycans” which, by definition, are those not removed by pre-analysis extractions. It is expected that some carbohydrates (i.e. glycans) will be in the “extractives” fraction and, thus, the values presented above represent minimum potential sugar yields per amount of biomass.

Acid-insoluble lignin (AIL) is the biomass component that is most commonly correlated with limitations in the biological reactivity of straws. Thus, it is an important component to discuss here. The AIL content of the commercial grass seed straws was significantly below that of wheat straw and some of the other grasses. It does not look as though there are many species which, when mature, have AIL values below that of the grass seed straws. Thus, it does not appear that this is a good target compound for breeding studies aimed at enhanced reactivity.

The last component of Table.1 that should be addressed in this report is “extractives”. “Extractives” are those components that are readily extracted from the straw with relatively little energy input. This fraction appears particularly important with respect to pre-gasification processing (see “Justification” above). The extractives content of the commercial grass seed straws is in the 30% range. This suggests that nearly one-third of the total solids may be extracted with relatively low energy input. Included in the “extractives” is a significant fraction of the overall mineral content (60-80% of the total inorganic matter originally associated with the grasses), at least a portion of which could be returned to the field should the extraction be done “on-farm”. It can be seen that the extractives content of the grass population tested ranged up to ~ 40%, although the highest values were associated with the less mature plants.

*Percent Glycan/Lignin/Extractives Content of Commercial Grass Species<sup>a</sup>*

Straw	Source	Total Glycan	Glucan (cellulose)	Lignin		Extractives <sup>b</sup>
				Acid Insoluble	Acid Soluble	
Perennial Ryegrass (PRG)	Willamette Valley	45.8	29.5	11.8	1.76	28.1
Kentucky						

Bluegrass (KBG) <sup>b</sup>	Spokane	45.4	26.8	11.1	1.77	29.2
Tall Fescue (TF)	USDA	41.0	26.0	10.7	1.95	29.4
Wheat Straw (WS)	USDA	53.8	34.1	14.0	1.62	16.3
Range of non-commercial grasses <sup>b</sup>	USDA	31.7- 49.7	18.7 – 31.2	6.4-14.6	1.6-4.4	20.3 – 41.6

<sup>a</sup> Analysis of samples following sequential (water, ethanol) 24-hour Soxhlet extraction. All values are % of dry weight of grass straw.

<sup>b</sup> values reflect the analysis of 39 non-commercial grasses previously determined to represent the range of compositions to be expected for Pacific Northwest relevant grass species.

Extraction Processes: A major emphasis over the past year has been to develop the methods necessary to systematically evaluate the extractives fraction of commercial grass seed straws. The methods are to be applied to four practical questions related to the extraction of commercial grass seed straws. First, to what extent are extraction yields dependent on pH and microbial growth. Second, what organic compounds (a) may be readily extracted at different pH and temperature combinations and (b) determine the buffering capacity of the commercial grass seed straws. Third, what mineral components may be readily extracted at different pH and temperature combinations, with an emphasis on the extraction of the major anti-quality inorganics (from a gasification perspective), particularly K<sup>+</sup>, Cl<sup>-</sup> and Si. Fourth, how might enzymes be used to enhance the extent of extractives recovery from commercial grass seed straws. Experiments addressing all of these questions are ongoing, as explained below.

Our initial studies in this area have focused on pH and temperature effects on water-recoverable extractives. An early complication arose regarding microbial growth. In general, straws suspended in water will result in pH values in the 6–7 range. Our early experiments, at temperatures from 30°–50° C, showed rapid reproducible declines in pH after approximately 6 hr. incubation. Tests with antimicrobials demonstrated that the change in pH was due to microbial metabolism. This finding led to an unexpected complexity – should anti-microbials be a part of these studies and, if so, which ones. It is unlikely that on-farm systems would include anti-microbials and yet microbial growth seriously complicates the systematic evaluation of the process (which is needed if the system is to be optimized). For example, to determine minimum extraction costs it is necessary to determine the properties that govern the buffer capacity of the different straws, and how buffer capacity is dependent on temperature. Anti-microbials, in general, are ionizable and, hence, have buffering capacity themselves, so their inclusion makes these experiments far more complicated. We have now worked out two experimental approaches, one with and one without antimicrobials. The approach(es) used will depend on the hypothesis being tested in the experiment.

In a separate set of experiments the extraction potential of water, in combination with an organic solvent (ethanol), is being evaluated. The results indicate that higher amounts of extractives may be obtained if water is used in combination with ethanol, but that the increase in the amount of extractives (26.7 → 29.0 percent) is unlikely to be cost effective. Confirmation of this will come when the identity of the ethanol-specific extractives are identified.

Studies have been, and continue, to evaluate the extractability of straw mineral/inorganic components. Combustion experiments indicate that the commercial straws, in combination with

the relevant PNW grass species, ranged from approximately 4-11 % total inorganics, and that following extraction the inorganics content of these same species dropped to 0.5-2.5 % total inorganics. The results are encouraging for pre-gasification removal of significant amounts of anti-quality inorganics. The focus of current work is the behavior of the silica component of the straws; these studies include analytical approaches to assess this component's solubility properties.

USDA-ARS (Corvallis) research contributions in support of the '05-'06 work for this project included coordinated data interpretation and selected instrumental analyses. USDA-ARS took the lead for the sample selection phase of the study in year 1. None of the funds received from GSCSSA were used to directly support the USDA-ARS contributions. USDA ARS and OSU are currently in the process of writing and joint publishing the results from these compositional analyses.

**Objective 2.** *Develop an on-farm scale gasification reactor that produces high quality syngas.* As in the previous year, the ARS cooperator utilized base funds to conduct the gasification research proposed in Objective 2 as part of assigned ARS in-house research. A summary of those results appear in the ARS progress report. Accordingly, all GSCSSA funds were utilized to expand the scope of the pre-gasification processing studies, as outlined in the FY 2005 proposal.

## INTERACTIONS

Work involving the "Investigators" and "Collaborators" is seamless. Samples, data, and expertise are shared between groups. In early 2006 Jeffrey Steiner (Co-PI) left the Corvallis USDA facility to take an administrative position in Washington, D.C. Dr. Stephen Griffith has taken on many of the projects that were previously under the direction of Dr. Steiner. Hence, OSU (M. H. Penner) is now working more closely with Dr. Griffith. Other scientists at Oregon State University and scientists and engineers at the National Renewable Energy Laboratory (NREL; Golden, CO) are sometimes involved in an advisory capacity.

## TIMELINE

*Nov. 2005 – present (done):* continue to obtain data on chemical composition of representative grass straws with emphasis on mass-balance closure for assessment of extraction and gasification potential.

*January 2006 – present (done):* Evaluate extraction schemes, including enzymatic saccharification, as pretreatments for processes focusing on value-added extractives from commercial grass straws

*Nov. 2006 – Nov. 2007 (to be done):* Continue the experimental study of issues related to "Objective 1", with an emphasis on those experiments addressing the four targeted questions dealing with "extractives" recovery (see above).

## PUBLICATIONS

- Masrungson, D. (2006) "Structural component composition of Pacific Northwest grass-derived biomass", M.S. Thesis, Oregon State University
- Masrungson, D., Smith, D., El-Nashaar, H. M., Griffith, S.M., Banowetz, G.M. and Penner, M.H. (2006) "Structural component composition of Pacific Northwest grass-derived biomass" *Biomass & Bioenergy* (in internal review process)