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Biomass Compositional Analysis Method Variability

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Motivation

- ***Compositional analysis data used in all steps of biomass to biofuels process research.***
- ***We would like to determine "typical" feedstock analytical wet chemistry errors.***
- ***Better able to match NIR calibration models to wet chemistry errors.***
- ***Identify and then control important sources of error.***

Method Background

Wet chemistry methods adapted from wood lignin methods.

1920's -1940's: *USDA Forest Products Lab (FPL) Applied H_2SO_4 lignin methods for US wood samples*
1954: *Adapted as TAPPI lignin standard method*
1967: *Procedures for the Chemical Analysis of Wood and Wood Products by Moore and Johnson (FPL)*
1970's -1990's: *Methods adapted to dietary fiber analyses (Uppsala Method for dietary fiber)*
1990's: *FPL/TAPPI/Uppsala methods applied to wood analysis at NREL for biofuels research (NREL LAPs)*
1993: *IEA/NREL round-robin compositional analysis*
1995: *ASTM adapted NREL LAPs as standard method*
2000's: *NREL adapted LAPs to herbaceous residues (corn stover). Continue to improve methods*

Experimental Conditions

Analysis material: Corn Stover (Pioneer 33B51)
- *Harvested 2003 from Northeast Colorado*
- *Milled (2mm) and sieved (-20/+80 mesh)*
- *900g sample coned and quartered 3X*
- *NIR check confirmed homogeneity*

Run in batches of 12 + NIST Bagasse (SRM #8491)
- *Limited by number of ASE positions*

14 batches (168) run by 8 analysts in 2 labs at NREL
- *Two analysts ran 4 batches split between both AFUF and FTLB labs*
- *Six analysts ran one batch each split between labs*
- *Designated autoclaves in AFUF (larger, built in) and FTLB (smaller, benchtop size)*
- *Triplicate sugar recovery standards (SRS) run with each batch to correct for losses during hydrolysis*

Complete solids composition including extractives

Method Scheme

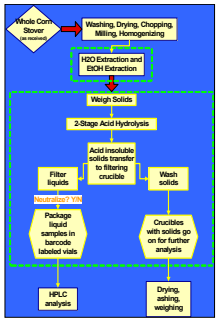
Sample preparation
- *Drying then milling*

Extraction
- *Water then ethanol*
- *Accelerated Solvent Extraction*

Two-stage hydrolysis
- *72% H_2SO_4 1hr, 30 ℃*
- *4% H_2SO_4*
- *Autoclave 1hr, 121 ℃*
- *SRS to correct for loss*

Gravimetric analysis
- *lignin*

HPLC analysis
- *As monomers*



Available at:
http://www.nrel.gov/biomass/analytical_procedures.html

Corn Stover Wet Chemistry Statistics

Sample Description	% Whole Ash	%Structural Inorganics	%Non-structural inorganics	%Structural Protein	% Sucrose	%Water Extractable Others	%Ethanol Extractives	% Lignin	% Glucan	% Xylan	% Galactan	% Arabinan	% Acetyl	% Total Component Closure
Within Batch Repeatability														
Grand average	4.78	1.67	3.11	1.08	7.24	10.14	2.58	12.29	33.96	19.15	1.05	2.50	2.88	97.41
pooled sd	0.10	0.09	0.14	0.04	0.37	0.56	0.12	0.12	0.36	0.23	0.05	0.10	0.14	0.62
Pooled n	136	136	136	115	135	134	136	124	128	131	135	135	123	130
pooled CV	2.10%	5.23%	4.39%	4.06%	5.08%	5.50%	4.72%	0.95%	1.06%	1.19%	4.61%	4.10%	4.78%	0.63%
Between Analyst Reproducibility (one sample per analyst)														
Reproducibility ave	4.78	1.67	3.11	1.08	7.24	10.14	2.58	12.29	33.96	19.16	1.05	2.50	2.87	97.43
Reproducibility sd	0.21	0.10	0.25	0.05	0.42	1.23	0.10	0.16	0.46	0.29	0.11	0.22	0.27	1.57
Reproducibility n	12	12	12	12	12	12	12	12	12	12	12	12	12	12
Reproducibility CV	4.36%	6.28%	8.20%	4.92%	5.78%	12.16%	4.07%	1.30%	1.35%	1.53%	10.78%	8.85%	9.52%	1.62%

Table 1. *Table showing within and between batch compositional analysis summary statistics for corn stover. Values for NIST Bagasse (SRM 8491) were similar (data not shown)*

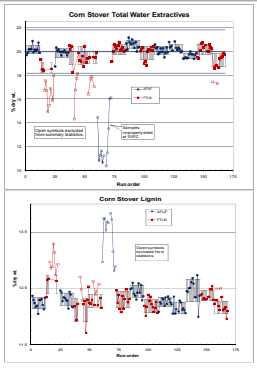


Fig 1. *Charts of corn stover water soluble material (upper) and whole-basis lignin (lower) shown in run order. The samples are grouped in batches run together by an analyst. Error bars are set at ± 1sd around each batch average. The error in water solubles dominated the overall errors. Samples with unusually low water extractives had high lignin values. The same effect is seen in glucan and xylan (data not shown). For water extractives, the average and ± 3 sd lines are shown. Samples (n=29) with water extractives below 3 sd are not included in final statistics.*

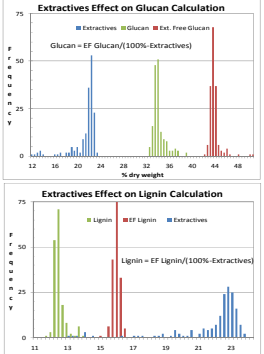


Fig 2. *Effect of variable extractives values on whole-basis glucan and lignin calculations. Extractives-free glucan and lignin (red bars) show narrow distribution. When converted to whole basis the glucan and lignin (yellow bars) take on the water extractives errors (blue bars). This shows the error comes from the extractives test not the glucan/lignin test. No effect of poor extraction seen in extractives free data.*

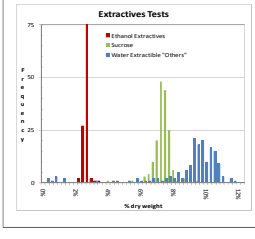


Fig 3. *Histograms of extractible components in corn stover. Ethanol extractives and sucrose show narrow distributions, while water extractible "others" shows wide distribution. Errors in water extraction not seen in sucrose and ethanol extractives.*

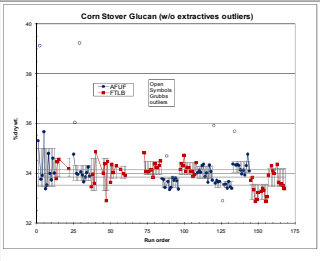


Fig 4. *Chart of corn stover glucan in run order (shown without extractives outliers). The average and ± 1 sd lines are shown. Seven samples (open symbols) are identified as outliers using the Grubbs test and not included in final statistics.*

Six samples are significantly above batch average. Sugars may have been concentrated in the lignin vacuum filtration step. A similar trend was seen in xylan and (weakly) in acetyl (data not shown), but not lignin (Fig 2).

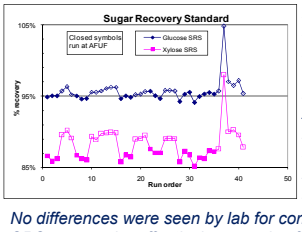


Fig 5. *Run chart of sugar recovery standards (SRS) run in triplicate with each batch. Samples run in AFUF (closed symbols) in larger autoclave showed significantly lower SRS recovery for both glucan and xylan.*

No differences were seen by lab for corn stover composition. SRS seem to be effectively correcting for autoclave differences.

Conclusions

- ***Reproducible results seen from 8 analysts in 2 labs.***
- ***No compositional difference seen between labs.***
- ***Errors in water extract not seen in ethanol extraction.***
- ***Error in water extractives dominated overall errors.***
- ***This effect was computational rather than physical as extractives free values showed good reproducibility.***
- ***Carbohydrates may be concentrated in hydrolysate liquor during lignin vacuum filtration step.***
- ***SRS effectively corrects for different autoclaves.***

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