

DIBANET: Collaboration in Biorefinery Research Between Europe and Latin America



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University of Limerick









SEVENTH FRAMEWORK PROGRAMME THEME: FP7-ENERGY.2008.3.2.1

"Enhancing international cooperation between the EU and Latin America in the field of biofuels"

DIBANET = Development of Integrated Biomass Approaches NETwork

"The production of Sustainable Diesel Miscible Biofuels from Europe and Latin America"



DIBANET Partners





There are 13 partners in the group, 5 from the EU & 8 from Latin America. The total budget for the 42 month project is €3.72m. DIBANET is co-ordinated by UL



5 Key Scientific Objectives

- 1. Optimise the yields of levulinic acid (and co-products), from the conversion of biomass, while minimising chemical/ energy requirements.
- 2. Improve the energy balance of the production of levulinic acid and the total biofuel yields possible from a feedstock by sustainably utilising the residues in pyrolysis/gasification processes.



- 3. Reduce the energy and chemical costs involved in producing ethyl-levulinate from levulinic acid and ethanol.
- Select key biomass feedstocks for conversion to levulinic acid, analyse these, and develop rapid analytical methods that can be used in an online process.
- 5. Analyse the DMBs produced for their compliance to EN590 requirements and, if non-compliant, suggest means to achieve compliance.



DIBANET processes & products & their linkages





- 1. Analysis of biomass and development of NIRS as a rapid primary analytical tool.
- 2. Development of pretreatment technologies for biomass.
- Production of levulinic acid, formic acid, furfural and ethyl levulinate from biomass.





- Carbolea developed standardised analytical methodologies for all DIBANET partners for important constituents:
 - C6 Sugars: Glucose, Galactose, Mannose
 - C5 Sugars: Arabinose, Xylose
 - Lignin content (acid soluble and insoluble)
 - Extractives
 - Ash.
 - Elemental analysis.
- Carbolea researchers have analysed over 1,000 samples via wet-chemical or NIRS.





NIRS - Concept

- NIR radiation can be absorbed by molecular bonds, resulting in vibrational movements.
- The radiation must be of the correct frequency/wavelength to allow absorption (quantum levels).







- A calibration set of samples with known compositions (determined via conventional methods) are used to develop the models.
- These models relate spectral variations to chemical variations using chemometric methods (e.g. PLS).
- The performance of the models is determined by testing them on the validation set; samples outside the calibration set.
- Important regression statistics:
 - R² for validation set (model predicted value vs. real value).
 - RMSEP/SEP standard error of prediction (error of estimate).



Application of NIRS in Carbolea



- We target the development of robust and accurate calibration equations for material that is wet and of a heterogeneous particle size.
- The vast majority of existing publications regarding the use of NIRS for the characterisation of lignocellulosic materials have focused on dry samples that have been ground down to a homogeneous particle size (< 1mm).
- They have preferred this method because the presence of water can mask the absorbance signal of some of the analytes of interest.

Sample Preparation



DIBONE.





ASTM Guidelines for NIRS Calibration

- The quality of the calibration is determined relative to the natural variation that exists for the components of that feedstock.
- A ratio is determined by dividing the range in concentration by the SEP.
- A ratio of 15+ is considered to be good for quantitative calibration.
- A ratio of 10-15 is considered good for screening control.
- E.g. if the cellulose content of Miscanthus varies between 40 and 50%. The maximum SEP permitted to allow a ratio of 15 is 0.67%. This shows the importance of **highly** accurate and reproducible lab methods.



Chemometric Models Developed at Carbolea

- Straws.
- Waste Papers.
- Peat.
- Pretreated Miscanthus.
- Residues and Hydrolysates from the DIBANET hydrolysis process.
- Hydrolysates from analytical hydrolysis.
- Miscanthus.
- A global dataset containing all samples.





Miscanthus Samples



- "I" = Internodes
- "N" = Nodes (each plant also sampled by the metre).
- "K" = Live leaves (>60% green by visual inspection)
- "M" = Live Sheaths
- "F" = Dead leaves (<60% green by visual inspection)
- "H" = Dead sheaths
- "FL" = Flowers
- "WP" = Whole plant (sometimes separate metre sections are collected)
- Over 700 such samples collected.







Glucose Models

DS

WU







Miscanthus Glucose Models



| | DS | DG | DU | WU |
|------------------------------|---------|---------|---------|---------|
| Calib:Valid | 159:42 | 125:45 | 128:44 | 147:42 |
| PLS Factors | 16 | 16 | 14 | 14 |
| CV - <i>R↓1</i> 2 | 0.9663 | 0.9435 | 0.9248 | 0.9545 |
| RMSECV | 0.9142 | 1.1394 | 1.3778 | 1.0823 |
| RER (CV) | 22.9086 | 18.0032 | 15.1918 | 19.3456 |
| Prediction - <i>R↓1</i> 2 | 0.9680 | 0.9483 | 0.8922 | 0.9305 |
| RMSEP | 0.8617 | 0.9680 | 1.2374 | 1.2663 |
| RER | 23.8086 | 21.2891 | 13.3996 | 16.2032 |



Miscanthus Xylose Models



| | DS | DG | DU | WU |
|-------------------|---------|---------|---------|---------|
| Calib:Valid | 149:42 | 125:45 | 128:44 | 147:42 |
| PLS Factors | 14 | 14 | 14 | 14 |
| CV - <i>R↓1</i> 2 | 0.9571 | 0.9565 | 0.9178 | 0.8605 |
| RMSECV | 0.4262 | 0.4547 | 0.6059 | 0.7757 |
| RER (CV) | 27.9720 | 26.1357 | 16.1676 | 15.3696 |
| Prediction - R↓12 | 0.9475 | 0.9392 | 0.9249 | 0.9292 |
| RMSEP | 0.4571 | 0.4664 | 0.6245 | 0.5317 |
| RER | 20.0524 | 20.6527 | 19.5001 | 17.0500 |



Klason Lignin Models (Gig)

| | DS | DG | DU | WU |
|------------------------------|---------|---------|---------|---------|
| Calib:Valid | 126:31 | 104:31 | 105:29 | 138:31 |
| PLS Factors | 8 | 8 | 8 | 10 |
| CV - <i>R</i> 112 | 0.9568 | 0.9541 | 0.9448 | 0.9173 |
| RMSECV | 0.5775 | 0.5596 | 0.5910 | 0.8055 |
| RER (CV) | 19.9707 | 20.5908 | 18.3601 | 14.3213 |
| Prediction - <i>R</i> ↓↑2 | 0.9747 | 0.9532 | 0.9666 | 0.9576 |
| RMSEP | 0.4812 | 0.6121 | 0.5198 | 0.5980 |
| RER | 18.4932 | 15.9996 | 20.9808 | 15.7505 |



Miscanthus Models - Summary

| | DS | DU | WU | RMSEP _{wu} | RER _{WU} |
|------------|------|----|----|---------------------|-------------------|
| Glucose | А | В | Α | 1.26% | 16.20 |
| Xylose | А | А | А | 0.53% | 17.05 |
| Rhamnos | e B | В | С | 0.06% | 8.38 |
| Mannose | e C | С | С | 0.07% | 5.52 |
| Arabinose | e B | В | В | 0.27% | 11.04 |
| Galactose | e C | С | С | 0.12% | 7.97 |
| Total Suga | rs A | В | Α | 1.21% | 18.59 |
| KL | А | Α | Α | 0.60% | 15.75 |
| ASL | А | В | В | 0.42% | 10.62 |
| Ash | А | В | В | 0.93% | 10.66 |
| EXTR_PD | В | В | С | 1.38% | 7.83 |
| Nitrogen | А | С | С | 0.28% | 6.84 |
| Moisture | . – | - | А | 2.52% | 23.80 |



Changes in Stem to Leaf Ratio





Early vs. Late Harvest – Whole Plant





Early vs. Late Harvest – Whole Plant (2)





Changes Over Window









DIBANET Biomass Report





Spin-Out Analysis Company



- Sugars
- Lignin (Klason and acid soluble)
- Ash
- Extractives (ethanol and water)
- Elemental
- More planned in mid-term.
- Accuracy of DIBANET methods has been identified as superior to other competing companies and the literature.
- Company will offer guarantees on precision of analysis.
- (2) NIR Analysis Predictions of the above based on models developed.





Current Work

- Daniel Hayes working at CTC (Brazil) as part of DIBANET for the development of NIR models for sugarcane bagasse.
- Includes the deployment of an online NIR system at a sugar-mill.







2. Pretreatment of Biomass







The Context



- Is there a process to :
 - Reduce Mechanical energy inputs (Grinding, Chopping)
 - Reduce Energy inputs (heat)
 - Increase biorefining yields
 - Environmentally sustainable
 - Cost effective
 - Capital, energy, rendering of output streams
 - Encompasses the best attributes of different approaches





✓ Suitable solvents for lignin such as formic and acetic acid, ethanol.

✓Selective dissolution and degradation of lignin.

✓Organic acids work as solvent and catalytic agent to break down lignocellulose: hemicellulose hydrolysis.

Swelling and interaction by hydrogen bonding.

| Formosolv | Alcell | Organocell | Milox |
|--|---|--|--|
| Formic acid reduces residual lignin to 4% in beech wood at 130°C | It uses aqueous ethanol at 180-200°C with additives such as H_2SO_4 and naphthol. | It uses aqueous methanol at 175-200°C with additional NaOH (~12%). | It uses solutions of peroxide (up to 2.5%) in aqueous formic acid in a three stage process. |



Oxidative Hydrolysis



- H2O2:
 - An oxidiser at ambient temperature in combination with an organic acid yields per-acid: effective lignin remover
 - Can be catalytically triggered to decompose rapidly (Fe, Transition metals, pH)
 - Decomposes Exothermically (pressure)
 - Environmental
 - Cost effective: available as a bulk chemical



 FA/H_2O_2



- Higher peroxide concentrations not used
 - Excessive oxidation of the lignin
 - Excessive degradation of holo-cellulose to undesired reaction products
- Typical milox process
 - Multi step at least 2 usually 3 at atmospheric pressure
 - Organosolv
 - Performic (1-2% Peroxide on biomass)
 - Alkaline oxidation
 - Residence times 1-3 hrs @ 70-130 °C



Fast Oxidative Fractionation of Biomass in Formic Acid



- ✓ Oxidative properties of H_2O_2 (bulk chemical) for the fast lignin fractionation: High recovery lignin yields.
- Exothermic reaction provides the energy for hemicellulose hydrolysis in the acidic medium.
- \checkmark High cellulosic pulp to facilitate further conversion.
- \checkmark Cost effective and sustainable.



Experimental Procedure





Temporal Evolution of the Liquor



- Once the secondary structure of the material collapses lignin and sugar release is triggered
 - Time to max liquor level dependent on concentration
 - At higher peroxide some degradation of the cellulose is beginning



Solids Analysis



| | Miscanthus | 2.50% | 5.00% | 7.50% |
|-------------|------------|-------|-------|-------|
| Glucose | 40.31 | 52.40 | 72.12 | 79.16 |
| Galactose | 0.64 | 0.53 | 0.14 | 0.04 |
| Mannose | 0.25 | 0.17 | 0.13 | 0.07 |
| Total C6 | 41.20 | 53.10 | 72.39 | 79.27 |
| Xylose | 19.38 | 22.72 | 11.95 | 4.92 |
| Arabinose | 2.15 | 2.11 | 0.43 | 0.12 |
| Rahmnose | 0.21 | 0.13 | 0.08 | 0.06 |
| Total C5 | 21.74 | 24.96 | 12.46 | 5.10 |
| K-Lignin | 21.79 | 5.95 | 4.47 | 6.02 |
| Extractives | 1.81 | 2.00 | 3.29 | 5.58 |



Mass Balance (1)



Unlike conventional milox: increased peroxide increases recoverability of lignin and hemi-cellulose from the liquor



Mass Balance (2)



Unlike conventional milox: increased peroxide increases recoverability of lignin and hemi-cellulose from the liquor



Mass Balance (3)



Unlike conventional milox: increased peroxide increases recoverability of lignin and hemi-cellulose from the liquor



Time of digestion: 24 hrs



Avicel 101



Time of digestion:48 hrs





2. Pretreatment: Summary

\checkmark Oxidative pretreatment of biomass

- Hydrogen Peroxide in Formic Acid treatment fractionates in a rapid process all components in lignocellulosic biomass into products for further transformation.
- Potential for reducing energy consumption (heat generated/no extensive biomass grinding) is attractive.
- Extensive separation of lignin is reached: Up to 90% of the lignin can be removed from the biomass.
- Process may be optimised through H₂O₂ concentration and residence time: appropriate temperature and residence time for pentoses conversion and lignin fractionation.



3. Acid Hydrolysis of Biomass





Levulinic acid (LA)



- Levulinic acid (LA):
 - is a major product of the hydrolysis of lignocellulosic biomass using an acid catalyst.
 - has two functional groups (carboxylic and ketone).



 has been identified as one of the top-twelve platform chemicals derived from biomass.

Werpy, et al. (2004) Top Value Added Chemicals from Biomass. National Renewable Energy Laboratory



Derivatives of Levulinic Acid





Conversions of LA to alternative fuels







Furfural and its Derivatives



Corma et al. (2007) Chem. Rev., 107(6), 2411-2502.







Effects of Temperature and Acid Concentration



Temperature, °C

- ✓ High acid concentration and mild to lower temperatures favour LA formation and reduce humin formation.
- ✓ Hemicellulose (Xylan) reacts rapidly at the these conditions: shorter residence times are required.



Effects of Temperature and Acid Concentration





Levulinic Acid from Brazilian Feedstocks





Levulinic Acid from Irish Feedstocks











Reaction Networks for Kinetic Study





Continuous Reactor













3. Hydrolysis: Summary

✓ Acid catalysed Hydrolysis of Biomass:

- Due to the complex nature of biomass, multiple reactions are occurring simultaneously during aqueous acid catalysed process at high temperature.
- Process can be optimised by controlling temperature, acid concentration and residence time towards Levulinic Acid and Furfural: Yields up to 75% mol for LevAc at 150° C and 0.5 M H_2SO_4 in 8 hours. Lower temperatures/longer residence time can improve LevAc yields.
- Solid loading is another important parameter during the process: lower initial glucan availability leads to higher levulinic acid yields.
- Solid loading should be considered in balanced insight: bulk material density of biomass, recovery and separation of products after process.



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Further Details







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Thanks!!

Questions?