

Dibanet Final Publishable Summary Report

Executive summary. The increasing reliance on imported diesel fuels, in addition to annual increases in the quantities of organic wastes are threats to the EU and LA. DIBANET will combat these threats and help to eliminate diesel imports by developing novel technologies that will allow the sustainable production of diesel miscible biofuels (DMBs) from wastes. It will build on the key, complementary, strengths of EU and LA researchers and industries to advance this field. This enhancement of co-operation will ensure that the whole process, from feedstock to process residues, is engineered for maximum efficiency. The links between regions will be further enhanced by the establishment of scholarships for LA students; 2 large brokerage events to engage all stakeholders; and a summer school for knowledge transfer.

DIBANET will improve the state of the art in the yield of levulinic acid, a valuable platform chemical, and other products, from biomass. Levulinic acid, when combined with ethanol, provides ethyl levulinate, a DMB that can be used in regular diesel car engines up to 20% (double the proposed 2020 EU mandate). DIBANET, will also improve the means for producing ethyl levulinate. Processes will be advanced to utilise the solid residue that remains after the acid-treatment. An energy carrier will result and also biochar which will be examined for use as a soil amender for enhanced biomass yields. This, excitingly, offers the potential for a carbon negative biofuel.

The objectives of DIBANET in WP3 was on the conversion of lignocellulosic biomass in the pretreatment and hydrolysis reactors. The key target was high yields of levulinic acid and furfural. In order to optimise the production of the target molecules it was necessary to construct a lab scale reactor unit with the capability of sampling the process at each stage of operation. This unit was to be used to improve our knowledge and understanding of the behaviour of the individual major components of the feedstock (cellulose, hemicellulose, monosaccharides) by developing a series of kinetic equations to describe how the yield of levulinic acid and furfural change as a function of process conditions (acid concentration, time, temperature). A wide range of real biomass feedstocks from EU and Brazil were to be assessed for their potential yield of levulinic acid. The kinetic equation would be used as the basis of a design of a “future” pilot scale process plant. Developing a Pretreatment technology to optimise the release the monosaccharides in order to give the highest yields of target molecules will be developed.

The DIBANET reactor system can be considered to be a “hydrolysis technology” since it involves the breakdown of the structural polysaccharides of the feedstock to their component sugars. Feedstocks with greater polysaccharide contents can allow for higher yields of the DIBANET target chemicals. In order to allow determinations of potential yields the following lignocellulosic components needed to be analysed for: glucose, arabinose, galactose, rhamnose, xylose, and mannose. Advanced analytical techniques to benefit levulinic acid yields will be developed and employed online to allow real-time adjustment of biomass conversion conditions. It was intended that WP2 could analyse more feedstocks than could be feasibly processed in WP3 and that the analytical results of WP2 could provide important indications of the yields that could be expected from these feedstocks if they were to be processed in WP3. This objective also involved the partners determining which feedstocks should be focused-on for near infrared (NIR) model development.

Thermal gasification and fast pyrolysis will be used to process the acid hydrolysis residue (AHR) in order to produce energy products which could be converted to diesel miscible biofuels (DMB) . New catalytic materials were to be developed to produce DMB's such as ethyl levulinate and upgraded fast pyrolysis oils which were to be tested to ensure EN590 compliance. The residue from these thermal processes is to be tested as a soil amendment to ensure environmental sustainability.

Finally, DIBANET ensures that the outputs of the research are fully exploited to the maximum benefit of both regions by developing a model for optimising the DIBANET process chain while maximising the socioeconomic impact and environmental sustainability leading to a strong future relationship in trade and research between EU and South America.

Summary description of the project context and the main objectives. (4 pages max).

Europe and Latin America share common needs and threats. The increasing reliance on **imported diesel fuels** is a problem for both regions. Many of the current feedstocks used for biofuel production have a variety of economic, technical and environmental problems and cannot satisfy our diesel needs (Table 1.1).

Table 1.1: Comparison of DIBANET feedstocks against first-generation crops

| | Sweet Sorghum (LA) | Maize (EU/LA) | Soya beans (EU/LA) | Rapeseed | DIBANET (residues and wastes) |
|---------------------------------|--------------------|-----------------|--------------------|------------|--------------------------------------|
| Energy Ratio (out vs in) | Medium | Low or negative | Low | Low | HIGH |
| Greenhouse gas saving potential | Medium | Low or negative | Medium | Medium | HIGH |
| Food vs Fuel? | YES | YES | YES | YES | NO |
| Can give a DMB? | NO | NO | YES | YES | YES |
| Feedstock Cost | Medium | HIGH | HIGH | HIGH | LOW |

Europe and Latin America (LA) are also experiencing annual **increases in** their quantities of **organic wastes**. Ideally these should be used to produce diesel fuels but there are technical limitations with waste-to-biofuel technologies in their current art (Table 1.2)

The objectives of DIBANET was to develop technologies to help reduce **the need for fossil diesel imports** in either region, improving the security of energy supply. This reflects a key philosophy of the Strategic Research Agenda of the European Biofuels Technology Platform (**BiofuelsTP**) which suggests that a significant part of biofuels should be targeted at diesel engines. DIBANET will achieve this by advancing the art in the production of **ethyl-levulinate** from **organic wastes and residues**. Ethyl levulinate (EL) is a novel diesel miscible biofuel (DMB) produced by esterifying ethanol with levulinic acid. The feedstock flexibility that allows the processing of wastes also reflects a key priority of the BiofuelsTP as well as the **EU Strategy for Biofuels COM(2006)**. The production of EL from indigenous wastes, coupled with a synergistic biofuel trading relationship with LA, will allow Europe to sustainably meet the 10% biofuels quotient mandated for 2020 in proposed **Directive 2008/0016**.

Table 1.2: Comparison of waste-processing technologies (FAME= fatty acid methyl esters).

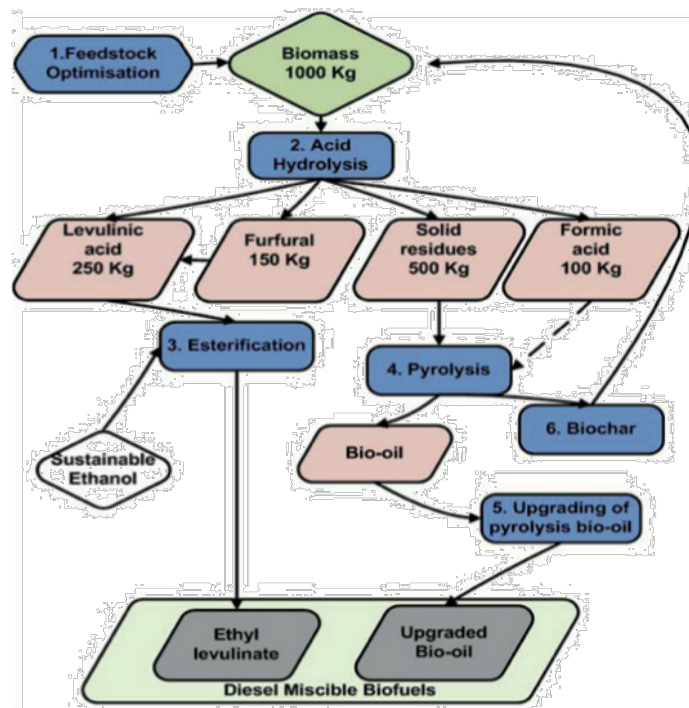
| | Enzymatic Hydrolysis | Gasification | FAME from wastes | Anaerobic digestion | DIBANET approach |
|---|---|----------------------------------|-----------------------------|----------------------------|-------------------------|
| Product: | Ethanol | Alcohols or FT diesel | Biodiesel | Biogas | DMB |
| Feasible waste feedstocks: | Straws, bagasse, wood | Woods | Fats and oils | Mostly grasses | All Lignocell. |
| Non-feasible feedstocks: | Municipal waste, mixtures | Municipal waste | Non-fats/oils | Dry biomass | Fats and Oils |
| Expands feedstock range? (Feedstock flexibility) | NO Enzyme specific to feedstock | NO (reactor sensitive) | YES (limited) | YES (limited) | YES |
| Can give a DMB? | NO | YES (FT-Diesel) | YES (up to 5% in EU) | NO | YES (up to 20%) |
| Processing Cost | HIGH | HIGH | LOW | LOW | LOW |
| Can have large impact on demand? | NO (few feedstocks) | NO (few feedstocks) | NO (few feedstocks) | Medium | YES |

The key Scientific Objectives (SO) of the DIBANET Project were:

1. **To improve the yields of levulinic acid** (and co-products), from the conversion of biomass, while minimising chemical/energy requirements.
2. Improve the **energy balance** of this process and the total **biofuel yields possible** from a feedstock by sustainably **utilising the residues** in **pyrolysis** processes to produce a **bio-oil** that can be **upgraded** to a DMB or a diesel fuel additive.
3. **Reduce** the energy and chemical **costs** involved in producing **ethyl-levulinate** from levulinic acid and ethanol.
4. Identify **key biomass feedstocks** for conversion to levulinic acid, analyse these, and develop **rapid analytical methods** that can be used online.
5. **Analyse the DMBs produced** for their compliance to EN590 requirements and, if non-compliant, suggest means to achieve compliance.

To achieve these scientific objectives DIBANET assembled a **well balanced** group of partners from both the EU and LA. DIBANET will **enhance co-operation** between partners and between the EU and LA in biofuels. It has four **Co-Operation Objectives**:

1. Develop a tightly-integrated online network of key players in the EU and LA
2. Organise public meetings/forums between key stakeholders from both regions.
3. **Train PhD and post-doctoral researchers** from the opposite region.
4. Develop an inter-regional **Technology Transfer Business Plan** for the most effective exploitation of the DIBANET technologies. This will consider the combined needs of the EU and LA and the potential for trade.



S&T Results for WP2

Identification of EU and Latin American Feedstocks Most Suitable for Processing by Acid Hydrolysis

The focus in DIBANET WP3 was on the conversion of biomass materials in the pre-treatment and hydrolysis reactors. The key target was high yields of levulinic acid, formic acid, and furfural. The DIBANET reactor system can be considered to be a “hydrolysis technology” since it involves the breakdown of the structural polysaccharides of the feedstock to their component sugars. Feedstocks with greater polysaccharide contents can allow for higher yields of the DIBANET target chemicals. In order to allow determinations of potential yields the following lignocellulosic components needed to be analysed for: glucose, arabinose, galactose, rhamnose, xylose, and mannose. The Klason lignin content of a sample is also important since this is a major output of the pre-treatment process. At the DIBANET kick-off meeting it was decided that, for WP3, a limited number of feedstocks (Miscanthus and sugarcane bagasse) would be processed. There would be extensive analysis of these feedstocks in WP2 with UL focussing on Miscanthus and CTC on bagasse.

It was planned that WP2 could analyse more feedstocks than could be feasibly processed in WP3. Indeed, the analytical results of WP2 could provide important indications of the yields that could be expected from these feedstocks if they were to be processed in WP3. Hence, it was necessary for WP2 researchers to identify what other feedstocks could be suitable for the DIBANET process and analysed in WP2. CTC as a group is solely focused on sugarcane and its products/residues, hence the only other suitable feedstock for analysis was sugarcane trash (field harvest residues). UL, UNICAMP, and Fundacion Chile (FUN), however, had a wide range of potential feedstocks from Europe and Latin America to consider. These partners conducted an extensive search of the literature for these, and there was a particular focus on wastes and agricultural residues. On the basis of this review UNICAMP selected 10 feedstocks (rice husks, sawdust, soy peel, coffee husks, bamboo, coconut shells, banana residues, grass, and acai seeds) and UL a larger number (samples included straws, animal slurries, spent mushroom compost, waste papers, switchgrass, short rotation coppices, municipal solid wastes, grasses, woods, leaves, and municipal composts). FUN provided advice to UNICAMP regarding which feedstocks would be environmentally and socioeconomically sustainable for use in biorefineries.

This objective also involved the partners determining which feedstocks should be focused-on for near infrared (NIR) model development. This would require that many more samples would need to be sampled and analysed for these feedstock types in order to construct robust and accurate models. The selection of feedstocks for this purpose would not only depend on whether their compositions were suitable for DIBANET-processing but also on whether there would be sufficient compositional variability between the samples for model development to be viable and warranted. After a literature review, UL decided that models would be developed for Miscanthus, waste papers, cereal straws, pre-treated Miscanthus (obtained from WP3), and a global dataset containing all samples. CTC decided to develop separate NIR models for bagasse and trash and UNICAMP decided, on consultation with FUN, to develop models for coffee residues, banana residues, and coconut residues.

Detailed Chemical and Spectral Characterisation of Feedstocks

Following the successful identification of feedstocks for analysis, UL, CTC, and UNICAMP proceeded to analyse these samples. A highly-detailed analytical methodology had been designed at UL, and this was demonstrated to the other WP2 analysis partners (CTC, UNICAMP) in a participatory workshop for biomass sampling and analysis. This knowledge transfer and inter-regional co-operation allowed for the methodologies to be standardised across the project. The protocols that were provided to these partners have been uploaded to the DIBANET website for use by the public. The analytical protocol is designed so that attempts at Near Infrared Spectroscopy (NIRS) calibration for the important chemical constituents can take place at various stages of sample preparation ranging from wet and unground (WU) heterogeneous samples to dry and sieved (DS) homogeneous samples

Following the standardisation of analytical methods the participants analysed a large number of samples for their polysaccharide sugars, Klason lignin, acid soluble lignin, ash, and ethanol-soluble extractives. The compositional data from the samples have been included in the DIBANET “Chemical Database” (see Figure below). This is an interactive piece of software that was built by UL using Microsoft Access and is free to download. This program was first uploaded to the DIBANET website on September 2012 and has been updated since then as additional data have been obtained. The software provides the wet-chemical data and/or the NIR-predicted compositions of samples. The program provides graphical representations of sample composition and allows users to sort samples according to composition or by numerous variables such as sample type and location (Europe or Latin America). It also provides summary statistics (average, maximum, minimum, range, and standard deviation) for the most important constituents for the filtered list of samples. The software provides the predicted chemical yields that could be obtained (theoretically) from processing these samples in the DIBANET process and a number of other representative conversion technologies. UL contributed 873 samples (694 of Miscanthus, 10 of other energy crops, 102 of agricultural residues, and 67 of wastes) to this database with CTC providing 456 samples (all of sugarcane residues) and UNICAMP 237 samples (235 agricultural residues and 2 energy crops).

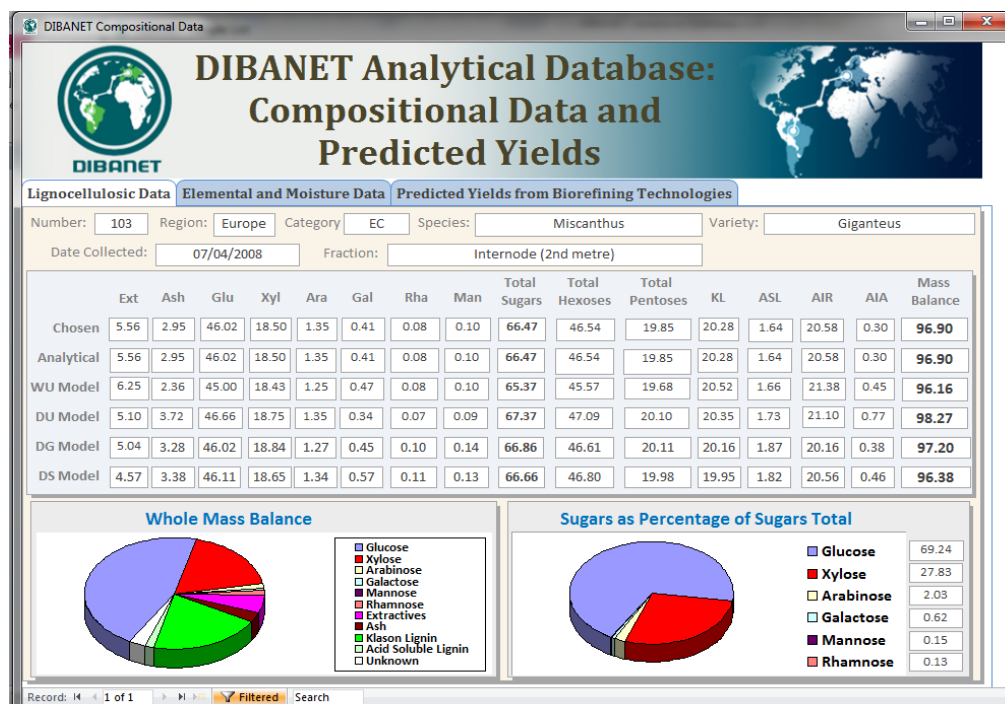


Figure: A screen of the freely-downloadable DIBANET Chemical Database.

In addition to the standard analyses (for sugars, ash, extractives, and lignin) other constituents were analysed for in subsets of samples. These included the crystallinity of cellulose for banana residues (UNICAMP), elemental (carbon, hydrogen, nitrogen) analysis (UL), and uronic acids (UL).

NIR spectra were collected for all samples. These were categorised according to the state of preparation of the sample with WU, DU (dry and unground), DG (dry and ground), DS, and DF (dry fines) spectra collected. Spectra were also collected during the reference analysis of samples to act as back-ups for moisture content analysis if the reference method was inaccurate. In total 9,650 lab spectra have been taken at UL, over 5,600 by CTC, and 1,944 by UNICAMP.

Set of Guidelines of Best Practice for Biomass Suppliers

To complement the Chemical Database a comprehensive report discussing the analytical results was written by UL, UNICAMP, and CTC. The 154 page report discussed, for both Europe (UL) and Latin America (UNICAMP, CTC) the initial evaluation of feedstocks and the samples that were selected for wet-chemical analysis and then discussed in greater detail the feedstocks that had been chosen for NIR model development. Histograms that described the compositional variability of these different feedstocks for the important constituents were presented along with critical evaluations of the suitability of these feedstocks for biorefining. The document also presented guidelines for feedstock suppliers that would ensure that the most suitable feedstocks could be provided to the biorefining facility.

The sections written by UL discussed at length the analytical results obtained for Miscanthus, cereal straws, and waste papers/cardboards. For Miscanthus it was observed that the *M. x*

giganteus variety provided the greatest per hectare yields in Ireland and offered the greatest hexose content, but its hemicellulose content was lower than other *Miscanthus* varieties (e.g. *M. x sinensis*). It was also noted that the composition of the harvestable crop changed significantly over the harvest window (October to April), a phenomenon mostly attributable to the loss of leaves over this period. For example, the total sugars content increased over the window, however this was not enough to counteract the loss of harvestable biomass, meaning that per hectare potential biorefinery yields were greatest in the early period of the harvest window.

The sections written by UNICAMP discussed in detail the results obtained for the residues from the banana, coconut, and coffee industries. It was found that, for the banana residues, the stem sections offered the greatest potential biorefinery yields whilst the leaves had a significantly lower total sugars content (of approximately 37%). For the coffee samples, only the husks had sufficient amounts of lignocellulosic sugars to justify their processing in hydrolysis biorefineries. In contrast, both the coconut husks and coirs had sufficient amounts of these sugars.

The CTC sections focussed on sugarcane bagasse and sugarcane trash. Both of these are considered to be good feedstocks for hydrolysis processes such as DIBANET. It was found that the ash content could vary significantly between bagasse samples and that there was a tendency for the ash contents of bagasse to be higher in some mills. Ash content can be particularly important for thermochemical biorefining technologies and also can affect the amount of acid required in acid-hydrolysis. It was therefore recommended that careful determinations and observations, over a period of time, of the ash contents, associated with the harvesting/milling process of any mill that is being considered for a biorefining scheme, should be carried out. It was also estimated that using practicable levels of the bagasse and trash resources could allow for massive levels of production of ethanol/levulinic-acid which could, in some cases, more than double the biofuel output from sugarcane in Brazil.

The full-length version of the report and a shortened (16 page) summary version are free to download from the DIBANET website.

Development of Predictive Calibrations Using NIR Spectra and Other Rapid Analysis Methods

The wet-chemical analysis of biomass is inherently costly and laborious. Therefore, a major focus of WP2 was on the development of rapid analytical methods, using the near infrared (NIR) spectra of samples. NIR models are built, using chemometric techniques, by linking the spectral differences in samples with their compositional differences. The derived relationships allow for the compositions of unknown samples to be predicted based solely on their spectra and these predictions can be tested by performing reference wet-chemical analysis on these samples. Prior to DIBANET the models that were developed for the constituents of lignocellulosic feedstocks of relevance for biorefining were based on samples that had their spectra collected when they were dry and of a homogeneous particle size distribution. DIBANET has not only developed models based on samples in this state but also from the spectra of wet samples of heterogeneous particle size distributions. While these models tended to be less accurate than those based on the spectra of the dry samples, their predictive abilities were, for some feedstocks, still impressive (e.g. an R^2 in validation of over 0.9 for the total sugars, glucose,

xylose, and Klason lignin contents of Miscanthus samples (UL)) and often high enough to be suitable for use in quantitative analysis and payment schemes. The ability to quantitatively characterise wet unprocessed samples means NIR analysis can be carried out in seconds rather than hours/days.

UL has developed over 240 models for Miscanthus. These covered the major constituents (e.g. glucose, Klason lignin) as well as minor constituents (e.g. rhamnose, mannose, acid soluble lignin). Accurate models were also developed for paper/cardboard samples and pre-treated Miscanthus. Models for cereal straws were less accurate for some constituents (e.g. sugars), primarily due to the lower compositional variability between these samples. Importantly, highly accurate models (e.g. a range error ratio of over 25 for total sugars, glucose, xylose, and Klason lignin) were developed based on a global dataset of the DS spectra of all samples analysed. Since those models covered wide compositional and spectral variability they are considered to be very robust and capable of predicting compositions of unknown samples.

UL also developed chemometric models to allow for the rapid prediction of the compositions of the process outputs (hydrolysates, pre-treatment pulps, acid hydrolysis residues) of WP3 and qualitative models that allowed for Miscanthus samples to be discriminated-between on the basis of: variety, anatomical fraction, stand age, and harvest period.

UNICAMP has developed 136 NIR models. Models have been built separately for each of the three chosen feedstocks (banana, coffee, and coconut residues) as well as on datasets including samples from more than one feedstock type. The UNICAMP models were also of a high quality, with an R^2 in validation of over 0.8 for most models. It was also found that the precision of the NIR methodology was better ($p < 0.05$) than the reference method for almost all the parameters, being worse only for moisture. Importantly, UNICAMP also developed cellulose crystallinity NIR models for samples of banana residues. These models were of a good quality and meant that low field NMR analysis (primarily used for rapid cellulose crystallinity measurement) would not be needed for this purpose.

CTC developed models for sugarcane bagasse and sugarcane trash. These feedstocks had the similar problem to the straw samples analysed at UL in that their compositional variability was limited. This meant that many of the models had relatively low R^2 values in validation, although excellent predictions for the Klason lignin and ash contents of trash samples were possible (even when using the WU spectra). It was considered that the high ash contents of some bagasse samples could hinder model development. For some constituents, the predictive abilities of the bagasse models improved when samples with high ash contents were excluded from the calibration sets.

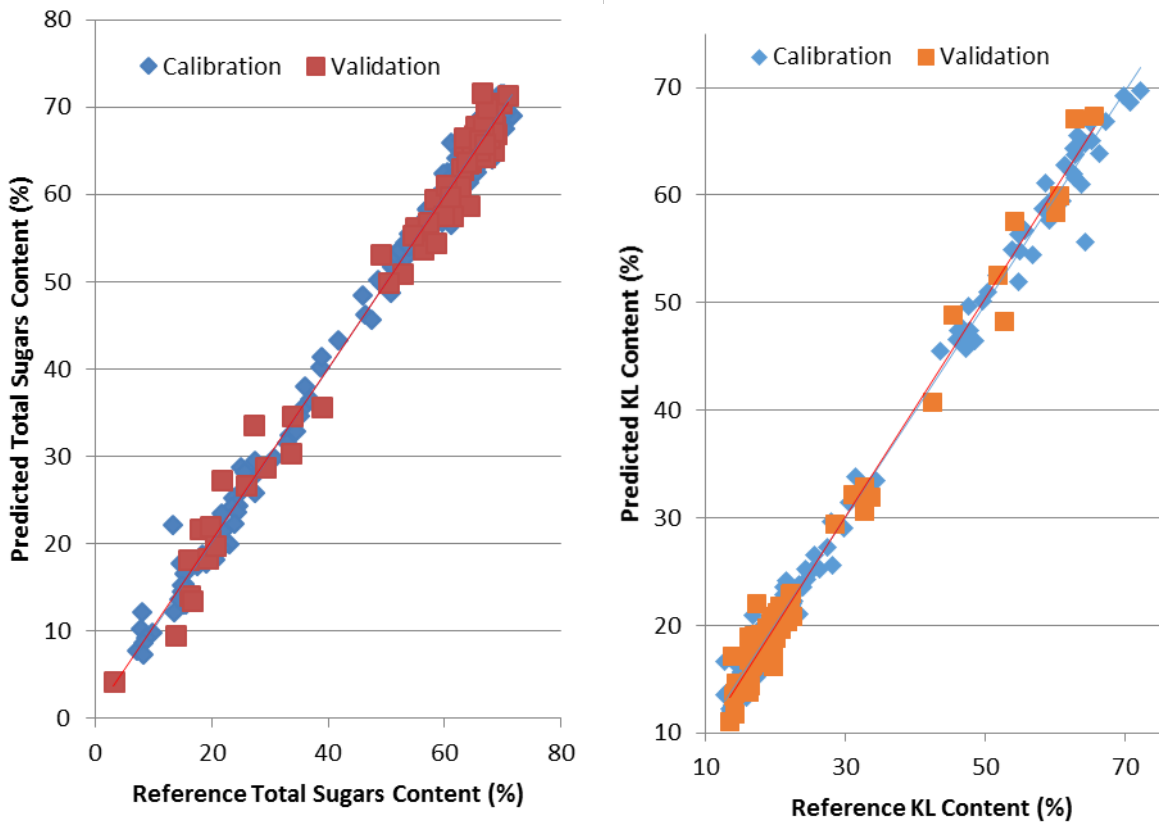


Figure: Regression plots for NIR models developed for a global set of samples analysed at UL.

In recognition of the great value presented by the proprietary NIR models and the accuracy and precision of the analytical methods developed during DIBANET, a spin-out company, Celnigis, has been developed in Limerick. This company will provide biomass analytical services based on the wet-chemical and NIR analysis of lignocellulosic feedstocks and is expected to commence services in the autumn of 2013.

Integration of an Online NIR System into a Sugar Mill for Bagasse Analysis

It was proposed that the NIR models that were developed in the laboratory could be transferred to spectra collected from an online NIR device and allow for the prediction, with a reasonable level of accuracy, of the composition of bagasse samples.

DIBANET partners FOSS delivered their diode-array detector ProFOSS online NIR system to CTC in 2012. This device was then integrated with the chute delivering the bagasse from the final mill of the sugar-mill. It was configured to automatically collect spectra every 15 minutes, which resulted in a total of 8,183 spectra being taken by the system. Furthermore, a sample collection protocol was also used, allowing for wet-chemical analysis of samples to be linked to a particular spectrum. A total of 239 samples were collected and each of these were analysed at the sugar

mill for their moisture and pol (sucrose) contents and were then taken to the CTC laboratory and scanned in the lab-NIR device (XDS) in the wet and unground (WU) form. A subset of samples were then processed for wet-chemical analysis (with further spectral collection along the preparation process).



Figure: Integration of the ProFOSS system with the bagasse chute in the sugar mill.

The transfer of models from the lab-NIR system to the online NIIR system first required that the wavelength region be trimmed to that of the ProFOSS (from 400-2500nm to 1100-1650nm). After this had been done models were developed based on these trimmed XDS spectra. It was found that the limited wavelength region did not adversely affect the predictive abilities of the models and, in some cases, slightly improved them (presumably due to a reduction in spectral complexity allowing for more constituent-based, rather than spectral-based, influence on the PLS loading vectors). As with the original models, the predictions of the limited-region models improved for some constituents (Klason lignin and glucose) when only samples with ash contents less than 5% were considered.

Unfortunately when the models, after spectral standardisation, were then applied to the ProFOSS spectra there were no significant regressions (with significant considered to be an R^2 value of over 0.5) for any of the constituents. Attempts were also made to develop primary

ProFOSS models by linking directly the ProFOSS spectral variability with sample composition (determined via reference analysis methods) but these were also unsuccessful for all constituents. It was considered that the added spectral heterogeneity provided by moving wet bagasse samples, in conjunction with the very limited compositional variability of these samples, made the development of successful models impossible.

This does not mean that online NIR analysis, for the parameters of importance for biorefineries, would not be possible for any feedstock. It could be viable for feedstocks that exhibit more compositional variability than bagasse and it could also offer value in being able to discriminate between feedstock types (in the case of a multi-feedstock biorefinery). Alternatively, at-line analysis could be employed at the facility, since DIBANET has demonstrated successful lab-based prediction for important feedstocks.

DIBANET Deliverable 2.4 considered the market potential for the use of FOSS devices (online and lab-based) in the developing second generation biofuels (biorefining) sector. The final report concluded that such devices could have value for a number of biorefining companies and biorefining facilities. As the second generation biofuels sector scales-up, and the number of commercial-scale facilities rapidly increases, FOSS will be in a strong position to provide valuable process-control equipment. DIBANET has played a valuable role in this regard by demonstrating the applicability of FOSS NIR analysis to biorefining feedstocks and lignocellulosic parameters. The importance of FOSS devices to DIBANET WP2 has been outlined in an article written for the FOSS "In Focus" trade magazine.

WP3 - Significant work/achievements from the work done

Work Package 3 (WP3) focused on the development and optimisation of a continuous process for the production of levulinic acid (LA) (and ethyl levulinate) from lignocellulosic biomass. This multistage activity involved evaluating existing pretreatment processes and developing an alternative to precondition the biomass making it more amenable to chemical hydrolysis. The work involved carrying out fundamental experiments to undertake real time evaluation of the processing condition on the products of chemical hydrolysis and the development of a kinetic model for the processing of cellulosic fraction of biomass into levulinic acid. These kinetic equations were used as the basis for developing a process model and simulation as well as the formulation of a process design for a pilot scale plant.

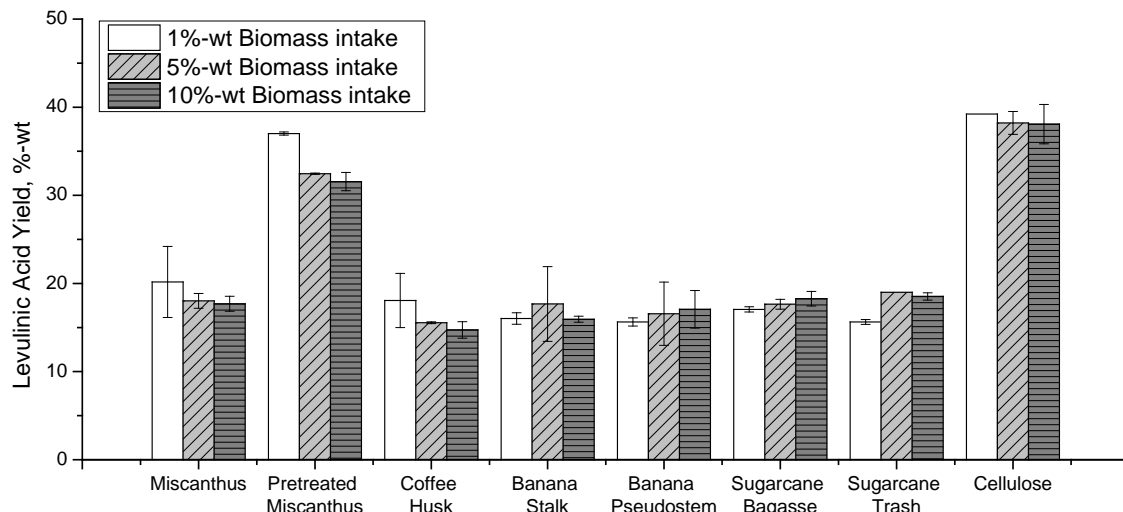
This workpackage comprised five tasks and UL was involved in each of these tasks. Initially UL researchers designed and built two laboratory scale reactors equipped with control systems and sampling capability. One reactor was an 8L batch high pressure system which allowed for continuous sampling of reagents and products, the other comprised a continuous (5kg/h) two stage process for the production of LA. The first stage is a high pressure plug flow reactor which can operate up to 230°C in order to hydrolyse the polysaccharide into soluble sugars and the products of this reaction are fed to a continuously stirred tank reactor where the glucose undergoes acid

dehydration to levulinic acid. The liquor stream containing LA is subsequently separated from the solid acid hydrolysis residue (AHR) by centrifuge.



An 8L high pressure batch reactor was also constructed to allow systematic kinetic experiments to be carried out by altering the reaction temperature, and the sulphuric acid concentration to establish the key reaction conditions and to develop a kinetic model for the chemical hydrolysis of lignocellulosic biomass to LA. The highest LA yield was obtained at 150°C and 0.55 M H₂SO₄ at 63 mol%.

For Task 3.3 UL researchers created a database of product range and yields of LA and other products obtained by experimentally processing a wide range of EU and LA biomass feedstocks under a variety of conditions of acid concentration, temperature, solid loading and pretreatment, taking into account the different carbohydrate and lignin content of these feedstocks and their possible effect on the LA Acid yields.

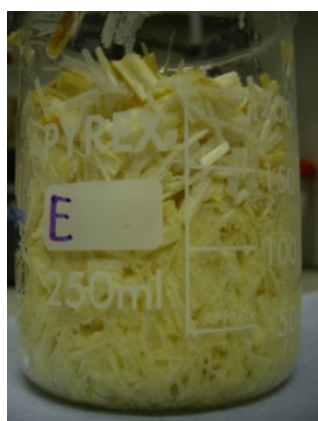


The Federal University of Rio de Janeiro (UFRJ) was responsible for the evaluation of suitable ionic liquids for advanced biomass conversion. UFRJ undertook an extensive review of the literature and found the most promising IL to be Butyl-methyl-imidazolium chloride (BMImCl). This solvent was tested in order to estimate the capacity of this solvent to digest biomass. However, the use of BMImCl for pretreating biomass was found to be uneconomic and resulted in a viscous and dark solution that made recovery of both sugars and solvent impossible.

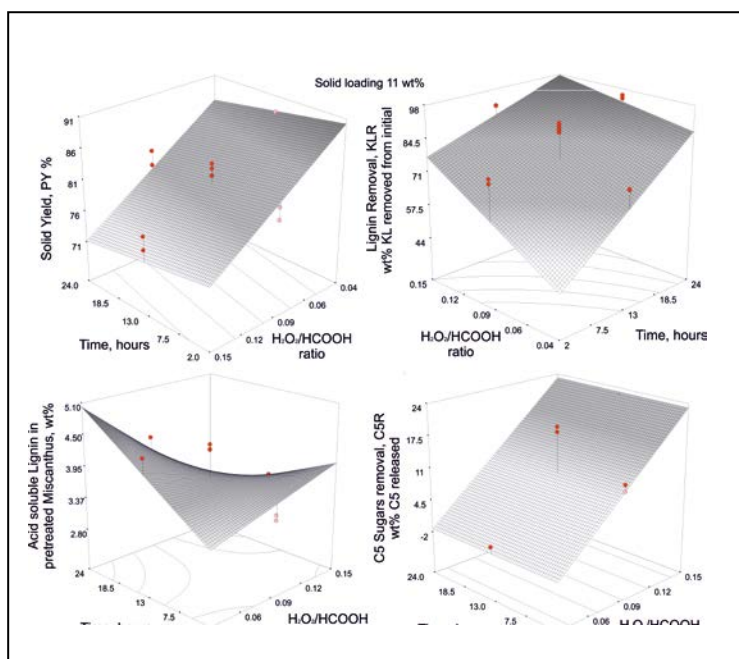


Initial appearance of BMImCl and mixture with Miscanthus after 24 hours.

Having evaluated potential ionic liquids as preconditioning swelling agents and found them to be technically difficult to recover and uneconomic UL researchers developed an alternative pretreatment based on recycling of formic acid which arises from the production of LA. This pretreatment is suitable for continuous operation and allows higher throughput of biomass at relatively low temperatures (155°C) which favours production of LA over undesirable AHRs. The pretreatment was tested for both batch and continuous operation and an EU patent application has been filed.



Miscanthus cellulosic fraction following pretreatment with hydrogen peroxide/HCOOH



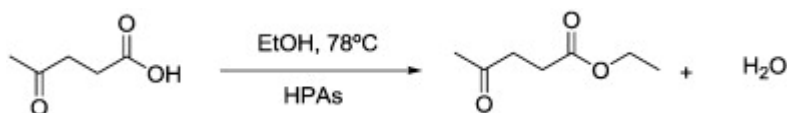
Esterification reactions are usually carried out in liquid-phase using mineral acids such as H_2SO_4 , H_3PO_4 or HCl , but substitution of homogeneous by heterogeneous catalysts is highly desirable because solids are easier to separate and there is no need for neutralization, can be used several times, and are less corrosive than mineral acids. UFRJ undertook the task of evaluating and comparing the activities of different zeolites (HUSY, HBEA, HMOR, HZSM-5, HMCM-22) and sulfated oxides (SnO_2 , ZrO_2 , Nb_2O_5 , TiO_2) against a commercial sulfonic resin (Amberlyst-15) for the esterification of levulinic acid with bio-ethanol. They found that Amberlyst-15 can be reused several times for the ethyl levulinate production under mild reaction conditions. The activity pattern for the non-zeolitic materials was Amberlyst-15 > SO_4/SnO_2 > SO_4/TiO_2 > SO_4/ZrO_2 > $\text{SO}_4/\text{Nb}_2\text{O}_5$ > SnO_2 , a pattern that correlates quite well with their total acidity. The association of the activity results of the re-sulfated stannias with their acidic site distribution shows that strong acidic sites are required to perform the levulinic acid esterification with ethanol. On the other hand, the activity of the zeolites seems to be related to their pore structure rather than to their total acidity, indicating that the formation of the transition states only takes place in the zeolites presenting large cavities such as MCM-22 and USY.

UFRJ prepared and characterised solid superacid catalysts for direct cellulose hydrolysis. Sulphated stannia can be classified as solid superacids and because published work in the literature indicated that acidic solids can perform satisfactorily, it was decided that the most acidic stannia SO_4/SnO_2 would be used. Preliminary results with sample SO_4/SnO_2 -3M showed that during the levulinic acid esterification the sample underwent leaching, with the loss of both acidity and catalytic activity. Since the carbohydrate conversion was to take place in aqueous solution it is reasonable to assume that leaching will also occur. Therefore, in order to avoid this problem and to increase the acidity of the material to a level comparable to that of Amberlyst 15. The major challenge was to produce a solid acid stannia catalyst resistant to leaching. This was successfully achieved by developing a novel route for the catalyst preparation.

Ethyl levulinate can be obtained by esterifying LA with ethanol in the presence of an acid catalyst such as sulphuric acid, however, one of the goals of DIBANET was to avoid the environmental problems associated with handling, containment, disposal and regeneration of homogeneous catalysts due to their corrosivity and toxicity and to develop solid acid heteropolyacids (HPAs) as a green alternative. HPAs have many advantages as solid acid catalysts over homogeneous liquid acid catalysis. They are non corrosive, cheap and environmentally friendly, presenting fewer disposal problems. However, their high solubility in water and polar solvents, as well as the low specific area of bulk HPAs, limits their application as heterogeneous catalysts necessitating their stabilisation by supporting them on carriers such as silica, alumina, titania. The interaction of the acids with these supports is known to improve the catalytic properties, however, the supported HPA catalysts obtained by impregnation techniques are unsuitable for use as in polar reaction media associated with the Dibanet project such as water or ethanol due to a continuous leaching of the HPAs.

The majority of catalytic applications of HPA's use the commercial Keggin-type structure but the application of phosphotungstic acid with Wells-Dawson structure as catalyst offers better catalytic performance in acid catalysis. UBA as part of Dibanet developed the first direct incorporation of a heteropolyacid with Wells-Dawson structure during the synthesis of silica by the sol-gel technique, in acidic media, using tetraethyl orthosilicate as the precursor material and its use as a catalytic material for the production of ethyl levulinate from levulinic acid. In order to avoid the problem of

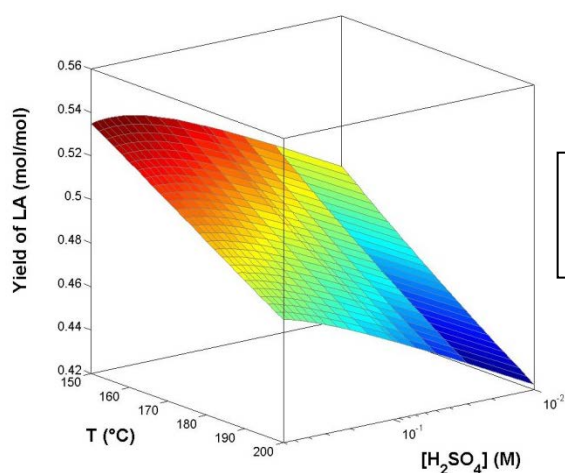
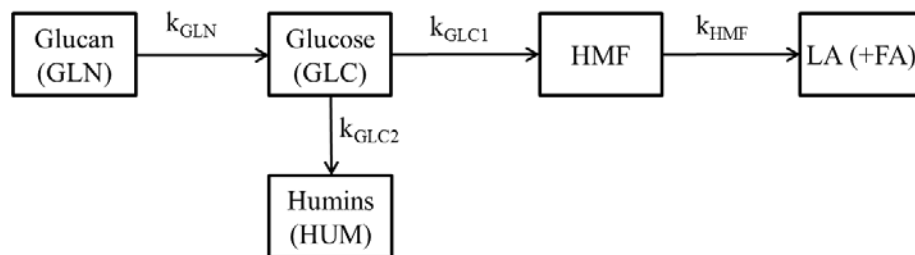
catalyst leaching from heteropolyacid acids in the polar media required for chemical hydrolysis a series of modified materials was prepared and characterised. This was the first recorded preparation of such materials by this method. This catalytic material underwent extensive structural characterization and was used to esterify the levulinic acid using ethanol at 78 °C, by incorporating the phosphotungstic HPA with Wells-Dawson structure (WD) as the active phase in a silica framework. Catalysts were synthesised with different amounts of WD acid included in the silica structure.



These HPA catalysts were 100% selective for ethyl levulinate with yields of 76% . To test for resistance to leaching in the polar media the catalysts were recycled and reuse over 4 cycles. The activity dropped from 76 to 68% yield of EL after the first cycle but no further deterioration of catalyst activity was observed confirming that these novel materials offer a potential alternative to conventional homogeneous catalysts.

UFRJ prepared and characterised solid superacid catalysts for direct cellulose hydrolysis. Sulphated stania can be classified as solid superacids and because published work in the literature indicated that acidic solids can perform satisfactorily, it was decided that the most acidic stania SO₄/SnO₂ would be used. Preliminary results with sample SO₄/SnO₂-3M showed that during the levulinic acid esterification the sample underwent leaching, with the loss of both acidity and catalytic activity. Since the carbohydrate conversion was to take place in aqueous solution it is reasonable to assume that leaching will also occur. Therefore, in order to avoid this problem and to increase the acidity of the material to a level comparable to that of Amberlyst 15. The major challenge was to produce a solid acid stania catalyst resistant to leaching This was successfully achieved by developing a novel route for the catalyst preparationUL researchers used the heteropoly acid solid acid catalysts prepared by UBA and amberlite to test for the direct conversion of carbohydrates to LA using the reactor, however, the yield of LA was in all cases lower than that achievable using sulphuric acid as the catalyst.

The hydrolysis of lignocellulosic biomass converts cellulose and hemicellulose fractions to various soluble low molecular weight components such as monosaccharides, organic acids including LA or furanic compounds. In Dibanet we focused on the aqueous phase processing of Sugar Cane Bagasse and Miscanthus using homogenous acid catalyst. The acid-catalysed hydrolysis of the lignocellulosic biomass takes place via complex reaction mechanisms . Kinetic studies were carried out by Dibanet partners to investigate the hydrolysis of Miscanthus and Sugarcane bagasse. Using the 8L batch reactor systematic kinetic experiments were carried out by altering the reaction temperature between 150 and 200°C, and the sulphuric acid concentration between 0.11 and 0.55 M to establish the key reaction conditions and to develop a kinetic model for the chemical hydrolysis of lignocellulosic biomass to LA. The highest LA yield was obtained at 150°C and 0.55 M H₂SO₄ at 63 mol%. The kinetic model developed (shown below) was in good agreement with the experimental data and can be applied over a wide range of hydrolysis reaction conditions for lignocellulosic biomass.

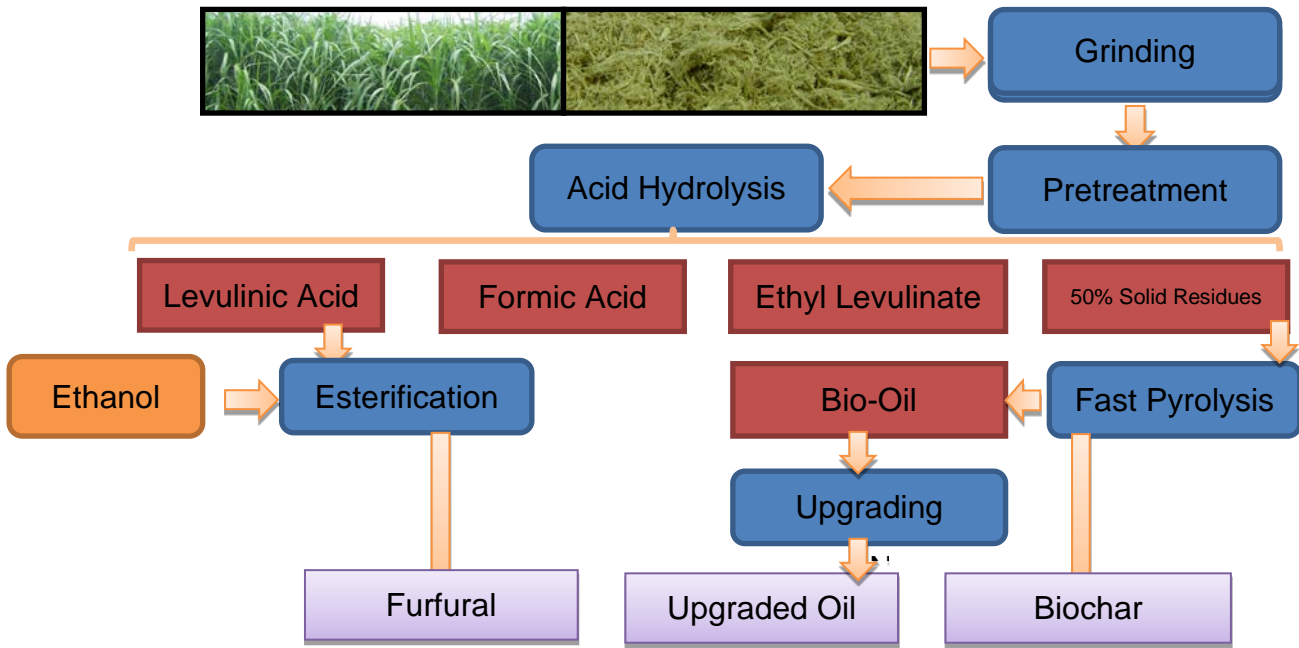


$$Y_{LA} = t(X_{GLN} = 99\%) \exp\left(\frac{T}{11.865} - 41.06\right) [H_2SO_4]^{1.59}$$

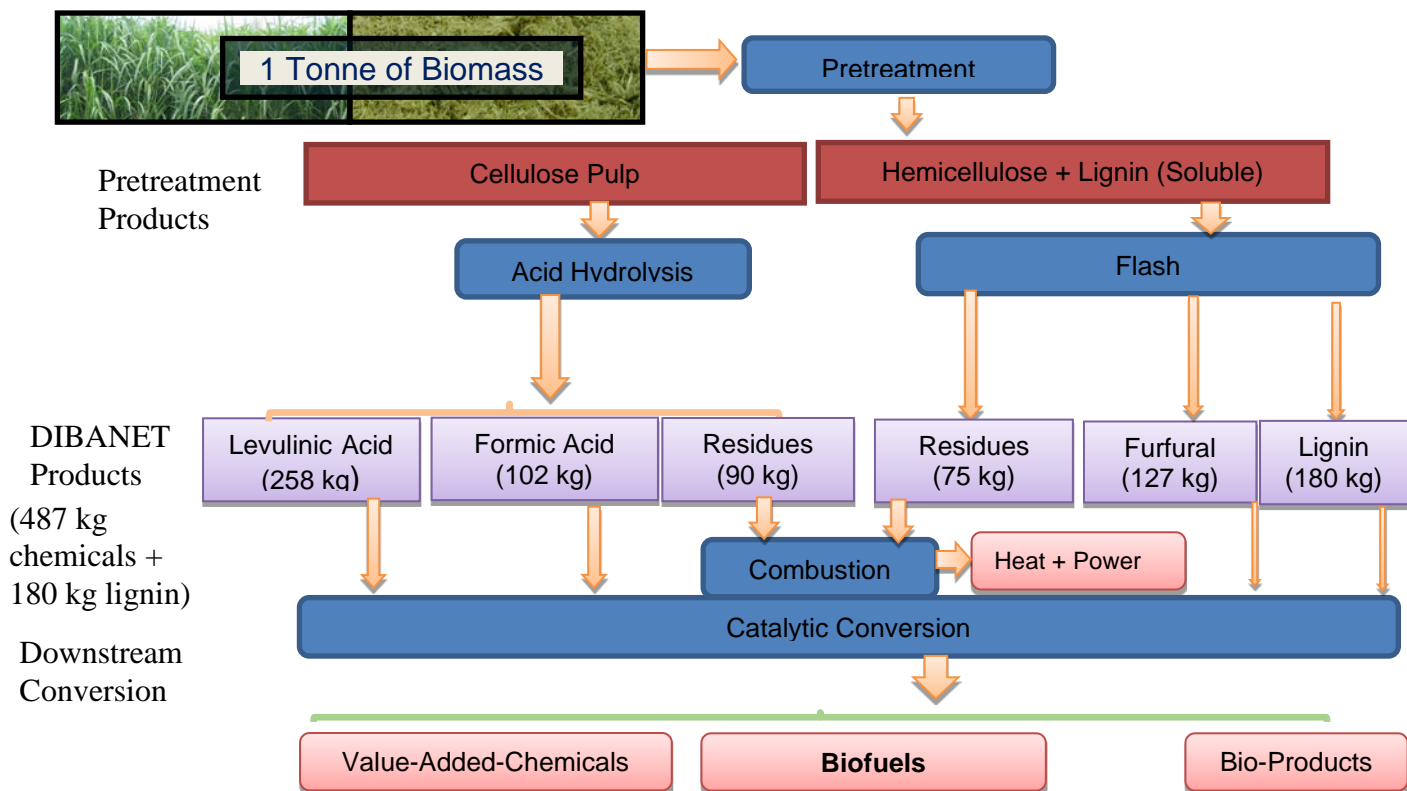
Based on the optimisation study carried out using our kinetic model, an empirical equation was proposed to predict the LA yield at a particular temperature and acid concentration.

The results of the kinetic study demonstrated that cellulose hydrolysis was the limiting reaction (high activation energy) and that temperature plays a vital role. Higher temperature reduces the yield of levulinic acid by favouring the production of unwanted humins over HMF. Lower temperatures require longer reaction times to achieve the same output however glucose concentration in solution is the key to the overall yield of LA so mass loading can be used to compensate for overall reduced rates at lower temperature. As expected the kinetic study confirmed that higher acid concentration increased rates for all reactions

The process data obtained from kinetic experiments was collated and compared on the basis of yields, energy costs, and sulphuric acid and the potential for scale-up to a commercial-scale system was evaluated. This required the partners to design a pilot-scale unit based on the modifications made to the laboratory scale continuous unit. The pilot-scale unit design allows for high levulinic acid yields with reduced environmental impacts and is of a suitable design for future scale-up to a cost-competitive commercial facility. The design plans incorporated a facility for the esterification of levulinic acid with ethanol. Key to the production of ethyl levulinate was the efficient conversion of biomass to levulinic acid which would then be esterified with ethanol to ethyl levulinate using an acid catalyst. Whereas the original proposal envisaged that up to 50% of the product would be acid hydrolysis residue of little value except as a fuel for combustion the new model which formed the basis of our design results in less than 17% AHR with a significantly higher amount of valuable fuel product or platform chemicals being recovered.



Original Dibanet model.



Dibanet Process which forms the basis of the process design.

A process simulation was created using ASPEN which allowed feedstocks and process parameters to be altered. The output from these was used in D5.3 to model to integrate the process modelling with the socio-economics model.

Highlights from WP3

* A functioning lab scale process for chemical hydrolysis of lignocellulosic biomass has been commissioned

* Yields of Levulinic acid have been obtained from raw untreated biomass which exceed or match the state of the art.

* A novel pretreatment process has been developed for swelling of lignocellulosic biomass which releases most of the lignin and gives higher yields of LA

* New hydrophobic HPA catalysts were developed which are active and selective for conversion of levulinic acid to ethyl levulinate. These catalysts also show activity for direct conversion of soluble sugars to LA. Novel sulphated stania catalysts have been prepared and characterized and will also be tested.

* A series of chemical kinetic equation have been calculated based on experiments and a kinetic model developed which will facilitate prediction of the optimum process conditions for maximizing yield of LA

WP4 - Significant work/achievements from the work done

The objective of the work in WP4 was to explore the upgrading of AHR by thermal and catalytic pyrolysis with a goal of producing a biofuel (biooil) that could be used either directly or after hydrotreating as a diesel miscible biofuel (DMB). However, after a review meeting and based on the AHR pyrolysis results a new objective was defined. This was to explore the AHR upgrading through steam gasification and catalytic steam gasification to produce a syn-gas rich in hydrogen. A final target was to derive an energy self sufficient biorefinery in which all the process heat and power requirements would be met from AHR. Combustion converts biomass directly into heat energy and ash, whereas both fast pyrolysis and gasification produce valuable intermediates that can be recovered and further processed to produce valuable fuels such as clean syngas or upgraded bio-oil. Therefore, fast pyrolysis and gasification were investigated in this work.

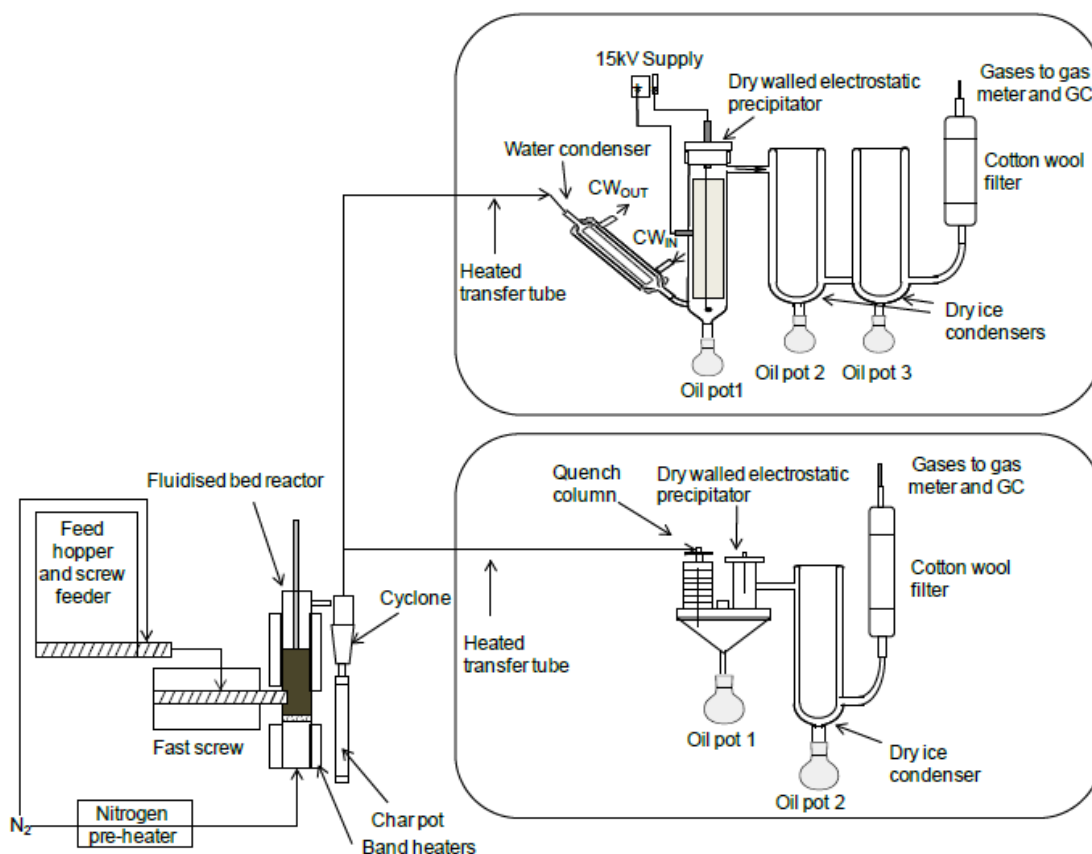
The main product from fast pyrolysis of biomass is bio-oil which is a dark brown free flowing liquid consisting of mainly organics and water. Liquid bio-oil is easier to transport and store than solid biomass as well as having the potential to be used as a fuel or a base for chemical production. The main components in bio-oil are acids, aldehydes, alcohols, sugars, esters, ketones, phenolics, oxygenates, hydrocarbons, and steroids. Although many applications of bio-oil exist, the Dibanet project initially focused on using fast pyrolysis to produce a bio-oil which could subsequently be upgraded to transportation fuels. Biomass gasification has been practised for decades with the aim of converting solid carbonaceous feedstocks into a combustible product gas at elevated temperatures. There are two modes of gasification which include pyrolytic gasification and oxidative gasification which are used to maximise gaseous products with a variety of uses such as power or electricity generation. Process heat for pyrolytic gasification is provided by combustion of recycled char and therefore reduces by-product yields. Product gases from pyrolytic gasification have a medium heating value (17-19 MJ/Nm³). On the other hand, oxidative gasification uses air, oxygen or steam. The product gas from air-blown gasification is diluted with nitrogen so has lower energy content (4-7 MJ/Nm³). However, product gas from oxygen or steam gasification has higher energy content (10-18 MJ/Nm³). Product gas from gasification can either be a fuel gas or syngas. Fuel gas is a low energy content gas from air-blown gasification usually containing CO, H₂, CO₂, CH₄ and small amounts of hydrocarbons such as ethene, ethane, propene, propane and water. As air is used, the combustible gas components in fuel gas are diluted with nitrogen which significantly lowers the gas HHV (4-7 MJ/Nm³). Fuel gas is suitable for boilers, engines and turbine operation to ultimately produce heat or electricity, but cannot be transported through dedicated pipelines. It can be used in diesel or gasoline engines with minor modifications. Syngas is a better quality medium energy content gas (10-18 MJ/Nm³) from oxygen blown or steam gasification containing mainly CO and H₂ and could be used to produce fuels (e.g. ethanol, methanol, naphtha, hydrogen, gasoline and diesel) or chemicals (e.g. acetic acid, dimethyl ether, and ammonia). Pyrolytic gasification, without an oxidant, can also produce gases with medium heating value (17-19 MJ/Nm³). A range of AHR and biomass samples were analysed to determine their suitability for thermal treatment.

Thermo Gravimetric Analysis (TGA) was used as a screening process to show how samples may behave under pyrolysis or gasification conditions. The AHR mainly consist of lignin and humins. Humins are carbonaceous dark coloured solids and are insoluble polymeric materials which have an

aromatic character. Humins are reported to be derived from glucose and 5-Hydroxy-methylfurfural and their formation is reported to limit levulinic acid yields. The TGA of biomass components, miscanthus and of AHR found that AHR decomposes at even higher temperatures than lignin suggesting that the presence of humins makes AHR even more difficult to thermally decompose. Higher temperatures are required to break the strong bonds between lignin and humins.

| Sample | Volatiles (%) | Char (%) | Fixed carbon (%) | Ash (%) |
|---|---------------|----------|------------------|---------|
| Untreated miscanthus | 73.66 | 26.34 | 22.74 | 3.60 |
| Untreated miscanthus pellets | 74.05 | 25.95 | 21.59 | 4.36 |
| AHR from miscanthus: 5% acid, 2h, 200°C | 38.05 | 61.95 | 58.50 | 3.45 |
| AHR from miscanthus: 1% acid, 3h, 150°C | 80.43 | 19.57 | 18.84 | 0.73 |
| AHR from miscanthus: 1% acid, 24h, 150°C | 73.70 | 26.30 | 24.96 | 1.33 |
| AHR from miscanthus: 1% H ₂ SO ₄ - 10 minutes - 200°C | 49.08 | 50.92 | 49.08 | 1.84 |
| AHR from miscanthus: 5% acid, 1h, 175°C | 40.07 | 59.93 | 58.39 | 1.54 |
| Untreated sugarcane bagasse | 82.40 | 17.60 | 14.78 | 2.82 |
| Untreated sugarcane bagasse pellets | 75.85 | 24.15 | 18.47 | 5.68 |
| AHR from sugarcane bagasse: 5% acid, 1h, 175°C | 36.17 | 63.83 | 56.80 | 7.03 |
| Untreated sugarcane trash | 74.14 | 25.86 | 19.46 | 6.40 |

Fast pyrolysis experiments were carried out on a 300g/h continuous fluidised bed rig with a K-Tron K-ML-KT20 gravimetric screw feeder to continuously feed the reactor. The reactor can be operated up to 650°C at atmospheric pressure which is ideal for pyrolysis. Char was separated using a cyclone and collected in a char pot. The liquid bio-oil was either collected by a quench column or a glassware collection system. These two systems are interchangeable. The non-condensable gases were sent through a gas meter and MicroGC. The concentration of hydrogen, carbon monoxide, methane, carbon dioxide, ethene, ethane, propene, propane and n-butane were analysed as was the bio-oil for solid content, water content and pH. The elemental content of bio-oil and char were analysed to determine the HHV of each.



The AHR pyrolysis worked was carried out using various AHRs provided by UL under different hydrolysis severities. These AHRs were fully characterized in CERTH and Aston then tested on a small scale pyrolysis unit using silica sand for the pyrolysis tests and different type of catalysts for the catalytic tests. Full mass balances were produced while the bio-oil was characterized with routine and advanced characterization methods. Pyrolysis results showed that the bio-oil yield is strongly related to the quality of AHR coming from the hydrolysis tests. AHR which originated from high severity hydrolysis tests give relatively low oil yield and more char. The AHR from low severity hydrolysis are suitable feeds since they can give up to 40% pyrolysis oil. From the catalytic tests it was demonstrated that ZSM-5 is the best catalyst and it can significantly reduce the oxygen in oil. However, with the refractory AHR the oil yield is even lower. Based on these results and the fact that the optimum AHR conditions for maximum LA production give the most refractory AHR it was concluded that the AHR pyrolysis process is not a suitable for a DMB production. For this reason it was decided to explore the use of this refractory AHR as feed in a high temperature pyrolysis and steam gasification process in order to maximize gas products with high heating value.

| Sample (treatment conditions) | C | H | N | O | S | Ash | HHV (MJ/kg) |
|--|-------|------|-------|-------|------|-------|----------------|
| Untreated miscanthus | 45.99 | 6.03 | 0.49 | 47.47 | nd | 4.94% | 18.25 |
| Untreated miscanthus pellets | 46.82 | 6.15 | 0.99 | 46.02 | nd | 4.54% | 18.82 |
| AHR from miscanthus (5% acid, 2h, 200°C) | 62.66 | 4.57 | 0 | 32.77 | nd | 2.69% | 23.86 |
| AHR from miscanthus (1% acid, 3h, 150°C) | 49.66 | 6.23 | 0.14 | 43.97 | nd | 0.41% | 20.13 |
| AHR from miscanthus (1% acid, 24h, 150°C) | 51.90 | 6.01 | 0.15 | 41.94 | nd | 0.38% | 20.86 |
| AHR from miscanthus (1% H ₂ SO ₄ - 10 minutes - 200°C) | 61.78 | 5.31 | 0.515 | 32.40 | nd | 0.93% | 24.46 |
| AHR from miscanthus (5% acid, 1h, 175°C) | 63.21 | 5.01 | 0.44 | 29.26 | 0.16 | 1.93 | 24.91 |
| Untreated sugarcane bagasse | 47.66 | 6.06 | 0.39 | 45.88 | nd | 3.19% | 19.03 |
| Untreated sugarcane bagasse pellets | 43.47 | 5.66 | 0.20 | 44.69 | 0.27 | 5.71 | 17.12 |
| AHR from sugarcane bagasse (5% acid, 1h, 175°C) | 62.61 | 5.00 | 0.15 | 26.07 | 0.18 | 6.00 | 24.94 |
| Untreated trash | 45.24 | 5.88 | 0.685 | 48.17 | nd | 6.03% | 17.72 |

The high temperature pyrolysis and the steam gasification tests were performed in a new batch unit in CERTH at temperatures between 650-950°C. It was shown that high temperature pyrolysis gives a high gas yield where the CO dominates, however, with very low H₂. The steam gasification of the AHR proved that this feed is suitable for gasification. The gas produced was very rich in H₂ and its HHV (excluding carrier nitrogen) was about 38 MJ/(Kg of AHR). Catalytic steam gasification of AHR was also investigated using two different types of catalyst (from CERTH and UBA). It was found that UBA catalyst is very beneficial for steam reforming since it gives a gas with more H₂, less CH₄ and more HHV compared to steam gasification without catalyst.

In Task 4.1.3 catalyst screen studies were undertaken targeting the selection of the best catalyst for the catalytic pyrolysis of acid hydrolysis residues (AHR). This process focused on the production of an upgraded biooil that could be used as diesel or diesel miscible biofuel and it is an upgrading process for AHR. The selection criteria for the best catalyst were the yield and the quality of the biooil produced (mainly its oxygen content). Moreover, in this task the evaluation of various AHR was performed targeting the selection of an AHR that could be used as potential feed in a pyrolysis or catalytic pyrolysis process. This selection can help to optimize the entire process chain from biomass to levulinic acid (LA) with the maximum valorization of the hydrolysis residues.

In this Task eleven (11) different biomass feeds were used. Four of these feeds were raw biomass feeds (from miscanthus, sugarcane and beechwood), four AHR produced from hydrolysis under different severities (hydrolysis conditions) and 3 pre-treated Miscanthus. All biomass feeds were fully characterized at CERTH using elemental analysis, moisture content, ash content, chemicals analysis as well as TGA analysis. The characterization results showed that the acid hydrolysis and the oxidative pre-treatment conditions have a significant impact on the actual structure of these feedstocks. The oxidative pretreatment appears to impact more the hemicellulose and the less

crystalline parts of cellulose. Regarding lignin, the severity of the conditions appears to cause further aromatization of the lignin structure. In this study we evaluated five different catalytic materials. Two of these catalysts were new catalysts synthesized at CERTH while the other 3 were commercially available catalysts. The catalytic materials were also fully characterized for surface area, pore size, pore volume and acidity. The pyrolysis experiments (thermal and catalytic) either for catalyst or for feedstock evaluation were carried on a pre-screening fixed bed pyrolysis unit. Full mass balances and biooil characterization results were obtained from these tests.

The objectives of this task were fully achieved. It was shown that the catalytic pyrolysis could be a potential upgrading process for AHR but only if the hydrolysis conditions (that produce the AHR) are mild. In this case oil yields up to about 40%wt (on AHR dry basis) can be produced. However, the quality of this thermal bio-oil is not satisfactory for a direct use as diesel miscible biofuel since it contains about 37%wt oxygen. Thus, a further downstream upgrading process is necessary.

The AHRs that are derived from more severe treatment conditions appear to be more coke like in nature, their pyrolysis yielding more solid product and the minimum of liquid biooil. For the upgrading of AHR through catalytic pyrolysis, the work showed that among the catalysts tested, the best catalyst is the ZSM-5. With this catalyst the oxygen in the oil is lowered but the overall yield of bio-oil is also reduced. Like the thermal bio-oil, the quality of AHR is also crucial for the catalytic pyrolysis. From the evaluation of the various AHRs it was shown that only the AHR produced after hydrolysis at 200°C with 1%wt H₂SO₄ and for 10 min could be used for upgrading through catalytic pyrolysis. In this case a bio-oil with 13.5%wt yield and 15.5%wt O₂ can be produced. The quality of this bio-oil is also interesting since it contains a lot of aromatics and phenols. However, the AHR that comes from a maximum LA process is not suitable for upgrading even with catalytic pyrolysis.

Task 4.1.4 focused on catalytic pyrolysis steam gasification of the AHRs. Both catalytic and non-catalytic gasification were investigated as possible processes for the exploitation of the AHR residue, towards the production of H₂. The AHR feed was used either as-received, or after carbonization at 800°C (C-AHR) and was compared against Lignocel, a beechwood derived biomass. The non-catalytic gasification was performed at 800, 850, 900 and 950°C using steam as a gasification agent at a rate of 0.5 or 1g/min, with or without the addition of air. In order to enhance the gas production, two catalysts were tested: NiO 10%-ZSM5 (CERTH) and NiMgAl (UBA), at the selected temperature of 900°C using steam at the above mentioned rates.

The gasification of C-AHR residue resulted in gas with H₂ as the main component. The gas yields increased by increasing the gasification temperature, but the increase in steam rate had a slight effect on the H₂ production, a more marked effect on CO and CO₂ production, while its effect on CH₄ production was also minor. The addition of air as a gasification agent caused a marginal increase in the amount of gases produced. The conversion of C-AHR was higher than 90%wt at 900 and 950°C. Regarding the relative volume ratios of the gases in the product, it should be mentioned that H₂ was the main component (50%vol at T>900°C) while CO was about 10%vol and CO₂ was about 12-15%vol, while the CH₄ vol% was very low. The catalysts were tested under air and steam 1g/min as gasification agents and as a result they did not enhance the production of H₂ probably due to deactivation, because of the conditions applied.

The gasification of as-received AHR and Lignocel was performed under the same conditions, but without the addition of air, as it proved ineffective. The results indicated that the H₂ production increased with the increase of temperature, but not with the increase in steam rate. Steam at a rate

of 0.5g/min resulted to the production of more H₂ for both feeds at all 5 temperatures. Above 850°C the CO production decreased, which was more obvious in the 1 g/min steam. It was concluded that the water gas shift reaction was promoted more above this temperature giving more H₂ and more CO₂. The adverse effect of steam rate was more pronounced in the case of AHR and Lignocel compared to the C-AHR. By comparing the steam gasification effect of the AHR and the biomass it was concluded that under the selected gasification conditions the AHR gasification resulted in higher gases production than Lignocel. It was clear that the richer in carbon AHR was better than the Lignocel for gasification run. In addition the C-AHR (that was richer in carbon than AHR) was an even better feedstock for a gasification process.

The selected catalysts were also tested for the gasification of AHR and Lignocel under steam, without the addition of air and their benefit on H₂ production became evident. In particular, at a steam rate of 0.5gr/min the NiMgAl catalyst results in the production of the highest amount of H₂. At more oxidizing conditions (steam 1cc/min) ZSM5 10%NiO performs better than NiMgAl, resulting in higher H₂ production. The catalytic effect on CO production is more pronounced at steam rate of 1cc/min, where it appears to be suppressed by the NiMgAl catalyst and enhanced by the ZSM5 10%NiO. The CO₂ formation is enhanced by both catalysts, but the CH₄ production is clearly suppressed by the NiMgAl catalyst. Comparing AHR to Lignocel, the first appears to be a more promising gasification feed as it results in the production of higher amounts of H₂, especially when catalysts are used. The overall result is that AHR is a suitable feedstock for a steam gasification process. The HHV value of the produced gases was calculated, excluding the carrier N₂. It seems that the optimum condition for a high HHV gas (for non-catalytic steam gasification) is the 0.5gr/min steam at a temperature around 900°C. Under these conditions a HHV=30 MJ/kg of AHR can be achieved (6.9 MJ/Nm³). Catalytic gasification with NiAlMg is even more beneficial giving a gas with HHV up to 40 MJ/kg of AHR (7.6MJ/Nm³). The oxidative gasification of AHR with air was also tested in this task. Product gas composition and HHV results at 950°C were representative of typical biomass air gasification producing a fuel gas with a HHV of approximately 5-7MJ/Nm³. Increasing reactor temperature reduced solid and liquid yields, but increased gas yield. AHR was more refractory than sugarcane bagasse and so rate of reaction was slower. Temperature, equivalence ratio and residence times were found to be important factors in maximising gas yields or HHV with the gas HHV increased with increasing reactor temperature. Tars were found unlikely to be problem with AHR gasification.

Biochar from pyrolysis of *Miscanthus*, sugarcane bagasse and acid hydrolysis residue (AHR) of sugarcane bagasse (slow pyrolysis of AHR) were tested as soil amendments. Pot experiments using the biochars were carried out to evaluate the N₂O emissions and plant production for these chars produced from different feedstocks under different pyrolysis conditions. The best pyrolysis conditions for the AHR was 450 °C for 30 min producing the most stable biochar at lowest energy input. Incubation experiments demonstrated the potential of the biochar to sequester carbon in the soil and the biochar decreased the K losses by leaching. However, a modification of the process is necessary to avoid the production of potentially toxic compounds. Agronomic evaluations of the AHR and biochar showed that these increase the soybean productivity and tree seedling biomass production. The economic evaluation confirms the economical viability of both AHR and biochar, specially taking in account the residual effect of the biochar (at least 3 years).

WP4 - Significant work/achievements from the work done

Significant and successful achievements include:

- * Fast pyrolysis of a range of feedstocks and residues at micro and laboratory scale
- * Catalytic fast pyrolysis of several feedstocks and residues at micro and laboratory scale
- * Production of a range of novel cracking, hydrotreating, esterification and upgrading catalysts
- * Successful testing of solid acid catalysts for production of esters from bio-oil
- * Development of robust analytical techniques for pyrolysis and upgraded pyrolysis products
- * Successful testing of biochar with crop yield improvements.

S&T Results for WP5

Analysis of the Biofuels Produced in DIBANET

The first task in WP5 involved the analysis of the biofuels that were produced in the other Work Packages of DIBANET. This analysis was carried out by the Technology Centre of DIBANET partner YPF S.A. in Buenos Aires, Argentina. Analysis took place for the pure product (ethyl levulinate, EL) as well as for mixtures of this product with existing transport fuels. Two series of samples of diesel and biodiesel containing 5% of EL were assessed according to standard EN590 and it was found that these met the required specifications. However, the resulting mixed fuel had a reduction of two points in cetane number, compared with the fossil fuel, and this would need to be compensated by adding approximately 500ppm of cetane improver additives. The addition of EL to biodiesel was shown to provide an improved performance in lubricity. Tests were also made on a mixture of EL (5%) with gasoline and it was found that this complied with EN228 specifications.

Evaluation of Non-Biofuel Markets for DIBANET Products

Levulinic acid can be used to synthesis a range of different biofuels, such as ethyl-levulinate, gamma valerolactone, and methyl tetrahydrofuran. However the biorefinery concept should also consider other applications for the chemicals produced from lignocellulosic biomass via the DIBANET processes. DIBANET partner Aston University carried out a literature review in order to identify the non-biofuel markets for the products of the DIBANET technologies (acid hydrolysis, pyrolysis, gasification) and their derivatives. It was found that there are significant markets for the co-products (furfural, formic acid, lignin) of levulinic acid in the acid hydrolysis process but that levulinic acid, in itself, has a limited market (but a high market price). The advantage of the DIBANET approach is that it allows for levulinic acid to be produced at a very low cost and this opens up a much wider market for the chemical and its derivatives. For example, diphenolic acid can be produced from levulinic acid and, at the levulinic acid production cost envisaged for a commercial-scale DIBANET unit, this

chemical could substitute for the petrochemically-derived mass-volume chemical Bisphenol A, which has applications in products such as resins and paints.

Modelling of the DIBANET Process Chain and Evaluation of Commercial Prospects

The DIBANET process can be separated into three distinct stages; (1) pre-treatment (to produce a cellulosic pulp, furfural, and lignin); (2) hydrolysis of cellulose for the production of levulinic acid and formic acid; and (3) esterification of levulinic acid for ethyl-levulinate production. These can be considered to be modular stages with a subsequent stage requiring the previous module(s) to be present but a given stage does not need later stages to be present in order to operate and generate saleable products.

For the optimal configuration of the DIBANET technologies, there were several variables that needed to be considered. These included:

- (1) How the acid hydrolysis residues (AHRs) should be utilised – should they be put through a fast pyrolysis process with the production of a bio-oil as a target, or put through a slow pyrolysis process to produce a biochar, or gasified to produce a syngas, or combusted to provide process energy?
- (2) Should the lignin from the pre-treatment be sold on the market or combusted to make up any internal energy shortfall in the process?
- (3) Is it more profitable to sell levulinic acid as a platform chemical or to esterify it with ethanol to produce, and then sell, ethyl-levulinate?
- (4) Can the pre-treatment process be economical without the following cellulose-hydrolysis stage?

This optimisation Task involved extensive modelling in order to answer these, and other, questions. This was necessary at the fundamental process level (using Aspen Plus) as well as on the financial level (using Microsoft-Excel financial accounting methods).

In order to encapsulate the different options, the modelling considered a number of scenarios for the DIBANET process scheme. These are summarised below:

“Pretreatment” Scenario – Only the pre-treatment stage is carried out. The saleable products are furfural, sold at its current market price, the organosolv-type lignin, and the cellulosic pulp. The lignin was assumed to be sold as a sustainable carbon source for fibre-board/plastics (with an assumed value of \$125/tonne). The cellulosic pulp is considered to be a highly valuable feedstock for second generation biorefining to ethanol and other products, hence a value of \$100 per dry tonne was assumed. In this scenario the AHRs are produced from the portion of the pentoses that produce condensation products (humins) and these are used to provide process heat with the combustion of additional biomass used to meet the energy shortfall (if it exists). If AHRs are produced in excess to the process needs then these are sold as fuel at a price of \$40/MT.

“Biorefining Scenario” – This incorporates the DIBANET pre-treatment, with the same prices applied to the furfural and lignin products. It then incorporates the DIBANET hydrolysis technology to process the pulp from the pre-treatment. The formic acid is sold as a commodity chemical (\$450/MT) and the levulinic acid is sold directly for \$500/MT,

significantly below the current market price, as a platform chemical. The AHRs from this scenario would come from the humins from the pre-treatment and hydrolysis, and these are used to provide process heat.

“Biofuels” Scenario – This scenario incorporates the pre-treatment, cellulose hydrolysis, and levulinic acid esterification stages. The ethyl-levulinate is sold for €790/MT and the furfural is sold for \$500/MT, much less than its current market price (\$1,200/MT), to be used as a biofuel precursor, whilst the lignin is combusted to provide process heat and energy. If there would be a quantity of lignin in excess to that which would be required to fuel the process, the excess would be sold as a solid fuel (at a value of \$40/MT).

“Combined” Scenario – This scenario has the same products as the “Biofuels” scenario, but it differs in its use of the lignin (sold at \$125/MT) and in the sales price of furfural (the current market price of \$1,200/MT is used, as in the “Pre-treatment” and “Biorefining” scenarios). Whereas the “Biofuels” scenario is unrealistically pessimistic, the “Combined” scenario represents the most likely configuration of a DIBANET facility producing ethyl-levulinate. In this configuration high value co-products are sold in addition to the biofuel, encapsulating the concept of a biorefinery. Process energy needs are supplied by the AHRs that are produced from the hexoses/pentoses that do not form the saleable products. Additional biomass is combusted or the surplus AHRs sold (\$40/MT), depending on the energy balance at this stage.

The modelling work showed that DIBANET, by virtue of its increased product yields and solid loadings, had much lower energy requirements than the Biofine process, an alternative technology for the production of levulinic acid. Furthermore, when a full energy analysis was carried out (considering the energy values of the chemical inputs as well as those of the outputs) it was found that the different configurations of the DIBANET process scheme had excellent energy ratios (when the energy value of the biomass used for acid hydrolysis was not considered) ranging from 2.7 to 13.6 (when Miscanthus was the feedstock). The figure below presents the total energy input, output, and balance for the different DIBANET scenarios.

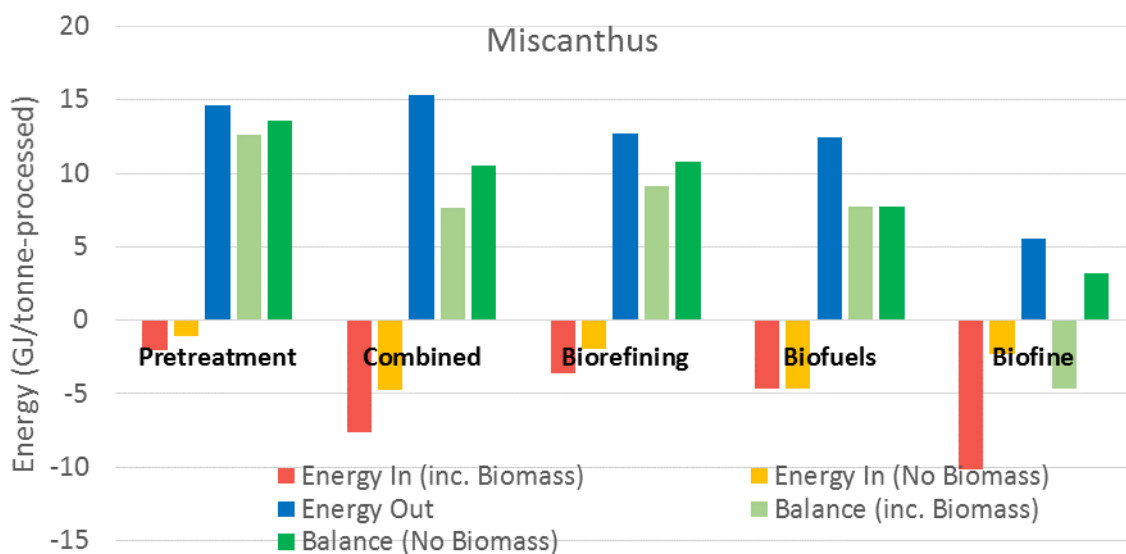


Figure: Graphical representation of the energy balances in the energy analysis, for the DIBANET scenarios and the Biofine process, when Miscanthus is the feedstock processed. Energy inputs/balances are presented when the energy value of the additional biomass required for process heat is considered (inc. Biomass) and when only the supply-cycle energy costs of this additional biomass is considered (No Biomass). All values are expressed on the basis of GJ per tonne of biomass processed through the biorefinery.

Regarding the best use of the AHRs, it was found that fast-pyrolysis experiments gave poor quality bio-oils at low yields, primarily due to the low hydrogen contents of these materials. On advice from an independent reviewer this option was dropped midway through the DIBANET project. The results from gasification also suffered due to the low hydrogen content of the feedstock, meaning that very large quantities of steam would be needed to produce a suitable syngas for upgrading. The biochar that was produced via the slow pyrolysis of AHRs was of a reasonable quality but its estimated value was relatively low. It was concluded that the best use for the AHRs would be in combustion to provide process heat and steam.

In any case, the importance of the use of AHRs in terms of the viability of the DIBANET process had been greatly reduced as a result of the significantly lower AHR yields that were achieved due to improvements in the yields saleable chemicals. Indeed, AHR production levels were so low that it was calculated that extra biomass (or the lignin product from pre-treatment) would need to be combusted to satisfy process energy requirements. The modelling showed that the internal energy balance of the process would be improved by combusting part of the lignin to make up the energy short-fall but it also showed that it is economically far superior to sell this lignin and to purchase additional biomass to fuel the process instead (even with feedstocks, such as Miscanthus, that have higher purchase costs).

The results of the financial modelling showed that the DIBANET process can be very profitable with highly attractive values for the IRR/ROI/NPV for most scenarios (see figure below). These values are far in excess of those possible from the Biofine process and also superior to many such values provided in the literature for other lignocellulosic biorefining technologies.

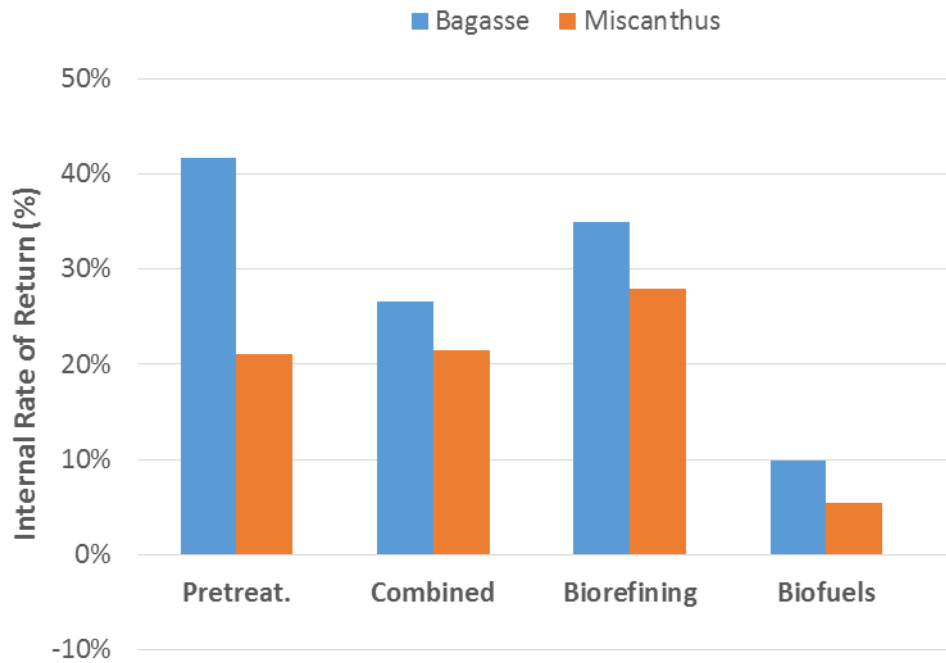


Figure: Internal rate of return (IRR) for the various DIBANET scenarios, using Miscanthus or sugarcane bagasse as feedstocks, assuming a biomass throughput (for the production of fuels and/or chemicals) of 475,000 dry tonnes per year.

It was demonstrated that the pre-treatment process can be a financially viable technology in its own right, particularly when feedstocks with high pentose contents (e.g. bagasse) are used. Combining the pre-treatment module of the DIBANET process scheme with the levulinic acid production/recovery module increases capital costs but also increases the annual profits and the NPV. Combining these two modules with the ethyl-levulinate production module can also be financially rewarding providing that the value of the furfural and lignin co-products are fully exploited (the “Combined” scenario).

The attractive financials of the DIBANET processes also mean that these can potentially be profitably operated at lower scales of operation than would be possible for many other lignocellulose-processing technologies (see figure below). Indeed, there are possible scenarios (based on the current market prices for levulinic acid and ethyl-levulinate) in which a demonstration-scale plant could pay back the investment cost and provide a healthy NPV in addition to proving the process on an enhanced scale.

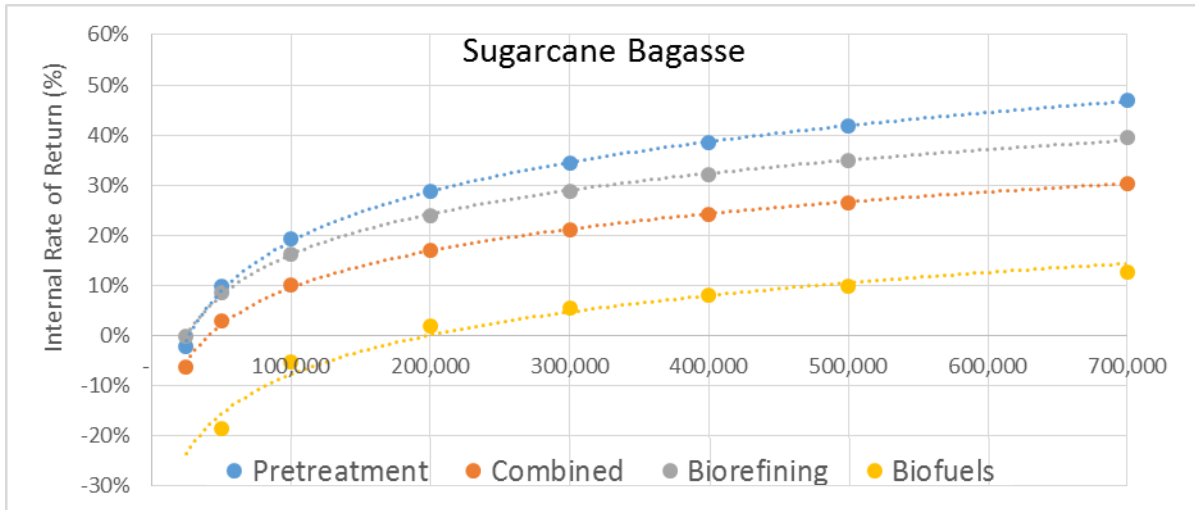


Figure: Internal rate of return (IRR) for the various technologies, using sugarcane bagasse, at various scales of operation (dry tonnes of feedstock processed per year; 100,000 tonnes per year is equivalent to 285 tonnes per day for a facility operational for 350 days per year).

The DIBANET processes also perform well when considered according to other, non-financial, parameters. For example, DIBANET process outputs can substitute for large quantities of fossil-fuel derived transport fuels and chemicals, so helping to reduce anthropogenic carbon dioxide emissions. A carbon balance was carried out and it was found that the carbon dioxide ratio (determined as emissions saved, through fossil fuel substitution, divided by the emissions produced from the process and from growing/transporting the feedstock) was extremely attractive, ranging from 7.5 to 10.9 (when Miscanthus was used).

Fundacion Chile also carried out a socioeconomic evaluation of the DIBANET process and concluded that the deployment of commercial-scale biorefineries based on the different DIBANET scenarios could result in significant employment. These scenarios also performed well when assessed according to the IDB Biofuels Sustainability Scorecard.

Development of a Business Plan for Exploitation of the DIBANET Advances

The final DIBANET Deliverable considered how to best proceed with the development of the IP beyond the end of the project. It was considered that the main IP suitable for development were the DIBANET pre-treatment/hydrolysis/esterification technologies and the proprietary near infrared models and refined wet-chemical methods that were developed, in WP2, for the analysis of lignocellulosic biomass. It has been decided that the analytical advances will be best exploited through the formation of a new spin-out company, Celignis (www.celignis.com), to provide analytical services and a detailed business plan has been prepared for this company. Celignis will be the first company, to date, to provide rapid low cost NIR analysis of lignocellulosic feedstocks for the compositional parameters of most relevance to second generation biorefining companies/facilities/researchers.

A business plan for developing the DIBANET biomass processing technology was also developed. It was recognised that this process has only been demonstrated to date on a pilot/lab-scale and that several stages of scale-ups would be needed before a commercial-scale facility could be built. These stages would be: full-pilot-scale (1-2 tonnes of biomass to be processed per day on a continuous basis); demonstration scale (in the order of 75 tonnes per day); ultimately followed by commercial-scale (in the order of 250+ tonnes per day). The modelling work showed that the DIBANET IP could be commercial with either the pre-treatment stage as the only module or with additional modules for: (1) acid hydrolysis of the pulp to obtain levulinic acid and; (2) esterification of that product to ethyl-levulinate. The business plan presented timelines and funding requirements for these different scenarios.

It was considered that the most appropriate means for developing the processing technology in the near term would be for a follow-on project funded in equal amounts by the EU and industrial partners. This project would be focused more on the demonstration of the technology at the pilot scale and less on fundamental R&D work (which has already taken place in DIBANET). The joining of the Brazilian energy company Petrobras to the DIBANET consortium in late 2012 was an important development in allowing for the project to be evaluated, and future plans considered, in a commercial context. There have been some initial discussions with industry and there seems to be considerable interest in the development of the DIBANET technologies towards ultimate commercialisation.

The figure below presents the conceptual timeline for such a follow-on project. It allows for the core modules of the integrated process to be developed in stages with the successful completion of each representing an important milestone for the project. DIBANET partner UFRJ carried out excellent work, within the project, on the development of improved catalytic methods for the esterification of levulinic acid with ethanol to produce ethyl-levulinate. It is recognised that there are a plethora of other valuable biofuels and chemicals that can be synthesised from levulinic acid via catalysis. Hence, an important element of the proposed future project would involve the further development by UFRJ of advanced catalytic mechanisms to allow significant enhancement of the potential markets-for, and revenue-from, levulinic acid.

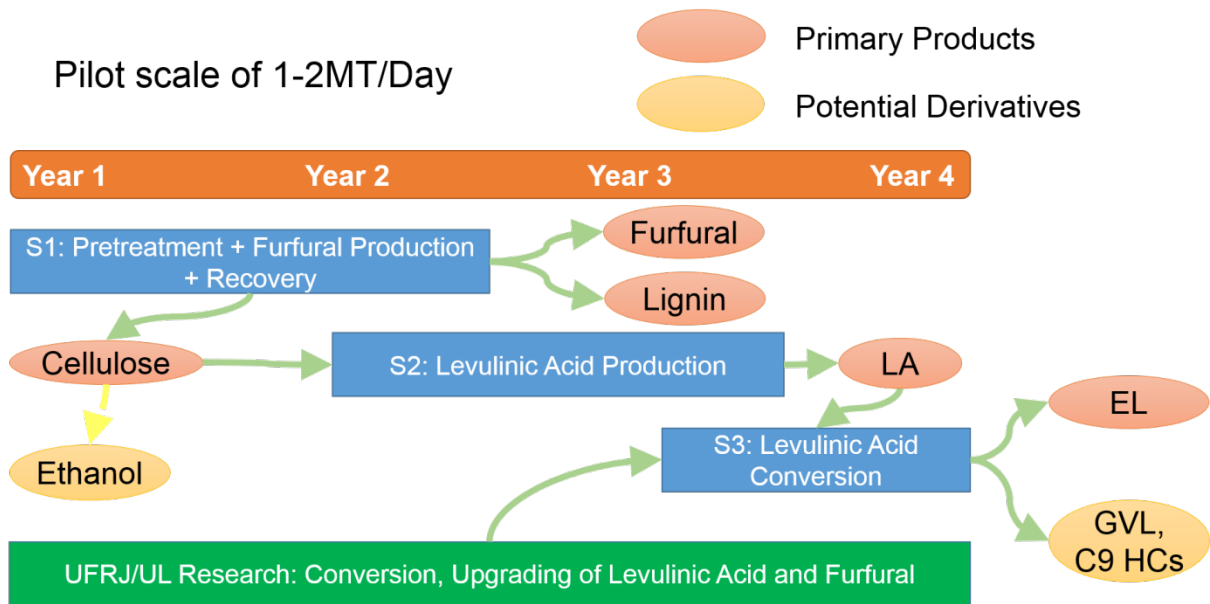


Figure: Conceptual timeline for a near-term follow on project to demonstrate the DIBANET IP on a pilot scale. There would subsequently be a demonstration scale facility, followed by commercial-scale plants. LA = levulinic acid; EL = ethyl-levulinate; GVL = gamma valerolactone; HC = hydrocarbons.

- **Description of the potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and the exploitation of results. (10 pages max).**

The potential impact of Dibanet research can have a strong socioeconomic and environmental benefit. The focus of the DIBANET project has changed significantly since its inception however the end result has nevertheless been the development of a core IP that has real potential for commercial deployment. This IP can also occupy an important niche in the biorefining sector in that it allows for the low-cost production of levulinic acid which is core platform chemical for the production of fuel additives or valuable chemical intermediates. The targets for the DIBANET process chain shifted substantially from those considered at the proposal stage. Instead of concentrating on how to utilise the AHRs by converting them to diesel miscible biofuels, the focus shifted to considering what would be the most profitable outputs of the pretreatment and hydrolysis processes and how these products from these processes should be utilised. For example: (i) should the lignin be sold on the market or used to make up the energy shortfall; (ii) is it more profitable to sell levulinic acid as a platform chemical or to esterify it with ethanol to produce, and then sell, ethyl-levulinate as a fuel additive and (iii) can the pretreatment process be economical as a stand-alone unit operation without the subsequent cellulose-hydrolysis stage.

Dibanet established that acid hydrolysis is an effective tool for developing sustainable and profitable routes for obtaining biofuels and platform chemicals from lignocellulosic biomass. It has shown that it would allow for a wide variety of different feedstocks to be processed and would also allow for the process conditions to be engineered so that levulinic acid could be produced in high yields from cellulose/hexoses (with formic acid as a co-product) and that furfural could be produced in high yields from hemicellulose/pentoses. These main products are of a higher value than ethanol and could also be used to synthesize biofuels.

UL researchers developed robust kinetic models for the acid degradation of biomass. These show the critical failings in the Biofine process that have meant it has never been successfully commercially deployed despite being developed as far back as 1988. Its process yields are too low and its energy demands are too high. The innovations developed during Dibanet will allow these shortcomings to be overcome. The DIBANET process can be separated into three distinct stages; (1) pre-treatment; (2) hydrolysis of cellulose for levulinic acid development; and (3) esterification of levulinic acid for ethyl-levulinate production. It has been demonstrated that the pre-treatment process can be a financially viable technology in its own right, particularly when feedstocks with high pentose contents (e.g. bagasse) are used. Combining stages (1) and (2) increases capital costs but also increases the annual profits and the NPV. Combining all three stages can also be financially rewarding providing that the value of the furfural and lignin co-products is fully exploited. The modelling has shown that the internal energy balance of the process is improved by combusting part of the lignin to make up the energy short-fall those results from the low amounts of AHRs that are produced. However, the modelling has also shown that it is economically far superior to sell this lignin and to purchase additional biomass to fuel the process instead (even with feedstocks, such as Miscanthus, that have higher costs). The cellulose obtained from the pre-treatment has been tested as a feedstock for enzymatic hydrolysis and the rate of glucose release was found to be in the order of 20 times greater than that for the raw biomass. Importantly, traces of the pre-treatment liquor within the pulp did not provide any inhibiting action or toxicity toward the microbial enzymes.

A Technology Transfer Business Plan for the most effective exploitation of the DIBANET technologies in both the EU and Latin America (LA) has been designed. This plan also considers wider issues such as: policy implications (particularly between the EU and LA); effects on trade, poverty, and social cohesion; and the total potential of an integrated biorefinery concept within a future European and LA bio-based Economy.

The current plans by the partners are to exploit the IP. So, the Business Plan considers that the main partner of relevance is UL and so will focus on their means to exploit three key areas of their outputs: a) the patented pretreatment technology. This IP is based on the work carried out at UL in WP 3; b) the DIBANET integrated process which includes the pretreatment and subsequent hydrolysis of biomass for the production of levulinic acid, formic acid, and furfural. This includes the potential for producing biofuels (e.g. ethyl levulinate) from these products and c) Biomass analysis services developed in WP2. UL plans to exploit these by offering analytical services on a commercial basis. Items (a), (b), and (c) will be exploited by a new company formed in Ireland (Celignis). It will carry out both the biomass analytical services and the development of the reactor technologies. It will be a spin-out from the University of Limerick. Regarding the plans within this company for the development of the reactor technologies, the next phases to follow are a Pilot-Scale plant, followed by a Demonstration-Scale plant and, finally, a Commercial plant. UL researchers have been in discussion with Petrobras to bring the innovations developed during this project to a commercial scale by investing in a pilot scale plant to demonstrate the commerciality of the Dibanet process.

The impact of Dibanet are to be seen in

- Improved the yields of Levulinic Acid, Furfural and Formic Acid beyond what was considered to be the state of the art were achieved.
- Patent filed on pretreatment process. The current plans by the partners are to exploit the IP in a commercial venture.
- By fractionating lignocellulosic biomass into its three main polymers (cellulose, hemicellulose, lignin) it has also allowed for lignin to be recovered and sold as a higher-value product.
- The amounts of acid hydrolysis residues (AHRs) that have been produced are significantly less than in the Biofine process. AHRs direct combustion is the most efficient means for providing process heat
- Fully modelled energy and chemical costs of process is available in Aspen Plus.
- Highly attractive economic returns whether as a biorefinery or as a biofuels factory.
- The TT Business Plan developed considers exploiting three key areas: a) the patented pretreatment technology; b) the DIBANET integrated process which includes the pretreatment and subsequent hydrolysis of biomass for the production of levulinic acid, formic acid, and furfural. This includes the potential for producing biofuels (e.g. ethyl levulinate) from these products and c) Biomass analysis services.
- The next phases to follow by the new company headed by UL are a Pilot-Scale plant, followed by a Demonstration-Scale plant and, finally, a Commercial plant. This process started with a presentation to Petrobras who subsequently requested samples of the pre-treatment pulp for evaluation in their own processing facilities

- greatly enhanced cooperation between the EU and LA in terms of R&D both for the the research community and industry. Very strong links have been created between the regions as well as inter-regionally. This has already shown fruits through the Science without Borders program whereby two Brazilian PhD students will join the Carbolea research group in UL as part of a program for joint supervision of early stage researchers between EU and Brazil.

The activities carried out in WP6 ensured that the findings of the project were disseminated in the key strategic areas and maximised the co-operation between EU and LA within the DIBANET project as well as setting-up lasting relationships and strategies to ensure that the project has a long-term legacy.

WP6 consisted of four main tasks: the Preparation of Dissemination and Exploitation (D&E) Plan, the Project website, the Information and Communication Tools and the Networking activities. All partners contributed to the WP tasks implementation.

The D&E plan prepared in the first year of the project implementation was extended during the project. Exploitation was considered more widely by all partners. It covered not only commercial exploitation of the results of DIBANET, but included other activities. By multiplication we understood the end-users adopting or applying the results. This is one area of exploitation where the most important method is the commercial application when the project partners with or without external parties find the way to exploit the results of the project on the market. The other main area of exploitation was mainstreaming which was understood as using results for policy development. The main method here is to develop policy recommendations, or introducing the results to policy makers through events, publications, and other means.

The following main exploitation routes were agreed to be followed:

Production of DMBs from AHRs: This has low potential for exploitation by the fast pyrolysis route or catalytic pyrolysis technologies and the focus changed following the mid-stage review of of DIBANET. The work was however published and the publications are available. The gasification route for AHRs offers better poteial for commercial exploitation. *Parallel to DIBANET (Blends for bio-oil, biodiesel and bioalcohols – patents applied in 2011 (Aston)*

New catalysts

- UBA and UFRJ have used several catalysts in the levulinic acid esterification and the most promising one, sulphated stania has some potential, further research is needed.
- UFRJ: after June 2012 – hydrogenation of levulinic acid to gamma-valerolactone: preliminary results show that a new catalyst, molybdenum carbide supported on activated carbon, is very active with high conversion and 100% selectivity towards the desired product. Further testing is needed, but if results are confirmed, there is a possibility for patent application.
- Scientific articles have been published on the use of sulphated stancias

Near Infrared Spectroscopy system to be applied for online rapid feedstock analysis and evaluation

- Equations have been developed from a calibration data set which links the variations in the spectra of samples and their corresponding reference (wet chemical) values.
- The various combinations of feedstock, chemical components, and sample state allow for a large number of NIR models.

Exploitation potential:

- Celnis (D2.3)
- FOSS's system; bench analyzer (online on a long term)
- Other organisations also have interest in NIR models for lignocellulosic energy crops and may offer a means for collaboration.

Potential Markets for the FOSS Systems

Online biomass analysis, BAS and CAS systems

- DIBANET widened the range of components predicted by the CAS and BAS to include biofuel feedstock parameters and potential yields in acid-hydrolysis, so adding value to Partner FOSS's equipment.
- Short-term potential: Payment analysis using the bench analyzer with FOSS's hardware and software together with the access to the calibration models and data
- The application of online NIR for analysis in DIBANET could set a precedent for establishing the technology

Patent

- Lignocellulose processing (UL) in preparation
- An application (PCT/IE2012/000014) was filed on 29/03/2012 on the Invention described in UL IDF 2006141. Priority claimed as of April 1, 2011 from Irish Application no.2011/0161.
- Currently awaiting international search report.

Designing a Pilot-Scale Ethyl Levulinate Facility

Pre-treatment process

- Owner: UL
- The technology can be licensed to interested bioethanol producers (in Europe and also USA)
- Developing a patent application based on the process for production of levulinic acid incorporating the pretreatment.
 - Partners are looking next steps financing models required for pilot plant construction – have met with Petrobras executives April 2013 to discuss investment options. Petrobras requested some additional materials for validation studies within their laboratories prior to commitments .
 - Next step would be to build a full pilot scale plant (before demonstration scale and full commercial scale)
 - Financial source would be Horizon 2020 and other public-private partnership; This pilot plant would be constructed close to an existing sugar/ethanol mill
 - spin-off company

- Owner: UL
Scientific research

- There is a requirement for scientific research related to optimise levulinic acid recovery and other valuable products generated in the process
- The chemical database with 1281 records at the moment in Microsoft Access file is available to download from the project website.

E-learning

- Public e-learning courses (hydrolysis, thermal processing)
- Creative Commons license applied

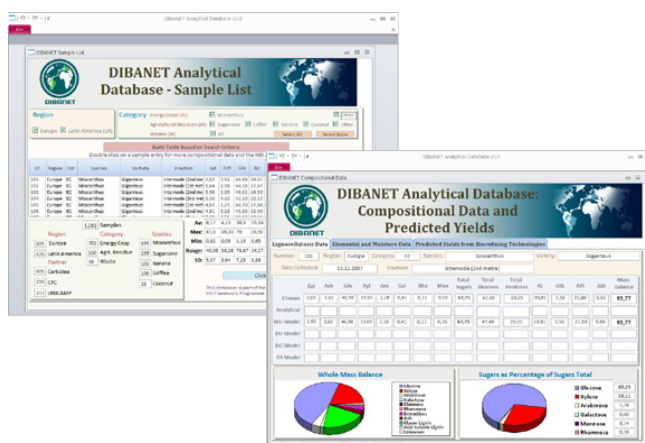
Other routes

- Staff exchange
- Cooperation with other EU projects (e.g. gasification experiments with BRISK; (one UL student & one Aston awarded Brisk travel grants for gasification others in process of evaluation) awarded Networking Day with SMART-CHP))
- Further research cooperation

The project's preliminary website was set up in order to raise interest and to start concentrate on possible essential stakeholders in the first year of the project and redesigned in the second reporting period and was regularly updated in line with the progress in the project activities. The current structure of the website is as follows:

- The website's visitors can find information on the DIBANET project; brief project introduction, objectives, proposed tasks, short description of the consortium members as well as the expected results of the projects.
- The website provides access to several project services:
 - The DIBANET Chemical Database provides information on the lignocellulosic, elemental and moisture contents of selected energy crops, agricultural residues and wastes of Europe and Latin America as well as on their predicted yields from biorefining technologies.
 - The DIBANET project offers two e-learning courses on diesel production from wastes and residues, free-of-charge. The courses on hydrolysis and thermal processing of biomass are available (after registration) to everyone interested in second generation diesel production.
 - The DIBANET Network and Contact Database provides networking opportunity after registration to all interested parties working with biofuels to present themselves as well as to look for potential future business partners.
 - Via the News session it is possible to follow the project progress and current activities and sign up for the bi-annual DIBANET Newsletter.
 - There are five discussion topics in the Dibanet Forum: Dibanet Publications, News related to biofuels, News on EU – LA research cooperation, biofuel related events, Dibanet events). The topics of DIBANET forum has been regularly monitored and updated.
- The Partner Area is restricted only for the consortium members. Partners can access project related documents and share bigger files among each other on a user friendly way.
- Public project results are available for download in the Download and Links section.

- Scientific publications of the project partners are summarised under the Publication menu.
- It is possible to contact the consortium via an online Contact Form.
- The summary and presentations of the DIBANET events (Networking days, Summer School) organised in October 2012 and December 2010 can be directly accessed via the event sessions.
- Selected photos of the main DIBANET activities (events, meetings) are published in the gallery session of the website.



The DIBANET website has three levels of access to the website contents:

- public access: available for everyone visiting the website
- public access through registration: available for everyone after registration
 - e-learning
 - DIBANET Network and Content Database
 - Forum
- restricted access for project partners: only project partners have access the documents and information and upload/share files within the consortium via the Partner Area

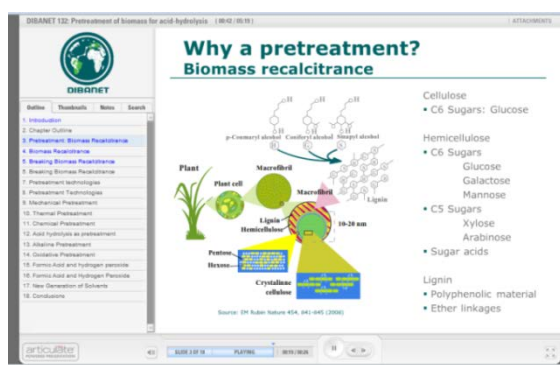
Chemical database

The DIBANET Chemical Database was launched in September 2012. It provides information on the lignocellulosic, elemental and moisture contents of selected energy crops (e.g. Miscanthus), agricultural residues (e.g. from sugarcane, coffee, banana and coconut) and wastes of Europe and Latin America as well as on their predicted yields from biorefining technologies. These technologies consist of, for instance, dilute acid and enzymatic hydrolysis of biomass, synthesis of mixed alcohols via catalytic processing of syngas derived from gasification of biomass, and Fischer-Tropsch synthesis of mixed range of linear hydrocarbons from biomass-derived syngas.

There are more than 1281 records in the database available in Microsoft Access 2010 format. Anyone can download the database without restrictions. Users can subscribe for updates, e.g. in case the database is extended with further items. A shorter and a longer guide is assisting the users how to use the database. The chemical database has received altogether 1225 views on the website and it was downloaded 123 times.

E-learning

The DIBANET project offers two e-learning courses on diesel production from wastes and residues. The courses are available after registration to everyone interested in second generation diesel production. The courses are built on the DIBANET Summer School structure



and consist of 6-5 modules on the hydrolysis as well as on thermal processing of biomass for second generation biofuel production. Each module includes chapters that are comprehensive units. Registered users can access all materials and search for specific information according to their interest.

The e-learning platform has been prepared in the second year of the project and it is running on the project website. The platform itself is php-based and provides a flexible interface to adapt the e-learning content to the target group's needs. It gives the opportunity to extend the content, manage user data and access rights to the courses. The e-learning chapters are prepared with the software Articulate that provides interactive learning opportunity with flash and sound animations. A 5 minutes long introduction presentation has been also prepared for the users. By the end of the project 209 participants used the e-learning services.

As protection, CC BY-NC-SA has been applied. This license lets others remix, tweak, and build upon your work non-commercially, as long as they credit you and license their new creations under the identical terms.

In terms of the information and communication tools that were developed during Dibanet, new, updated project brochure, new editions of the project newsletters and a video have been created. An event flyer, agenda of the Networking day have been prepared in electronic and printed format and distributed to the main target groups to inform them about the final public project event.

There were Dibanet brochures at months 5,15,25,35 and a general 2-page and an extended 6-page project brochure were prepared in the first two years of the project presenting the project consortium and its activities. A 2-page project brochure and a 1-page poster were prepared in English describing the new DIBANET processes and providing information on the final Networking event in Thessaloniki, Greece during the final period of the project. The project brochures were provided electronically in PDF format to all partners in addition to the printed versions for the Networking event participants. Partners were asked to disseminate the pdf brochures within their contacts, mailing lists, conference presentations, etc.

- **DIBANET Newsletters**
(Month 6, 12, 18, 24, 30)

A bi-annual electronic newsletter that summarise the actual main project activities are published for stakeholders in EU and LA. The content of the four, fifth and an extra edition in Month 37 were created. The documents were finalised based on the partners' feedback sent to the subscribers as well as to the project partners to send the final version to their local and international contacts. Any interested person can subscribe to the Newsletter via the project website and the previous versions of the Newsletters are



available on the DIBANET website in English, Portuguese and Spanish.

DIBANET Video

Based on the requests of the project partners, Geonardo created a flashed based short video presenting the activities, partners and expected results of the project. The aim was to support the partners in disseminating the project on different conferences as well as online.



DIBANET Publications

Publications submitted to high-impact international refereed scientific journals as well as to key commercial or commerce related journals played a crucial role in the DIBANET dissemination activities. SMEs and industrial partners had to submit at least one publication to a commercial journal related to energy and environment. Partners from academia have to submit at least two publications in a scientific journal and this is progressing very well with . The following scientific articles have been published so far in the DIBANET project in the last project period:

- Mass and Compositional Changes, Relevant to Biorefining, in *Miscanthus x giganteus* Plants over the Harvest Window, Hayes DJ, Bioresource Technology, Accepted pending minor revisions
- Development of near infrared spectroscopy models for the quantitative prediction of the lignocellulosic components of wet *Miscanthus* samples, Hayes, DJ Bioresource Technology, 119 (2012) 393-405.
- An integrated process for the production of platform chemicals and diesel miscible fuels by acid-catalyzed hydrolysis and downstream upgrading of the acid hydrolysis residues with thermal and catalytic pyrolysis. Girisuta, Buana; Kalogiannis, Konstantinos G.; Dussan, Karla; BIORESOURCE TECHNOLOGY Volume: 126, 92-100 (2012)
- Autothermal, single-stage, performic acid pretreatment of *Miscanthus x giganteus* for the rapid fractionation of its biomass components into a lignin/hemicellulose-rich liquor and a cellulase-digestible pulp, Haverty, D; Dussan, K; Piterina, AV; Leahy, JJ; Hayes, MHB; Bioresource Technology 109 (2012) 173–177.
- In situ catalytic upgrading of bio-oil using supported molybdenum carbide; Patel, M. A.; Baldanza, M. A. S.; Teixeira da Silva, V.; et al. APPLIED CATALYSIS A-GENERAL Volume: 458 Pages: 48-54 (2013)
- Characterisation of the products from pyrolysis of residues after acid hydrolysis of *Miscanthus*. Melligan, F; Dussan, K; Auccaise, R; Novotny, EH; Leahy, JJ; Hayes, MHB; Kwapinski, W. Bioresource Technology, 108 (2012) 258–263.
- Biochar and soil nitrous oxide emissions, Alho, CFBV; Cardoso, AS; Alves, Bruno JR; Novotny, EH. Pesquisa Agropecuária Brasileira, 47 (2012) 722-725.
- Reproducing the organic matter model of anthropogenic dark earth of Amazonia and testing the ecotoxicity of functionalized charcoal compounds, Linhares, CR; Lemke, J; Auccaise, R; Duó, DA; Ziolli, RL; Kwapinski, W; Novotny, EH. Pesquisa Agropecuária Brasileira. 47 (2012) 693-698.
- Context and importance of biochar research, Madari, BE; Maia, CMBF; Novotny, EH. Pesquisa Agropecuária Brasileira. 47 (2012) i-ii.
- Catalytic upgrading of levulinic acid to ethyl levulinate using reusable silica-included Wells-Dawson heteropolyacid as catalyst, Pasquale, G; Vazquez, P; Romanelli, G; Baronetti, G, Catalysis Communications 18 (2012) 115–120.

- Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts, Fernandes, DR; Rocha, AS; Maia, EF; Motab, CJA; da Silva, VT, Applied Catalysis A: General 425– 426 (2012) 199– 204.
- Advances in Biochar Research in Brazil, Maia, CMBF; Madari, BE; Novotny, EH. (2011) Dynamic Soil, Dynamic Plant, 5 (Special Issue 1). 53-58.
- Pressurised Pyrolysis of Miscanthus using a Fixed Bed Reactor. Melligan, F; Auccaise, R; Novotny, EH; Leahy, JJ; Hayes, MHB; Kwapinski, W; Bioresource Technology 102 (2011) 3466-3470.

Apart from the project partners website, articles have been published on the project for example in the following electronic and printed media in the last period of the project:

- Greencarcongress: <http://www.greencarcongress.com/2013/03/dibanet-20130312.html>
- Linked
In: http://www.linkedin.com/osview/canvas?_ch_page_id=1&_ch_panel_id=1&_ch_app_id=2000&_applicationId=2000&_ownerId=0&_appParams={%22event%22%3A%221090547%22%2C%22page%22%3A%22event%22}&trk=
- Cordis: <http://cordis.europa.eu/wire/index.cfm?fuseaction=main.detail&rcn=31609&rev=0>
- Conference locate: <http://www.clocate.com/conference/Diesel-miscible-fuels-from-wastes-residues-and-non-food-crops-of-Latin-America-and-Europe-2012/32786>
- SMART CHP project: <http://smartchp.eng.auth.gr/en/news/?id=25>
- BiofuelSTP: <http://www.biofuelstp.eu/events.html>
- WBC- INCO NET: <http://wbc-inco.net/object/event/10527>
- Sustainable Industries: <http://sustainableindustries.com/events/dibanet-and-smart-chp-networking-day>
- All conferences: <http://www.allconferences.com/c/dibanet-networking-event-on-diesel-miscible-fuel-production-2012-october-31>
- Environmental Research web: <http://environmentalresearchweb.org/cws/event/241614>
- Biorefinery: <https://biorefinery.crowdmap.com/reports/view/47>
- Biomass Energy
Centre: http://www.biomassenergycentre.org.uk/portal/page?_pageid=74,413187&_dad=portal&_schema=PORTAL#Liquid
- Bioenergy Site: <http://www.thebioenergysite.com/events/>
- Environmental Expert: <http://www.environmental-expert.com/events/dibanet-networking-event-on-diesel-miscible-fuel-production-13438>
- Follow Science: <http://www.followscience.com/event/dibanet-networking-event-on-diesel-miscible-fuel-production-41522>
- ManageEnergy: <http://www.managenergy.net/events>
- Twitter: https://twitter.com/EU_Funds/status/235303243746516992
- European Agenda: <http://www.europeanagenda.eu/events/33486.php>
- Enter Network: [http://www.enter-network.eu/index.php?id=164&tx_cal_controller\[getdate\]=20121031&tx_cal_controller\[view\]=event&tx_cal_controller\[type\]=tx_cal_phpicalendar&tx_cal_controller\[uid\]=135&tx_cal_controller\[lastview\]=view-month|page_id-164&cHash=ff7de8eb16](http://www.enter-network.eu/index.php?id=164&tx_cal_controller[getdate]=20121031&tx_cal_controller[view]=event&tx_cal_controller[type]=tx_cal_phpicalendar&tx_cal_controller[uid]=135&tx_cal_controller[lastview]=view-month|page_id-164&cHash=ff7de8eb16)
- GConference: http://www.gconference.net/eng/conference_view.html?no=33906&location=02&rDay=10312012
- HighBeam Research: <http://www.highbeam.com/doc/1G1-214528134.html>
- EUTrainingSite: <http://www.eustrainingsite.com/blog.php?id=66>

- AtlanticCities: <http://atlanticcities.wordpress.com/2012/10/02/dibanet-and-smart-chp-networking-day/>
- Radio interview, Klubradio, Hungary

DIBANET Presentations

Information on the project activities and its available results has been presented on different events such as:

- 9-12 December 2012, 21st Panhellenic Chemistry Conference, Thessaloniki, Greece (CERTH)
- November 2012, Advances in the DIBANET project, Technical Diffusion in the Technology Division, YPF, (YPF)
- 19-21 November 2012, III Latin American Congress Biorefineries, Pucon, Chile (UL)
- 24-26 October 2012, 1st Iberoamerican Congress on Biorefineries, Los Cabos, Mexico (UL)
- October 2012, University of La Plata, Argentina, (UBA)
- 3-7 October 2011, IX Encontro Brasileiro de Substâncias Húmicas, Aracaju/SE, Brazil (EMBARPA)
- 20-21 September 2011, 2nd European GCxGC Symposium, Regensburg, Germany (CERTH)
- 6, 14 September 2012, Information Day at National Innovation Office, Budapest; Association of Environmental Enterprises, Budapest, Hungary (GEONARDO)
- September 2012, XXIII Congreso Iberoamericano de Catálisis, Santa Fe, Argentina (UFRJ)
- 8-11 July 2012, Cat4Bio Conference, Thessaloniki, Greece (CERTH, UFRJ)
- 19-25 JUNE 2012, CAC-2012, XIII Chemometrics in Analytical Chemistry, Budapest, Hungary (UNICAMP)
- 18-22 June 2012, 20th European Biomass Conference, Milan, Italy (CERTH)
- 22 May 2012, Pyrolysis 2012, Linz, Austria (ASTON)
- 21-15 May 2012, 19th International Symposium on Analytical and Applied Pyrolysis, Linz, Austria (ASTON)
- 11 May 2012, Renexpo, Budapest, Hungary (GEONARDO)
- February 2012, University Federal of Sao Carlos, Brazil (UBA)
- 25-26 Nov 2011, 1st Workshop on Green Chemistry Scientific Community, Argentina (UBA) October 2012, Congreso Argentino de Catalisis -VI Congreso de Catalisis del Mercosur, Salta, Argentina (UBA)
- 5-8 November 2011, Latin American Symposium of Food Science, Campinas, Brazil (UNICAMP)
- 2-6 October 2011, 16th Brazilian Congress on Catalysis, Campos do Jordao, Brazil, (UFRJ)
- October 2011, First International Congress on Biorefineries (CatBior 2011), Malaga, Spain (UBA)
- 28-30 September 2011, International Conference on Thermochemical Biomass Conversion Science (tcbiomass 2011), Chicago, USA (ASTON)
- 20-22 September 2011 – Short course on “Catalytic Transformations of Biomass” during the Week of Studies in Chemistry in Federal University of OuroPreto, Brazil (UFRJ);
- 7-8 September 2011, COST FP0901 Joint analysis effort/biorefinery analytics meeting, Viterbo, Italy (UL)
- 29 August - 1 September 2011, First European Biorefinery training course, Paris, France (UL)

- 28 August - 2 September 2011, EuropacatX Congress, Glasgow, UK, (UFRJ)
- July 2011, 12th International Congress on Catalysis, Munich, Germany (UFRJ)
- 21-22 July 2011, Brazilian Congress of Chemical Engineering Students, Curitiba, Brazil (UFRJ)

In terms of Networking Activities a Networking event was organised on 31 October 2012.

DIBANET EU-LA Networking Day – Thessaloniki, Greece, 31 October 2012

The last Networking event was hosted by CERTH in Thessaloniki, Greece on 31 October 2012. It was co-organised with the LIFE project „SMART - CHP Demonstration of a Small scale Mobile Agricultural Residue gasification unit for decentralized Combined Heat and Power production”. The event was followed by "UBIOCHEM-III: Sustainable production of fuels/energy, materials & chemicals from biomass", the third International Workshop of COST Action CM0903 held in Thessaloniki, Greece on 1-3 November 2012.



List of lecturers:

- Dr. Donncha Haverty, University of Limerick, Ireland
- Prof. Michael H. B. Hayes, University of Limerick, Ireland
- Dr. Daniel Hayes, University of Limerick, Ireland
- Dr. Angelos Lappas, CERTH, Greece
- Prof. Costas Kiparissidis, Aristotle University of Thessaloniki, Greece
- Emeritus Prof. Spyros Kyritsis, Agricultural University of Athens, Greece
- Dr. Danial Nowakowski on behalf of Prof. A.V. Bridgwater, Aston University, the United Kingdom
- Prof. Victor Teixeira da Silva, Federal University of Rio de Janeiro, Brazil
- Bellis Vasileios, Chemical Engineer, ANKA, Greece
- Assoc. Prof. Anastasia Zabaniotou, Aristotle University of Thessaloniki, Greece

The event consists of presentations of the project activities and available results as well as a poster session to demonstrate the project activities. 66 participants attended the event from Argentina, Brazil, Chile, Columbia, Cyprus, Ireland, Greece, Hungary, Norway, Macedonia, Spain, Sweden, the United Kingdom and UK.

Prior to the event, many people indicated that they are interested in the event, however, they cannot attend it. Therefore, the presentations have been recorded and uploaded to the project website, YouTube, Slideshare and Scribd. The presentations were watched 622 times on Slideshare, 222 times on Scribd and 143 times on YouTube.



The D&E activities were implemented in the last year of the project within the modified timeframe. The extra dissemination activities, such as the development of the DIBANET video as well as recording and making the last Networking event presentations online caused extra costs. However,

these activities were required for the successful implementation of the project. Therefore the last report contains staff and other costs not planned in the period originally.

The main focus was on the networking activities in the last period of the project combined with interactive use of Information and Communication Technologies. The key activities were organising the DIBANET Networking Day in Thessaloniki, Greece in October 2012 that required an intense interaction with the relevant target groups and extension of the project website services in line with the planned D&E activities.

The main achievements of the work package in the third reporting period are the followings:

- The DIBANET EU-LA Networking Day in Thessaloniki has been organised for the relevant stakeholders in October 2012. The recorded presentations have been made available online after the event.
- PETROBRAS, a major Brazilian energy corporation, has joined the consortium.
- The two e-learning courses on hydrolysis and thermal processing of biomass for second generation biofuel production have been launched.
- The Chemical database has been uploaded to the project website.
- The fourth, fifth and an extra sixth edition of DIBANET Newsletter have been designed and distributed.
- The DIBANET project website has been extended and regularly updated.