Analysis of European Biomass Feedstocks and Development of Near Infrared Spectroscopy as a Rapid Analytical Tool

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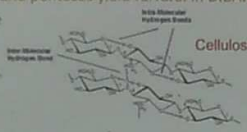
Biomass Composition and Feedstocks

Work Package 2 (WP2) involved the analysis, via wet-chemical and spectroscopic means, and the evaluation of a range of potential biomass feedstocks. Important chemical properties include:

Polysaccharides (hexoses yield levulinic acid + formic acid and pentoses yield furfural in DIBANET)

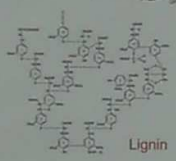
Cellulose (a homopolysaccharide made up of glucose (hexose) monomers).

Hemicelluloses (contain the hexoses galactose, mannose, rhamnose, glucose, and the pentoses arabinose and xylose).



Lignin

Klason lignin and acid-soluble lignin. Will form part of the acid hydrolysis residues in DIBANET.



Extractives

Interfere with analytical-hydrolysis results for sugars and lignin; ethanol-soluble extractives were removed.

Ash

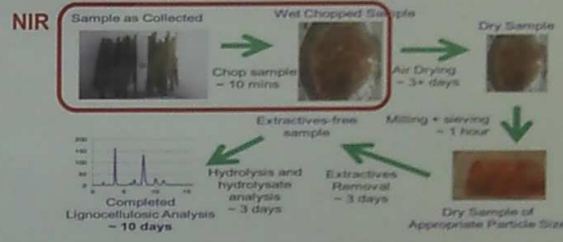
Standardised analytical methodologies were prepared at Carbolea and introduced to WP2 partners CTC and UNICAMP at a Biomass Analysis Workshop in Dec 2009. These methodologies and the associated data recording sheets can be downloaded from the DIBANET website.

Carbolea researchers were responsible for the analysis of feedstocks relevant to Europe. Some of these feedstocks are listed, according to category, below:

Energy Crops	Agricultural Residues	Wastes
Miscanthus	Cereal Straws	Municipal solid wastes
Switchgrass	Animal Excreta	Waste Papers
Reed Canary Grass	Spent Mushroom Compost	Garden Wastes/Composts
Short Rotation Coppices (SRC)	Forestry Residues	Sewage Sludge
		Food Waste

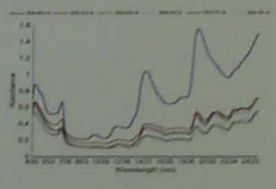
Near Infrared Spectroscopy (NIRS)

As shown below, the wet-chemical analysis of biomass for lignocellulosic constituents is costly and time consuming. Near infrared spectroscopy (NIRS) provides spectra based on the absorbance of near infrared light by samples. Chemometric models can be used to relate the spectral variations with the chemical variations seen in the calibration set. From these models the compositions of unknown samples can be predicted. A target in DIBANET was to develop models based on the spectra of wet samples with heterogeneous particle sizes. Something that has not been achieved accurately for lignocellulosic biomass in the past.



Several NIR spectra were collected for each sample, according to sample state:

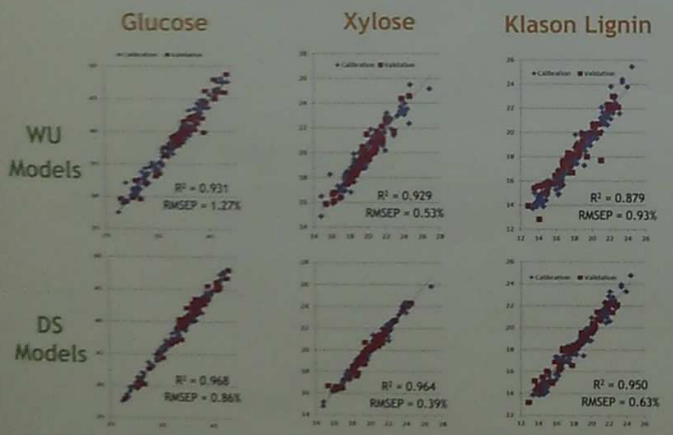
- WU = Wet and unground
- DU = Air-dried and unground
- DG = Dried and ground (<850µm)
- DS = 180 µm < x < 850 µm
- DF = <180 µm



NIR models were then built based on the wet-chemical data of samples in the DS state.

NIRS Models for Miscanthus

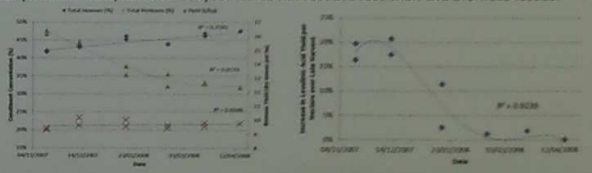
The most accurate quantitative models were developed based on the DS spectra, however the predictions from WU (wet) spectra were still of a high accuracy and show that NIRS has potential as a true rapid analysis tool both in the laboratory and, potentially, on an online basis in biorefineries. Some regression plots, with statistics for the validation set, are included below:



Models were also developed for: galactose, arabinose, rhamnose, mannose, total sugars, acid soluble lignin, acid insoluble residue, acid insoluble ash, nitrogen, ash, ethanol-soluble extractives.

Use of Models to Predict Biorefinery Yields

NIR models were applied to Miscanthus samples collected over the harvest window (Nov-April). During this time leaves are lost (biomass yield decreases) but the hexose and total sugars content of the harvestable biomass increases. This means the losses in potential biorefinery yields (levulinic acid, ethanol etc.) for a late harvest are less than the biomass losses.



Formation of Analysis Spin-Out Company

As a result of the successful development of wet-chemical and NIR methods during DIBANET, a spin-out company has been registered. The Biomass Analysis Centre of Ireland (BACI) will offer numerous analytical services to characterise lignocellulosic biomass, including the determination of:

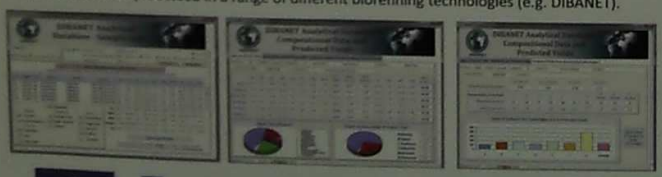
- Lignocellulosic sugars (glucose, xylose, mannose, rhamnose, galactose, arabinose).
- Klason lignin and acid soluble lignin.
- Ash (including acid-insoluble and ethanol-insoluble ash).
- Extractives (various kinds including ethanol and water-soluble).

NIR predictions for the above constituents will also be offered as a single package based on either the spectra of wet (Miscanthus, peat, and sugarcane-residues only) or dried samples.

baci Biomass analysis centre of Ireland

Downloadable Analytical Database

A database containing all of the wet-chemical data and all of the NIR-predicted compositional values can be downloaded from the DIBANET website. It contains a total of 1,281 samples from Europe and Latin America. Samples can be sorted according to location, sample type, and property. Predicted values are also presented for the yields that could be obtained if these samples were to be processed in a range of different biorefining technologies (e.g. DIBANET).



Additional Outputs

There have been numerous other valuable outputs from Carbolea's contribution to WP2:

- Quantitative NIR models for waste papers, cereal, straws, and a global dataset of all DS spectra.
- NIR models for the composition of pretreated Miscanthus and acid hydrolysis residues (WP3).
- NIR models to discriminate between samples. E.g. between Miscanthus plant fractions, varieties, harvest periods, and stand ages.
- Chemometric models to predict the concentrations of products including levulinic acid, formic acid, furfural, hydroxymethylfurfural, and acetic acid in process hydrolysates from WP3 based on their ultraviolet transmission spectra.
- Models to predict the hexose and pentose contents of biomass analytical hydrolysates from WP2 using ultraviolet transmission spectra; a rapid means of analysis prior to chromatography.

References:

Hayes, D. J. M. (2012), Development of near infrared spectroscopy models for the quantitative prediction of the lignocellulosic components of wet Miscanthus samples, **Bioresource Technology**, 119: 393-405

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