BIOREFINERIES AND NEW TECHNOLOGIES FOR PRODUCTION OF ALKYL LACTATES

J. Beckmann[1], B. Kamm[2]

[1] biorefinery.de GmbH, Stiftstraße 2, D-14471 Potsdam, Germany, e-mail: kamm@biorefinery.de

[2] Research Institute Bioaktive Polymer Systems e.V. and Brandenburg University of Technology Cottbus, Kantstrasse 55, D-14513 Teltow, Germany, e-mail: kamm@biopos.de

Plant biomass always consists of the basic precursors carbohydrates, lignin, proteins and fats, beside various substances such as vitamins, dyes, flavours, aromatic essences of most different chemical structure. Biorefineries combine the essential technologies between biological raw materials and the industrial intermediates and final products. Biorefineries combine necessary technologies between biological raw material and the industrial intermediates and final products. Worldwide have been developed the biorefinery systems green biorefinery and lignocellulosec feedstock biorefinery [1]. In the lecture have been presented precursors-containing biomasses with preference of carbohydrate line and in particular on platform chemical lactic acid and their sequence products, e.g. polylactide, ethyl lactate, butyl lactate.

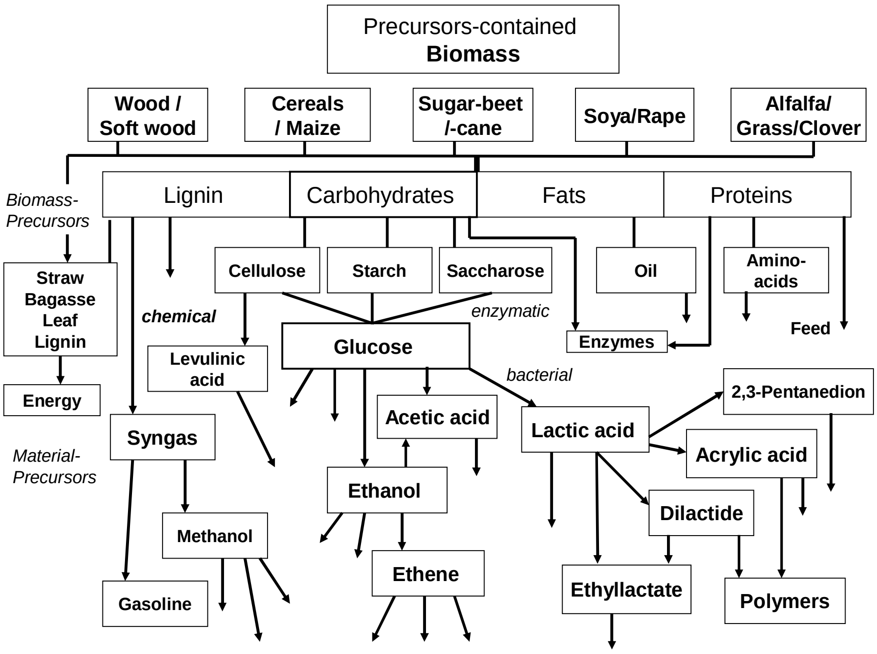


Abb.: Biorefinery-scheme for precursors -containing biomasses with preference of carbohydrate line

We have found together with Grace Company a new catalytic process for efficiently production of alkyl lacates for application as 'green' solvents [2]. The new technology, products, and prices are presented.

[1] Kamm, B.; Gruber, P.; Kamm, M.; Biorefineries, Industrial Processes and Products, ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY, WILEY-VCH, 2007

[2] Kamm, B.; Kamm, M.; Schönicke, P.; Bohnen, F.; Verfahren zur Veresterung organischer Säuren, Patentanmeldung Az.10 2007 063 507.0, 28.12.2007

Turning waste into fuel: The microbial production of bioethanol from deproteinized whey concentrate.

Christian Benecke[1], Sascha Beutel[1], Heinrich Buchholz[2], Thomas Scheper[1]

[1.] Institut für Technische Chemie der Leibniz Universität Hannover, Callinstraße 5, 30167 Hannover
[2.] Biolac GmbH & Co. KG, Am Bahnhof 1, 31097 Harbarnsen

Due to the limited reserves of fossil fuels and concurrent worldwide increasing demand, the need of alternative fuels from renewable resources is obvious. The so called 1st generation biofuels, (e.g. bioethanol from sugar cane or biodiesel from palm oil) lead to ethic discussions because of the competitive occupation of cultivable land with the production of food, because the growing of energy crops increases the benefit of the farmer, compared to edibles. Therefore, the 2nd generation biofuels, which are obtained from waste or residual materials, became attractive research objectives.

In this research project, the microbial production of bioethanol from deproteinized whey concentrate is investigated. This residual whey concentrate is waste material from the production of whey proteins and lactose and it still contains up to 10 % of the original amount of lactose. Due to this high amount of ca. 200 g/L of carbon source, this whey concentrate represents a problematic waste on the one hand, but also probably an attractive substrate for suitable microorganisms on the other. For the conversion of lactose to bioethanol, the yeast *Kluyveromyces marxianus* DSM 5422 showed the best results in preliminary tests in shaking flasks. This yeast was able to convert lactose to ethanol up to a concentration of more than 60 g/L (7.2 %Vol.) in a fed batch process. As a suitable value of initial sugar concentration, an amount of ca. 140 g/L lactose was determined. Higher concentrations cause a radical reduction of growth, probably by osmotic stress. The variance of the pH value from pH 4 – 8 shows no significant change in the growth rate. So that it is not necessary to adjust the pH value of the whey concentrate to a predefined value, but the natural pH value of the whey concentrate of ca. 5.6 is sufficient. The necessity of sterilization of the whey concentrate was also investigated. The results showed that there is no significant difference in lactose consumption and biomass growth in sterilized whey concentrate compared with unsterile material.

OPTIMIZATION-BASED IDENTIFICATION OF PROMISING REACTION PATHWAY ALTERNATIVES

Anna Besler, Andreas Harwardt, Wolfgang Marquardt

Aachener Verfahrenstechnik – Prozesstechnik, RWTH Aachen University,
Templergraben 55, 52056 Aachen, Germany
E-Mail: Wolfgang.Marquardt@avt.rwth-aachen.de

Keywords: biofuel, process synthesis, reaction network

Innovative and sustainable processes for the conversion of whole plants into fuels are developed in the cluster of excellence "Tailor-Made Fuels from Biomass (TMFB)" at RWTH Aachen University.

To guarantee an efficient production, a large number of process alternatives needs to be evaluated systematically at an early design stage. Therefore a rapid screening method is derived from metabolic pathway analysis [1]. Networks of all possible reactions are evaluated based on mole balances for each substance taking stoichiometric coefficients into account. Further connection rules can be implemented to describe reaction directions, yields or separation tasks.

As this system of equations is generally under-determined, room for optimization is given. In a first step the yield of a target component is maximized. The solution space is evaluated using mixed integer programming to find all alternate optima [2]. Then economic, energetic and ecological criteria are introduced for secondary discrimination. Based on this knowledge the most promising reaction pathways are chosen for further analysis, e.g. process design by short-cut methods and a detailed economic evaluation.

The fermentation of green biomass to itaconic acid and the following chemical conversion to target molecules are investigated as example. The most promising reactions are identified from a network including more than 200 reactions and a first benchmarking of the entire process is presented.

References:

[1] Schilling, C., Palsson, B.: The underlying pathway structure of biochemical reaction networks, *Proc. Natl. Acad. Sci.* (95) 1998, 4193-4198

[2] Lee, S., Phalakornkule, C., Domach, M., Grossmann, I.: Recursive MILP model for finding all the alternate optima in LP models for metabolic networks, Computers and Chemical Engineering. *24* (2000), 711-716

Bioconversion of rye straw at elevated temperatures

Vera Bockemühl[1], Thomas Ingram[2], Tim Rogalinski[2], Lutz Popper[3], Gerd Brunner[2], Garabed Antranikian[1]

[1]Institute of Technical Microbiology, Hamburg University of Technology, Hamburg, Germany
[2]Institute of Thermal Separation Processes, Hamburg University of Technology, Hamburg, Germany
[3]Research and Development, SternEnzym, Ahrensburg, Germany

Due to the shortage of fossil resources the bioconversion of biomass to high value products such as fine chemicals and biofuels has recently attracted the interest of scientists from academia and industry. The choice of the most suitable substrate and the process will be crucial for the success of the future biobased industry. In mainstream processes large quantities of chemicals, such as sulfuric acid, are added to hydrolyze the cellulosic material in order to make it accessible for enzyme action. Here, we propose a novel process that allows the efficient conversion of rye straw to utilizable products without the use of chemicals. Liquid hot water treatment at elevated temperatures and a pressure of 50 bar is used to make the cellulosic material accessible for hydrolytic enzymes. The resulting liquid hydrolyzates as well as the solid residues were enzymatically converted to monomeric sugars (xylose/glucose) using mesophilic enzymes from *Penicillium janthinellum* (at 50℃ and pH 4.0) and thermoactive enzymes from *Myceliophthora thermophila* (at 60℃ and pH 4.0). These enzyme systems contain ed endoglucanase, exoglucanase, β-glucosidase, endoxylanase and β-xylosidase activities. HPLC analysis showed that glucose, xylose and arabinose are the major products formed and 95% of the initial xylan and 92% of the glucan was converted to monomeric sugars using a pretreatment temperature of 200℃-215℃. The described process using a fixed-bed reactor combines several advantages compared to other reactor types, namely significant energy savings since no biomass comminution is necessary, high solid-to-water-ratios and reduces by-product formation.

We thank the Deutsche Bundesstiftung Umwelt (DBU) for the financial support (AZ 13157-32)

Fucus vesiculosus as resource for medical applications - chances and obstacles -

Andrea Holtkamp[1], Linda Kilian[1], Svenja Kelly[2], Roland Ulber[2] and Siegmund Lang[1]

[1]Technische Universität, Institut f. Biochemie u. Biotechnologie, Spielmannstr. 7; 38106 Braunschweig;
[2]Technische Universität, FB Maschinenbau u. Verfahrenstechnik, Lehrgebiet Bioverfahrenstechnik, Gottlieb-Daimler-Str., 67663 Kaiserslautern.
a.holtkamp@tu-bs.de

Fucus vesiculosus (bladder wrack) is a ubiquitous macro algae that can be found on various coast around the globe. One interesting compound of the alga is fucoidan which is stated to posses several bioactive capacities (Cumashi et al., 2007). It is a sulphated polysaccharide which consists mainly of Fucose. Other saccharides are mainly connected to the Fucose backbone by 1,3-α-glycosidic bonds.

In the work presented, fucoidan was extracted from *Fucus vesiculosus* collected at the North Sea Coast, Germany. Extraction procedure was optimized to gain higher yields, reproducible quality and molecular size cuts of the material. Tests were performed to gather information of the bioactivity of the produced fucoidans. As already stated in literature (Holtkamp et al., 2008) fucoidan showed an anticoagulant effect like heparin does. Another even more interesting result was the influence of fucoidan against HCMV (human cytomegalo virus). In the tests performed fucoidan exceeded the bioactivity of ganciclovir which is already used as a virus statica. Any negative effects on the cells could not be detected. Analysis using fucoidan as anti tumour agent do also show an influence of fucoidan against tumour formation.

Hence, fucoidan has a high potential to act as a new sustainable drug. Its different application possibilities make it an interesting research tool. The bottleneck of this work lies in the raw material. Analysis was performed to produce a cleaving enzyme (fucoidanase) as well as methods had to be developed to gain information about the constitution of the wanted sugars. Suitable screening methods and large scale reproducible extraction is needed to exploit this valuable source.

Acknowledgement: We would like to thank the group of Prof. Dr. R. Buchholz (Uni Erlangen, Lehrstuhl f. Bioverfahrenstechnik) for HCMV studies.

Literature:

Cumashi, A., Ushakova, N. A., Preobrazhenskaya, M. E., D'Incecco, A., Piccoli, A., Totani, L., Tinari, N., Morozevich, G. E., Berman, A. E., Bilan, M. I., Usov, A. I., Ustyuzhanina, N. E., Grachev, A. A., Sanderson, C. J., Kelly, M., Rabinovich, G. A., Iacobelli, S., and Nifantiev, N. E. (2007). A comparative study of the anti-inflammatory, anticoagulant, antiangiogenic, and antiadhesive activities of nine different fucoidans from brown seaweeds. *Glycobiology* **17,** 541-552.

Holtkamp, A., Kelly, S., Ulber, R., and Lang, S. (2008). Fucoidan and Fucoidanases. *Applied Microbiology and Biotechnology* **submitted**.

Biomass Fractionation by an Organosolv Process for Co-Production of Fuels and Chemicals

W.J.J. Huijgen*, R.R. van der Laan & J.H. Reith

Energy Research Centre of the Netherlands (ECN), Biomass, Coal & Environmental Research, P.O. Box 1, 1755 ZG Petten, The Netherlands.
* Corresponding author: Wouter Huijgen, Phone: +31 224 568162, Fax: +31 224 568487, E-mail: huijgen@ecn.nl

Abstract

In this work, we present a fractionation process for co-production of fermentable sugars (e.g. for bioethanol production) and high quality lignin from lignocellulosic biomass. The function of the pre-treatment process is to increase the accessibility of the cellulose polymers for subsequent enzymatic hydrolysis as well as hydrolysis of the hemicellulose fraction and separation of the lignin fraction. Most pre-treatment technologies are optimized for sugar production only and produce a residue that is only suited for heat and power generation. The goal of the organosolv process studied by ECN is to achieve full fractionation of all biomass fractions, including lignin, in a sufficient quality for production of (bio)chemicals.

Experiments on willow wood showed substantial hydrolysis of hemicellulose to sugar monomers and low formation of most potentially inhibiting degradation products. Enzymatic hydrolysis tests showed a 4 to 5 fold higher glucose yield from pre-treated willow as compared to untreated wood, which indicates a strongly improved accessibility of the cellulose fraction for the enzymes. As a way to improve particularly the delignification during organosolv the use of other solvents than ethanol was studied as well as the application of catalysts. Results will be presented at the conference. This work was performed within the EU-FP6 BioSynergy and NL-EOS LignoValue projects.

Separation and Purification of 1,18-Octadecenedioic acid

Dipl.-Ing. H.-J. Körner, Dr.-Ing. G. Deerberg
Fraunhofer-Institut für Umwelt-, Sicherheits- und Energietechnik UMSICHT,
Osterfelder Straße 3, 46047 Oberhausen, Germany
www.umsicht.fraunhofer.de

Biotechnological processes are becoming increasingly important for the manufacture of chemical products such as special polymers, fine chemicals and pharmaceuticals. Therefore, in the mid of 2005, eight Fraunhofer institutes joined to form a research alliance. The research activities are geared towards developing and establishing a technology platform for the integrated manufacture of bio-based chemical products using biotechnological processes, with optimum utilization of natural synthesis. Plant oils and fats are being used as model systems. As an example, the components of the fats (fatty acids/ monocarboxylic acids) are transformed by biotechnological means into α,ω-dicarboxylic acids (1,18-octadcenedioic acid). These chemicals are then converted into polymeric products.

The success of biotechnological processes is determined by the chosen bioconversion step as well as by the processes for product isolation and purification. Following the bioconversion, the raw product mixtures typically only contain low concentrations of the desired product. At the same time, there are great requirements on the purity of the final product. These conditions place high demands on the selection and optimal setup of the necessary separation and purification technology.

As the experiments showed, Carboxylic acids, particularly dicarboxylic acids, can be separated from a fermentation broth by adjusting the pH of the fermentation broth and heating the broth to a temperature sufficient to cause formation of three immiscible phases. One of these phases is an organic phase containing the carboxylic and dicarboxylic acids and can be separated from the two other phases.

The separation of the carboxylic acids / dicarboxylic acids from unreacted starting materials and reaction by-products can be achieved by extracting with an organic solvent. The following purification is characterised by the recovering of the organic solvent and the separation of monoand dicarboxylic acids by distillation.

'High value chemicals' biorefinery: developing adaptive processes for recovery of high value compounds

Alexei Lapkin

Centre for Sustainable Chemical Technologies
Department of Chemical Engineering
University of Bath, Bath BA2 7AY, UK
S.Chemat@bath.ac.uk

Natural factories – plants – are capable of synthesising very complex functional molecules, which are then often mimicked for their function (as a drug, a fragrance, etc) through chemical synthesis. Hence, using natural feedstocks as libraries of unique high-value molecules, and as factories that can be optimised to produce higher quantities of the desired molecules, is the approach that is potentially hugely rewarding, leading to creation of new markets. This route may also lead to the reduction of environmental impact of chemical technologies through avoiding the use of non-renewable feedstocks, complete utilisation of plant biomass and integrating plant feedstocks utilisation with energy and fertiliser technologies.

The major scientific and technical barrier is, however, the step of initial extraction/fractionation of compounds from biomass. Complex mixtures, difficult mass transport processes, variability in composition all add to the overall complexity of the problem.

In this presentation we will describe an approach to developing an integrated supply chain of chemical feedstocks (Figure 1), which starts from an adaptive extraction technology. A combination of computational and experimental techniques are employed to develop the extraction process, using 'green' solvents and process intensification principles.

The example of extraction and the approach to whole-plant utilization using *Artemisia annua,* will be discussed in detail.

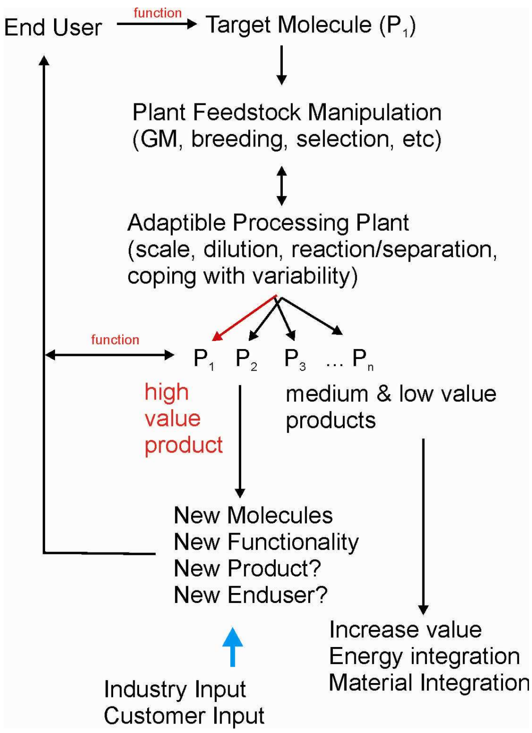


Figure 1: Scheme of supply chain integration from end-user and user-defined product function, to plant development through to processing technology.

Reactions in Ionic Liquids – Dehydration of Carbohydrates to 5-Hydroxymethylfurfural

J. Lifka, A. Stark, B. Ondruschka

5-Hydroxymethylfurfural (HMF), obtained from renewable biomass-derived carbohydrates, has the potential as platform chemical to provide sustainable substitutes for petroleum-based building blocks used in production of fine chemicals and polymers. Presently, the efficient production of HMF is not satisfactory due to the insufficient product purity requiring various purification steps; neutralisation, ion exchange chromatography, crystallisation. We have studied the production of HMF by dehydration of carbohydrates using commercially available ionic liquids such as 1-butyl 3-methylimidazoliummethanosulfonate. In these reaction system, the ionic liquid acts as solvent, catalyst, and also as water scavenger.

The influence of different reaction parameters on the dehydration was investigated. When the reaction is carried out under optimal conditions, a yield of HMF as high as 90% can be achieved within 60 minutes.

In particular, the studies clarify the following questions: What are the fundamentals of catalytic activity of ionic liquid in the reaction system? Can we use then another ionic liquid system (i. e. other alkyl imidazolium derivates)? How can the work-up and purification procedure be optimised? Different solvents for extraction were examined concerning their extraction selectivity and general efficiency.

In a first step, the reaction was investigated in a batch reactor, and the results transposed to a continuous reaction set-up. In a second step, the reaction parameters were optimised to a mini-plant working on the principles of reactive extraction technology.

Fermentative production of α,ω-di-carboxylic acids for the synthesis of bio-based plastics

Sabine Löffler[2], Wenke Wagner[1], Susanne Zibek[1], Thomas Hirth[1,2], Steffen Rupp[1]

[1] *Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB, Stuttgart*
[2] *Institute of Interfacial Engineering IGVT, University Stuttgart, Germany*
steffen.rupp@igb.fraunhofer.de

KEY WORDS: DICARBOXYLIC ACIDS, *CANDIDA* SP., BIOBASED PLASTICS, OMEGA OXIDATION

For the production of polyesters, diols and di-carboxylic acids are used. Short-chain di-carboxylic acids can still be made easily and at low cost from petrochemical raw materials. In contrast the production of long-chain di-carboxylic acids with more than 12 carbon atoms is quite difficult and very expensive. These long-chain building blocks can be used to create new materials with improved characteristics for products like thermoplastics or coatings among others.

The goal within our network (BioProChem) is to evaluate the production process of these new polymers along the entire value chain, starting from the selection of the raw material to the final product. Our part in this research project is to develop biotechnological methods for production of long-chain di-carboxylic acids. For this purpose the metabolic pathway of omega-oxidation is exploited. In several yeast species of the genus *Candida* for instance this pathway is present and enables the microorganism to convert fatty acids into di-carboxylic acids. As renewable raw materials we use plant oils or by-products from technological processes like olein, a by-product of the reprocessing of tallow and technical fats. We established a biotransformation process using the yeast *C. tropicalis* and produced octadecenedioic acid from oleic acid derived from different substrates like rapeseed oil (including in process use of lipases), rapeseed oil methylester and olein. Biotransformation processes using different yeast species are currently under development.

Presentation: New Chitinases for the Industrial Biotechnology

Karin Moß[2], Susanne Zibek[1], Thomas Hirth[1,2], Steffen Rupp[2]
[1] *Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB, Stuttgart*
[2] *Institute of Interfacial Engineering IGVT, University Stuttgart, Germany*
steffen.rupp@igb.fraunhofer.de

Key Words: CHITIN, ENZYME SCREENING, N-ACETYLGLUCOSAMINE

In today's daylife many petroleum-based materials ensure our living standard. As crude oil resources are running short, we have to identify renewable raw-materials in order to create alternatives for production of materials equivalent to the nowadays commonly use of petroleum based materials to keep our living standards. Chitin, the second most abundant biopolymer after cellulose, could be such an alternative. It is found for example in crustaceans' and insects' carapace. Being a major component in the shellfish-waste it is cheap and easily accessible for production processes. Built of N-acetylglucosamine (NAG) monomers Chitin in contrast to glucose provides a naturally occurring resource for molecules containing nitrogen, which may be used for the production of high-value building blocks such as pyrrols. In our research we aim on the development of biotechnological processes to convert chitin to its monomer NAG. Therefore we search for new powerful Chitin-degrading microorganisms and enzymes (Chitinases EC 3.2.1.14) including their encoding DNA-sequence. Using enrichment cultures and metagenomic libraries we could identify 2 new chitinolytic organisms and new enzymes. The comparison of the DNA-sequence of one of the enzymes identified revealed a new chitinase with low similarity to known ones. The production process of NAG is developed as a two-step-process were in the first step chitinases are produced by the microorganisms on basis of either glucose or chitin and in the second step after separation of the enzyme-producing cells crab-shells or other chitin containing substrates are enzymatically degraded to the monomer NAG. We aim at a process in which no waste products as acid or lime will have to be handled. NAG then could be used as a basic chemical for further conversion e.g. to pyrrole or furan derivates.

Development of advanced biorefinery schemes to be integrated into existing industrial fuel producing complexes

Hamid Mozaffarian (project coordinator)

Energy research Centre of the Netherlands (ECN), Unit Policy Studies
P.O. Box 1, 1755 ZG Petten, the Netherlands
Phone: +31 224 564262 / Fax: +31 224 568338
E-mail: mozaffarian@ecn.nl

BIOREF-INTEG is a CSA (Coordination & Support Action) project, within the framework of the FP7 Programme (Theme Energy). The overall aim of BIOREF-INTEG is to develop advanced biorefinery schemes to be integrated into existing industrial fuel producing complexes. The Scientific and Technological project objectives are:

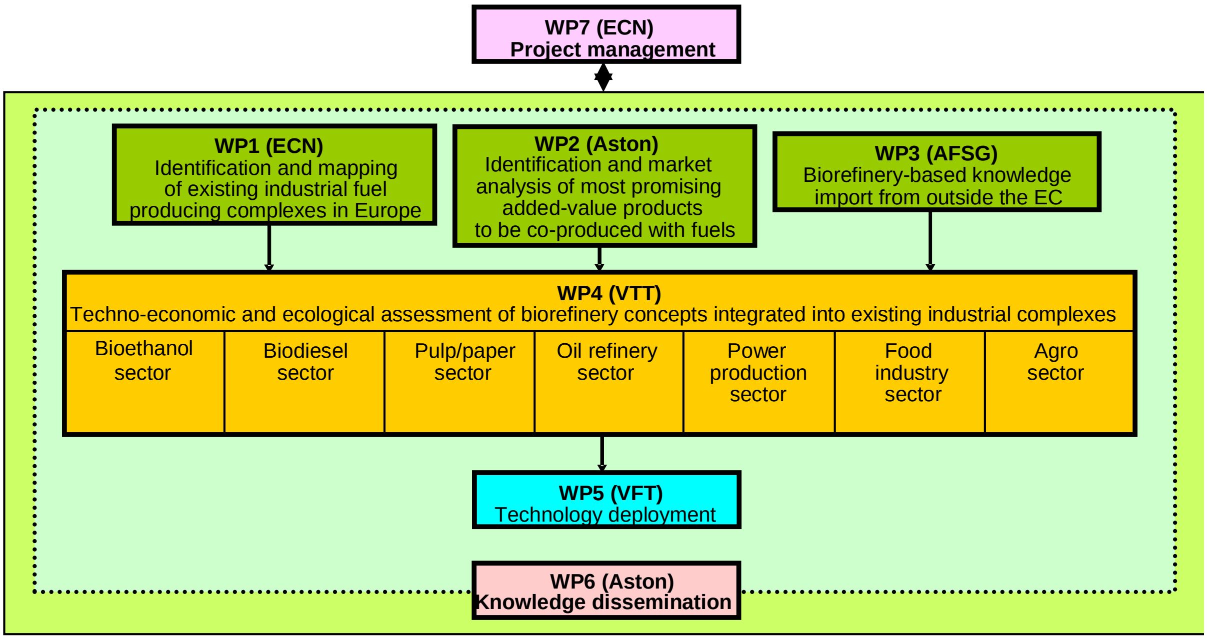
- To make the production of biofuels more competitive;
- To identify and develop the optimal integrated biorefinery schemes for the production of best suited "building blocks" in terms of processes and bioproducts;
- To identify opportunities of various biomass-based sectors to produce fuels while increasing their market competitiveness by co-producing added-value products.

Sectors dealt with are: sugar/starch (bioethanol), biodiesel, pulp & paper, conventional oil refinery, power production, food industry, and agrosector. The project is performed by 7 separate but strongly interrelated workpackages dealing with:

- Mapping of existing industrial fuel complexes in Europe (reference-cases);
- Definition of most promising added-value bioproducts;
- Knowledge import from outside the EC;
- Integral technical, economic and ecological system assessments to select most promising market specific integrated biorefineries;
- Technology deployment;
- Knowledge dissemination and training;
- Project management.

The project is co-ordinated by Energy research Centre of the Netherlands, ECN. Other participants involved are 4 SMEs: ETC (SE / forest-based biorefinery), Ten Kate (NL / high quality fats & proteins), VFT (BE / industrial marketing services with focus on renewable resource materials), Bioro (BE / biodiesel), 3 industries: Abengoa Bioenergy New Technologies (ES / bioethanol), Cehave (NL / high quality animal feed), Repsol (ES / conventional oil refinery), 2 universities: Aston (UK) and University of Ghent (BE), and 3 RTD institutes: VTT (FI), AFSG (NL), and STFI (SE / pulp & paper). Project duration is 2 years (June 2008 – May 2010).

In this poster the project framework, objectives, expected results, and the related dissemination activities would be presented.



BIOREF-INTEG Work Packages and their interdependencies

Microalgae as CO_2 sink in the biogas process

Noke, A; Kontradowitz, C.;. Klöck, G.

University of Applied Sciences Bremen, Germany

Key Words: biogas, microalgae,

Abstract:

The digestion of renewable primary products like maize silage leads to the production of biogas with a relatively high content on carbon dioxide (up to 50%) and 50 – 54% of methane. For the safe operation of a combined heat and power unit (CHP) it is necessary to reach a constant concentration of methane of at least 52%.

The intention of our research is to increase the content of methane by the decrease of the CO_2 content. Thereby a safe running and a higher effectiveness of the CHP is ensured.

The produced gas of the biogas plant will be conveyed through a gas scrubber to dissolve the CO_2 in the watery phase and will be fixed later in algae biomass. Thus potentially explosive mixtures of CH_4 and O_2 will be avoided. Thereby other troublesome elements like hydrosulphide and ammonia will be removed. Finally a pilot plant will be build up and operated nearby a biogas plant.

The growth of the microalgae will be enhanced and valuable products will be produced by the selected alga species. Resources like poly unsaturated fatty acids (PUFA), which are essential for human nutrition, or different pigments (e.g. carotenoids) may be extracted from the biomass. Different microalgae of the class of haptophyta (coccolithophores) will be tested because they are able to fix high amounts of CO_2 by calcification. Green algae (e.g. *Scenedesmus* sp.) may be also interesting because of their high CO_2-binding and growth rate and their production of high valuable carotenoids. Less valuable fractions can by used as feed for the biogas plant. By this the cycle of matter will be closed.

The research is embedded in the cooperation project ALGENBIOGAS between 2 Universities of Applied Sciences and 4 companies and is funded by the German Federal Ministry of Education and Research (FHprofUnd").

Conversion of Poplar Wood into Platform Chemicals after Organosolv Pretreatment

Juergen Puls and Bodo Saake

vTI Institute for Wood Technology and Wood Biology, 21031 Hamburg, juergen.puls@vti.bund.fe

In a joint project coordinated by Dechema and funded by FNR including chemical companies, different universities and research institutes, a process has been developed for the conversion of beech and poplar wood into platform chemicals. Based on an accurate literature study an organosolv process based on ethanol and water was chosen as the basic procedure for component separation. The process should allow an effective utilization of all wood components cellulose, hemicelluloses, lignin including the extractives. Indeed the procedure chosen by the research consortium allows the separation of the extractives using the same solvent, which is required for the component separation into the wood polysaccharides and sulphur-free lignin.

Based on a factorial design the optimal parameters (ethanol: water ratio, temperature, time, liquor:wood ratio, addition of catalysts) were identified with regards to accessibility of the cellulose fraction for cellulolytic enzymes as well as for lignin recovery and hemicellulose fermentability. Optimization of pulping parameters was achieved in the 100g scale and verified in the 1kg scale. Taking poplar from a short rotation plantation as a example a quantification of the individual wood fractions will be given in addition to qualitative data on the extractives fraction, the cellulosic fibre fraction, the water-soluble hemicellulose material and the recovered alkali-soluble lignin.

Phenolic compounds from *Quercus suber L.*

Sónia A. O. Santos, Paula C. R.O. Pinto, Armando J.D. Silvestre, Carlos Pascoal Neto

CICECO and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Byproducts of the forestry industry have been attracting increasing interest in recent years as a renewable source of chemicals within the Biorefinery concept [1]. Considering the environmental restrictions of sustainable development and the instability of the crude oil prices dictated by *geo-politics*, the upgrading of all the by-products generated, within the scope of the biorefinery in forest-based industries, represents a valuable contribution for the gradual implementation of this concept.

Cork industry is one of the most important sectors of the Portuguese economy, with an annual production of *Quercus suber* cork of about 185 000 tons / year (about 50% of world production). However, this industry generates considerable amounts of residues, such as “cork powder” (about 40 000 tons/year), during the processing of cork stoppers and agglomerates production. These residues are, nowadays, mostly burned to produce energy.

The detailed study of chemical composition of cork is a fundamental step to evaluate the viability of extracting new added-value chemicals from cork by-products. The potential of such waste as a source of triterpenic components [2] and suberine [3] is well established. On the contrary, the phenolic fraction of the cork is still poorly studied.

In this paper we report a detailed study of the composition of the phenolic fraction of cork products. This study involved successive extraction methods and fractionation, followed by a detailed chemical analysis by GC-MS and HPLC-MS. The total phenolic content and antioxidant activity of the extracts were evaluated following standard procedures. The compounds identified included several phenolic acids, flavonoids and aldehydes.

[1] B. Kamm, P. Gruber M. Kamm (Eds). Biorefineries- Industrial Processes and Products, Wiley VCH, Weinheim, 2006;

[2] A.F. Sousa, P.C.R. O.Pinto, A.J.D. Silvestre, C. Pascoal Neto, *J Agric. Food Chem.* 2006, **54**, 6888;

[3] A. Gandini, C. Pascoal Neto, A.J.D. Silvestre. *Progr. Polym. Sci.* 2006, **31**, 878.

The application potential of chemical functionalizised xylans

Katrin Schwikal[1], Katrin Petzold[1], Thomas Heinze[1], Bodo Saake[2]

[1]Centre of Competence for Polysaccharide Research,
Friedrich Schiller University Jena / TITK-Rudolstadt, Germany;
[2] Department of Wood Chemistry and Chemical Technology of Wood,
Johann Heinrich von Thünen Institute, Germany

Abstract

There are various processes like pulping or steam treatment of wood and one year plants yielding hemicellulose, e.g., xylans of different mol. wt. and structure. Recently, the xylans gain an increasing importance as basis for new biopolymeric materials and functional polymers accessible by chemical modification reactions. Various routes for prepg. anionic and cationic derivatives including detailed studies on the distribution of the functional groups revealed by NMR spectroscopy and HPLC after hydrolytic chain degradation will be and their potential for some applications will be discussed.

Succinic acid esters as intermediates for the synthesis of polyamide 44

Dr. Inna Bechthold, Dr. Karlheinz Bretz, Dr. Andrea Springer, Dr. Stephan Kabasci

Fraunhofer-Institut für Umwelt-, Sicherheits- und Energietechnik UMSICHT,
Osterfelder Straße 3, 46047 Oberhausen, Germany

Succinic acid is predicted to be one of the future platform chemicals that can be derived from renewable resources.

The development of a process chain from natural resources to new polymers like polyamide 44 is the main research objective of the scientists group »C4-GAIN« at Fraunhofer UMSICHT. This project is funded by the BMELV/FNR (FKZ 220-249-05).

One part of the process chain is the conversion of succinic acid to its dialkyl esters and their following polycondensation to polyamide 44. Dialkyl esters of natural organic acids are known as environmentally friendly, non toxic solvents, and they also represent interesting monomers for syntheses of polyamides or polyesters. In the esterification of succinic acid the formation of byproducts like monoesters and anhydride must be considered. As the experiments showed, diethyl esters of succinic acid could be produced under optimised reaction conditions with a yield of more than 98 %. Furthermore, it could be revealed, that the following polymerisation can utilise the raw effluent from the esterification reaction without further purification.

Polyamide 44 was synthesised by polycondensation of succinic acid diethyl ester with 1,4-butanediamine. Its melting point was measured as high as 305 ℃ due to the high density of hydrogen bonds between the amide groups in the polymeric chains. The IR-spectra show, that unwanted side-reactions in the polycondensation, like e. g. the typical chain interruption reactions caused by formation of imides, can effectively be suppressed, if diethyl esters are used as monomers.

Towards the fermentative production of fine chemicals: utilization of crude glycerol from biodiesel production by recombinant *Escherichia coli* strains

Ullrich K., Albermann C., Sprenger G. A.,

Institute of Microbiology, University of Stuttgart

Glycerol is a valuable renewable resource, which is a well-known C-source for the cultivation of microorganisms and especially for *E. coli*. The increasing production of biodiesel results in a surplus of crude glycerol in the coming years. Therefore, new applications are desirable for this then abundant carbon and energy source, e.g. utilization by *E. coli*. The aerobic dissimilation of glycerol in *E. coli* proceeds via uptake through facilitated diffusion (GlpF) and activation by an ATP-dependent glycerol kinase (GlpK) to glycerol-3-phosphate (G3P). G3P is then oxidised to dihydroxyacetone phosphate (DHAP) by glycerol-3P dehydrogenase (GlpD, or GlpABC) [1]. Subsequently, DHAP enters the central metabolism. In the genome of *E. coli* K-12, a cryptic pathway for the dissimilation of glycerol exists. Glycerol could be oxidised by glycerol dehydrogenase (GldA) and subsequently phosphorylated to DHAP by a PEP-dependent dihydroxyacetone kinase (DhaKLM). This way of glycerol dissimilation is usually inactive in *E. coli*, but can be activated by mutation [2].

In order to get high efficiency in the conversion of glycerol we constructed various *E. coli* strains either by deletion of chromosomal genes [3] or by site-directed integration of the appropriate genes into the chromosome (“knock-in by knock-out”). Results of the conversion of glycerol and crude glycerol into production of aromatic amino acids, and the comparison to a glucose-based production will be presented.

[1] Lin et al., 1990 *J Bacteriol*. 172(1):179-84

[2] Tang et al., 1979 *J Bacteriol* 140(1):182-7

[3] Datsenko, K.A. and Wanner, B.L., 2000 *PNAS* 97(12): 6640-6645

ADVANTAGES AND DISADVANTAGES OF THE INDUSTRIAL PROCESSING Of WHOLE CANE.

Antonio Valdés Delgado*, Hector Fiandor Rosario* *

* Center for Priority Programs and Projects
Calle 20 No. 4112 e/41 y 47 Playa, Ciudad Habana Cuba
Fax: 0 537 229372, E-mail: avaldes@ geprop.cu
** Division of Integral Studies
Calle Industria esq. Barcelona Habana Vieja, Ciudad Habana Cuba
E-mail: hfiandor@infomed .sld.cu

ABSTRACT

The industrial processing of the whole cane –stalk, leaves and tops – increases the quantity of biomass that can be obtained for its use as fuel; this renewable fuel, can substitute fossil fuel in different productions, meaning an increase of the added value to the sugar production including the access of carbon credits as the quantity of electric energy generated can be increased using this non polluting, renewable fuel.

However also different affectations exist to the technological process as is: a) the increase of the period of operation on account of an additional fibrous material to the processed with cane -with scarce content of sucrose and a higher content of non sugars- b) an increase in the sucrose losses in the bagasse and in the final molasses. These affectations present a certain economic valor, its comparison with the advantages of an additional fuel determines the possibility of its use. In this work the technologic and economic results –in a case study considered- are exposed for the use of the Whole Cane.

The Whole Cane Processing indicates the advantage of obtaining a higher quantity of biomass that can be employed as fuel.

The Whole Cane Processing indicates as disadvantage an increase in the sucrose losses in the bagasse and in final molasses.

The economic valuation for determined prices in the world market for sugar and fuel oil, indicates that from an industrial standpoint it can be economically advantageous to carry out the processing of Whole Cane. It is recommended to make an industrial test to precise these results and to determine the quantity of these residues recommended to be left at the field.

Membrane-aided clean-up and fractionation of fatty acid esters produced from waste fats – a feasibility study –

Taher Sahlabji, Hubertus Wichmann, Muefit Bahadir

Technische Universitaet Braunschweig Institute of Ecological Chemistry and Waste Analysis Hagenring 30, 38106 Braunschweig, Germany

Efforts are made to replace mineral oil by renewable raw materials in technical products like lubricating oils. Energy- and cost-effective production and refinement routes for e.g. fatty acid esters are under progress. In this context, a feasibility study was performed, whether the application of membrane-aided separation procedures for the hydrophobic matrix of fatty acid methylesters are suitable. It was found, that an enrichment of saturated acid esters from 28 to 51 % was possible in an unsaturated fatty acid ester matrix in just three steps. The content of free fatty acids (FFA) could be reduced to a considerable extent as well, e.g. to 6% of the initial value of 7.8 mg FFA/g ester. This clean-up effect was enhanced by the addition of a basic additive. In general, the good clean-up potential of the procedure, concerning expected impurities like water, salts, oligo- and polymers of fatty acids, coloring matter, phospholipids etc. was demonstrated.

In the course of this feasibility study on the use of membrane techniques for the production of technical ester oils, interesting effects concerning the separation of saturated from unsaturated fatty acid esters and of FFA from the oils were determined that appear worth being investigated in detail in the future. Nevertheless, these effects are far from practical industrial application, yet. The flux through the membranes has to be improved. The solvent recovery by distillation after dialysis is still an energy consuming step. This could likely be avoided by performing a nano filtration (pressure, no solvent) instead of dialysis. But in general, membrane processes appear to be applicable for the production of special customized technical ester oils in small charges of up to a few thousand tons per year and plant, whereby continuous operation procedures will be preferred to batch working as demonstrated here by preliminary lab-scale experiments.

BIOGENOUS MATERIALS FOR INDUSTRIAL APPLICATIONS – SUSTAINABLE COOLANTS FOR MACHINING

Christoph Herrmann, André Zein

Institute of Machine Tools and Production Technology, Technische Universität Braunschweig,
38106 Braunschweig, Langer Kamp 19b, GERMANY

ABSTRACT

Considering economic and environmental aspects of machining, fundamental concerns are linked to the use of coolants. Cutting fluids can have severe influences on the environment. Apart from the extraction of nonrenewable resources as mineral oil, cutting fluid use, preparation, cleaning and recycling in production companies are directly connected to liquid and hazardous waste and health, environmental, economic and safety issues. Up to 30 % of coolant in machine tools can be lost through vaporization (which can be harmful to workers if substances are inhaled), adherences on work pieces and swarf or in the worst case through leakage. Against this background, possible solutions focus on the implementation of dry machining operations or minimum quantity lubrication (less than 50 ml/h) and the substitution of coolants through environmentally friendly coolants.

Dry machining (sufficiency) and minimum quantity lubrication (efficiency) are possible solutions to impede or at least reduce the issues of coolants. However, these strategies centre the problem but are often not realized or applicable on a comprehensive industrial scale. Especially grinding processes still depend on the use of coolants as over 90 % of the grinding power is converted into frictional heat and has to be absorbed. So far the removal of the induced heat in industrial grinding operations is yet not realized with dry machining technology or with reduced lubrication.

In addition to avoiding coolants, research activities at the IWF have focused on the development of alternative coolants with minimum environmental impact. These have to be considered within a life cycle management framework (technological, ecological, economic and social aspects) in order to avoid the shift of risks and problems from one life cycle phase to another. While it is easy to simply exchange mineral oil for substances (e.g. plant seed oil), the economic and ecologic impacts of these coolants have to be observed for benefits or detriments of product use over all life cycle spans from raw material extraction, to use and disposal. This includes also local and global aspects as raw material availability.

As a current example, the use of rapeseed or palm oil as an alternative energy and coolant resource lead to a competitive situation with food provision and induced a drastic rise of prices. New substitutes for mineral oil coolants are water miscible bio polymers. The bio polymers are natural resources with a high industrial availability. They dissolve in water and can be used - enriched with additives - to set up clear water based lubricants (share of water > 90 %) with a higher specific heat capacity compared to mineral oil. Technical grinding experiments have proven even higher performance capability. Apart from reduced grinding forces in operation, the polymer fluid also enables to reduce the energy demand (e.g. no extra cooling necessary) and environmental impacts.