



Second-generation biofuels and bio-products: an overview of recent projects at IFPEN

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Second-generation biofuels produced from lignocellulosic biomass (forest residues, straw, high yield crops,...) are now one of the main technological options for reducing the climatic impacts imposed by fuels used in transportation. Two main types of process are used to convert lignocellulosic biomass into biofuels: biochemical and thermochemical processes. Today the main product from the biochemical route is known as 'cellulosic ethanol', produced from hydrolysis of polysaccharides and fermentation of extracted sugars. In the thermochemical processes, the initial structure of lignocellulosic solid matrix is broken down by gasification (BtL process) to produce a synthesis gas which can be converted by Fischer-Tropsch synthesis, after purification, into very high quality biodiesel and biokerosene. Bio-liquids can be also produced from other thermal treatments such as fast pyrolysis or hydroconversion. The choice of biomass valorization process depends on the characteristics of the input biomass, its availability and the type of output fuel required. Production of bio-based chemical intermediates using lignocellulosic resources is another major topic issue to deal with, in response to the need to find sustainable alternative sourcing channels for petrochemical intermediates (ethylene, propylene, etc.). A real opportunity exists to further develop a new chemical industry based on processing non-food biomass.

Lignocellulosic transformation in biofuels or platform biomolecules is performed by multi-steps processes and involves complex chemical reaction pathways. The resulting aqueous or organic solutions are composed of a large diversity of oxygenated compounds (*i.e.* alcohols, sugars, carboxylic acids, carbonyls and phenols) whose characterization is essential to assist conversion reactions. Relevant analytical methodologies based on sample pretreatment and complementary chromatographic techniques are required to provide a detailed description of the chemical composition of these oxygenated matrices.

This presentation provides an overview of some recent projects and studies in which IFP Energies nouvelles is involved to produce 2G biofuels and bio-products. A special attention will be paid on the products quality from a technical point of view, showing that analytical characterization of biomass derived liquids is a key point to get a better knowledge of their chemical composition and in this way to contribute on developing new processes for biomass transformation.



Biorefineries: The Central Role of Catalysis

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The development and implementation of biorefinery processes is of the utmost importance to meet the vision towards a sustainable economy based on bio-resources [1,2]. In this context, catalysis, either enzymatic, heterogeneous or homogeneous is playing a major role like this is already the case in a 'conventional' refinery based on the treatment and the conversion of petro-resources. Nevertheless, contrary to petro-resources of which the nature and composition variations are 'relatively' limited, under the term 'bio-resource' or 'biomass' are gathered compounds of very different natures, namely cellulose, hemicellulose, oils, lignin and so on... Thus, a complete set of specific technologies must be developed in order to convert each fraction as smartly as possible. This implies, among others, the elaboration of a lot of processes based on catalysis. These latter constitute core technologies that will be implemented in the so-called 'biorefineries'. Within this frame, the present author coordinated the elaboration and the development of the EuroBioRef concept 'EUROpean multilevel integrated BIOREFinery design for sustainable biomass processing' (www.eurobioref.org), as a 'large-scale' European project (2010-2014). EuroBioRef is a new highly integrated, diversified and sustainable concept, which involves all the biomass sector stakeholders. The potential of all the fractions issued from the various types of biomass is used to yield a value-added as high as possible in a sustainable and economical way. The overall efficiency of this approach is a vast improvement to the existing situation and considers options such as: Production and use of a high diversity of sustainable biomass adapted for European regions / Production and use of high specific energy bio-aviation fuels (42 MJ/kg) / Production of multiple products (chemicals, polymers, materials) in a flexible and optimized way that takes advantage of the differences in biomass components and intermediates / Improvement of the cost efficiency by as much as 30 per cent through improved reaction and separation effectiveness, reduced capital investments, improved plant and feedstock flexibility and reduction of production time and logistics / Reduction by 30 per cent of the required energy / Zero waste production and reduction of feedstock consumption.

The EuroBioRef novel concept will be presented, after a general introduction on biomass, biorefineries and catalysis of which the central and key role will be discussed. Then, the next important developments for the next decade concerning catalysis for biorefineries will be presented. First, a new high throughput approach for catalysts developments materialized by the REALCAT platform [3] will be described, and then, the new concept of hybrid catalysis [4-6], integrating in one-pot chemo- and bio-catalysis, taking advantage of both technologies by creating synergies, will be presented.

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Biocatalytic enzyme processes for CO₂ conversion and lignin modification

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Global anthropogenic carbon dioxide (CO₂) emissions recently reached a record high level of 35.7 billion tons per year. An agreement to achieve zero net greenhouse gas emissions and pursue efforts to limit the temperature increase to 1.5 °C during the 21st century was negotiated recently at the 2015 United Nations Climate Change Conference, COP 21, in Paris, France. Enzyme catalysis (biocatalysis) may offer new solutions to help lower CO₂ emissions by *removing* the CO₂ and actually use CO₂ as a carbon substrate for production of chemicals: A designed biocatalytic cascade system based on reverse enzymatic catalysis by formate dehydrogenase (EC 1.2.1.2), formaldehyde dehydrogenase (EC 1.2.1.46), and alcohol dehydrogenase (EC 1.1.1.1) can convert CO₂ to methanol (CH₃OH) via formation of formic acid (HCOOH) and formaldehyde (HCHO) during equimolar cofactor oxidation of NADH to NAD⁺. This reaction is appealing because it represents a double gain: 1. Reduction of CO₂ and 2. An alternative production route to fossil oil derived chemicals. The talk will present the efficiency of different immobilized enzyme systems and reaction designs that have been explored for optimizing this sequential enzymatic conversion of CO₂ to CH₃OH, and present data we have obtained at DTU from enzymes immobilized in membranes [1]. The talk will also highlight some recent important learnings we have achieved in relation to enzymatic modification of lignin, a lignocellulosic biomass conversion residue, and notably address how laccase enzymes (EC 1.10.3.2) work to oxidize phenolic substrates using oxygen and whether laccases can really act upon lignin [2].

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Switching to Nano: Switchable Ionic Liquids in Biorefining provides the toolbox - from fractionation and pretreatment to catalysis and nanocellulose

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For centuries the Nordic countries have been relying on their natural resources, particularly forest, to make value-added products exported throughout the world and, at the same time, helping the societies to create wealth, job opportunities and social welfare. The global changes taking place today have gradually rendered these industries less competitive and profitable upon increasing competition from, particularly, Asia and South America when the consumption of such bulk products like paper and pulp have declined in the western world. The rise of the digital era, i.e. increasing use of electronic information and documentation, has meant that the volumes needed are in the decline in the developed world whereas the developing world still has room for growth in these products. Consequently, the industry has been forced to adapt and change, moving a lot of production capacity to there were the demand is. At the same time, increasing efforts are made to transform and trim the production in the original 'homeland' mills partly towards new, more innovative and more sophisticated products but also 'back-to-basics' i.e. packaging solutions based on cellulose. Moreover, importantly, there is a strong incentive and drive to move towards production of various value-added, modern biorefining solutions covering the areas of bio-based energy, transportation and chemical commodities. To meet the future challenges we have been developing an entirely new concept for biorefining utilizing 'switchable' ionic liquids (SILs) to fractionate biomass to its constituents while still to a large extent retaining their native structure [1-11]. Further, the very same SIL technology can be used for CO₂ or other acid gas capture and mitigation, productions of superior nanocellulose, as a medium of catalytic reactions including both bio- and supported heterogeneous catalysis as well as pre-processing/pretreatment and detoxification of biomass for e.g. fermentation processes.

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Low-temperature transformation of biomass: challenge for chemical reaction engineering

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The global tendency towards the use of renewable sources is a big challenge not only for conceptual chemical technology, but to chemical engineering, too. We are shifting from relatively simple molecular structures appearing in crude oil and natural gas to the very complex ones in biomass. Molecules originating from biomass are, typically polyfunctional macromolecules. On the other hand, biomass is a well-organized entity, consisting mainly of cellulose, hemicelluloses and lignin. The sugar platform of a future biorefinery is based on bio-chemical conversion processes of biomass to sugar feedstocks, while the syngas, pyrolysis platform is based on thermo-chemical conversion processes of biomass to synthesis gas or pyrolysis oils for chemicals, materials and fuels.

There are still several problems to be solved to make the mild-temperature sugar platform working in practice. One of the key issues is the catalyst development. In order to obtain platform chemicals from cellulose and hemicellulose, the glycosidic bonds should be broken by hydrolysis. Several catalysts have been proposed, such as homogeneous mineral and organic acids, heterogenized acid catalysts on carbon support, cation exchange resins as well as enzymes. The hydrolysis kinetics of polysaccharides in the presence of several catalysts is considered, along with kinetic modelling of autocatalytic phenomena appearing in the hydrolysis of polysaccharides. A new kinetic model for the hydrolysis kinetics has been developed, taking into account the differences in the reactivities of the glycosidic bonds in the polymer chain.

From the mild-temperature hydrolysis process, valuable monomeric sugars are obtained: besides glucose, polyfunctional molecules, such as arabinose, galactose, mannose and xylose are obtained. These molecules can be used as such, or refined further, e.g. by hydrogenation, oxidation and isomerization. The process intensification approach starts with catalyst selection and optimization, kinetic studies, investigation of physical properties as well as mass and heat transfer phenomena. In general, it can be stated that the interaction of chemical reaction kinetics and internal mass transfer effects in the pores of solid catalysts plays a crucial role in the transformation of molecules from biomass. In many cases, catalyst deactivation interferes with kinetic and mass transfer phenomena.

Several examples of the application of continuous structured reactors on the transformation of sugars to value-added molecules are shown in the lecture. The approach covers the following possible aspects: from the optimization of catalyst nanoparticles to the design of structured elements, kinetic and mass transfer studies, mathematical modelling of individual catalyst particles and continuous reactors. A general research strategy will be presented: from reaction kinetics to reactor design.

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Design of bio-based solvents

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The European consumption of solvents is significant, with about 6 million metric tons out of the 28 million tons worldwide consumed in 2012.^[1] They are used in many applications such as the formulations of pesticides, inks, and paints, or for industrial cleaning, extraction / separation processes and syntheses. The depletion of fossil resources, stricter regulations and collective awareness for the environmental protection incite the development of alternatives to the use of petrochemical solvents. Therefore, the chemical industry shows a growing interest in designing bio-based solvents made from renewable raw materials and supposed to prevent hazards in the field of health, safety and environment.

Two methodologies different from the trial and error approach, were developed to design these novel bioproducts. The first methodology, predictive, is based on the properties prediction thanks to various models ^[2] before the synthesis of the molecules. The reverse design is, in turn, an innovative methodology to design molecules of biosolvents through a virtual laboratory. Stages of generation of molecular structures and properties prediction are integrated in a computer-aided molecular design tool (CAMD) providing solutions that meet the outlined specifications. This tool is able to help the chemist to find out the optimal structures in agreement with defined specifications in terms of physico-chemical properties (Hansen solubility parameters, boiling point, melting point, vapor pressure, and flash point), toxicity and ecotoxicity.^[3]

These methodologies lead to identify a pool of candidate molecules derived from a bio-based building block that may act as a solvent for the target applications. Then, the relevance of these best candidates is checked with respect to their ability to be synthesized according to the green chemistry principles and their real performance in the target application. The feasibility of their syntheses is studied by retrosynthetic analyses.

The reverse design approach is more rational and efficient to find the best molecules suitable for the application: it presents the advantages to generate time, energy and cost-savings. Only potentially interesting molecules (with predicted properties meeting the specifications) are synthesized and validated in application.

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Moving from black to green Development of biorefinery processes and products in Norway

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Norway has significant forestry resources and ever since the late 18th century pulp and paper production has been central to the on-shore national value creation, ensuring activities along the whole forest based value chain. In 1969 oil was discovered on the Norwegian continental shelf, and since the early 1970s the expanding oil industry has ensured long-term wealth and welfare to the Norwegian society. During recent decades, however, increasing environmental concern has shifted the focus of research and innovation to strengthen the development of novel, environmentally benign processes and products based on biomass.

Paper and Fibre Research Institute (PFI) is a central stakeholder focusing on research and development of new processing schemes and products based on green biomass resources. PFI is an independent research institute and has performed research on biomass conversion ever since its establishment in 1923. Since 2004 PFI has been part of the Swedish INNVENTIA group, an internationally leading concern in biomass conversion/biorefining.

Today PFI's research is centered around 4 focus areas:

- Fibre and paper
- Biorefinery and bioenergy
- Biocomposites
- Nanocellulose and carbohydrate polymers

The presentation will give examples of PFI's research activities within all these areas.

In 2013-2014 PFI initiated and coordinated the establishment of the central national infrastructure project NorBioLab (Norwegian Biorefinery Laboratory), funded by the Norwegian Government through the Research Council of Norway. NorBioLab is a national infrastructure for biorefining, accessible to national and international stakeholders for the development of processes for the sustainable conversion of land and marine biomass to novel, environmentally benign biochemicals, biomaterials and bioenergy products. NorBioLab is headed by PFI and gathers central Norwegian stakeholders in the biomass conversion area, including The Norwegian Univ. of Science and Technology (NTNU), The Norwegian Univ. of Life Sciences (NMBU) and SINTEF. By uniting existing knowledge and infrastructures as well as supporting the establishment of novel research tools, NorBioLab shall allow for internationally leading research on new, innovative biorefinery processes.

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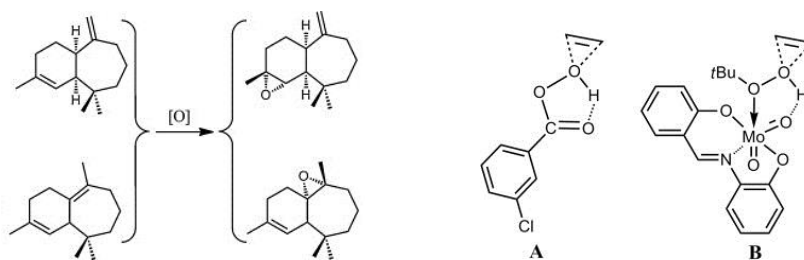
Organic solvent-free olefin epoxidation catalyzed by molybdenum complexes: Greener transformation of natural substrates.

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We are currently developing innovative greener chemical processes to (ep)oxidize organic compounds. Thus, several molybdenum based catalysts have been tested with very low catalyst loading (<0.1%) under organic solvent-free conditions, using cyclooctene as substrate and TBHP in water as oxidizing agent.[1-7] Theoretical calculations realized with $[\text{MoO}_2(\text{SAP})]_2$ catalyst exhibited a mechanism (**B**) similar to the one described by Bartlett (**A**) using *m*-CPBA in organic solvent.[5] From this similarity, we compared both methods with sesquiterpenes issued from a Moroccan tree.[8] The greener transformation gave similar results without potentially toxic organic solvent and less workup.



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Intensified Technologies for Green Process Engineering

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The LGC (Laboratoire de Génie Chimique 5503 CNRS/INPT/UPS) is a chemical and process engineering research centre at the Institut National Polytechnique de Toulouse, which is part of the University of Toulouse, France. It has approximately 160 permanent staff members and 125 graduate and post-doctorate researchers.

The research activities carried out in the department of Science and Technology for Process Intensification (STPI) within the LGC focus on the design, scale-up, operation and safety of intensified processes involving multifunctional equipment, green solvents, energy efficiency, and bio-sourced carbon. Research concerns industrial scale processes, associating equipment design and technology, as well as final product specifications. The members have long-time expertise in the characterisation of hydrodynamics, mixing and related transport phenomena (in single and multiphase flows, using both Newtonian and non-Newtonian fluids), as well as in reactor design and scale-up. They also have experience with diverse reactor types, including batch and continuous reactors, microreactors, and other novel devices for process intensification, including continuous oscillatory baffled reactors (COBR), microwave reactors, heat exchanger reactors and centrifugal reactors. They also have solid experience in a range of experimental techniques, including Particle Image Velocimetry (PIV), micro-PIV, Planar Laser Induced Fluorescence (PLIF) and high-speed digital imaging for flow visualisation and measurement, and in Computation Fluid Dynamics that can be used for reactor design and understanding.

Some examples of recent work include the design and characterization of microreactors for gas-liquid applications (1-3), biodiesel production using intensified process equipment including COBR, microwave reactors, and microreactors (4-7) and the design and construction of a continuous miniaturised microwave reactor for green chemistry. The department members are also editors of a recent book on Green Process Engineering (8).

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High value molecules obtained from a selective biomass extrusion process

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Polyphenols are natural compounds characterized by a high structural diversity and their common occurrence in plants renders them intrinsic dietary components. They are found only in plants and certain fungal species and are not synthesized neither by animals nor by humans. At present, polyphenols are looked upon as secondary metabolites characterized by a wide spectrum of physiological functions. The number of phenolic compounds identified in plant extracts has already exceeded 8000. Despite its enormous popularity, resveratrol is not a unique interesting polyphenol in a large, structurally diverse class of oligomeric stilbenoids (viniferin, Vitisin B) that are present in the wines and foods that we consume. Until recently, access to these oligomeric natural products was limited to isolation from natural sources, which severely hampered their biological evaluation. The scientific interest in resveratrol has undoubtedly instigated the renewed attention in these compounds by the chemical community. Currently, the extraction methods of polyphenols are based on the principle of maceration in a suitable solvent. These methods use a large amount of solvent, are discontinuous, expensive and require considerable energy for low extraction yields.

VALAGRO developed Biomext, a patented technology concerning a novel and innovative method of polyphenols extraction from biomass (grape cane) based on extrusion defibration. This technology requires a smaller amount of solvent, and can be carried out continuously. The Biomext technology comprises 4 steps; 1/ optional drying of the feedstock, 2/ grinding of the raw material, 3/ defibrating of grinded raw material into an extruder in the presence of a solvent and 4/ separating the soluble phase containing polyphenols from the fibers. A crude extract containing a mixture of polyphenols can be used as such or as a purified cocktail *via* preparative chromatography or centrifugal partition chromatography. For example, with grape cane coproducts, viniferin and trans-resveratrol are obtained after simple purification with a good yield. The residual solid fraction contains non-degraded cellulose and can be transformed into ethanol by enzymatic hydrolysis and fermentation.

The technology developed by VALAGRO is a continuous and economical process which requires the use of a low amount of solvent as compared to prior processes. Moreover the recovery of significant amounts of polyphenols and the viniferin yield are much higher than those obtained by infusion. The Biomext technology is patented (WO 2014076425) and used to obtain viniferin and trans-resveratrol from *Melon de Bourgogne* vine shoots with a higher efficiency in less severe experimental conditions. Extraction yields, compared to those issued from infusion technology are the following ones: The Viniferin and trans-resveratrol contents in the crude extract measured by HPLC are respectively of 984 and 7400ppm from an extrusion process and of 764 and 5468 ppm from an infusion procedure.

Finally the extrusion extraction of viniferin is now done by ECOETHANOL at a pilot scale (500 g to 1kg per day of viniferine will be obtained). Moreover, other developments are currently done by extrusion to extract other high value molecules (suberin, cutin...) from biomass.



Enhancement of enzymatic synthesis of 6-O-Dodecanoyl-D-glucopyranose with modified lipases.

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Esters derived from sugars and fatty acids are of great interest due to their surface and organoleptic properties. They are non-ionic surfactants derived from natural sources, renewable and therefore environmentally friendly. These non-ionic surfactants have large structural feature that allows their use in various areas (detergents, cosmetics and pharmaceuticals). Their synthesis is carried out either chemically or enzymatically.

Enzymatic esterification in organic solvents has recently received much attention by bio-industries. Enzymes such as lipases often exhibit innovative catalytic functions in organic solvents as improvement the solubility of hydrophobic substrates and facilitation of product recovery. Modification of the surface of lipase to protect it from denaturation in an organic solvent has widely been achieved. Surfactant-coated lipase and lipase immobilization appear to be the most promising methods although some other proposed methods for protecting lipases.

The concept of “modified lipase” could be better explored for the production of sugar esters. In this context, the efficiency of different preparations of lipase from *Pancreatic porc* (PPL) and *Candida cylindracea* (CCL) was evaluated and the specific activities were compared in ethylmethylketone (EMK) to crude powder.

In this work, lipolytic esterification of glucose and lauric acid in EMK was investigated. Immobilized and surfactant-coated lipases from PPL and CCL were designed to enhance the esterification. *Candida cylindracea* and *Pancreatic porc* lipases interacted with the surfactant Span 80 in a buffer of pH 6.9 to form Surfactant-coated lipases. The same enzymes were immobilized on celite. It was found that the catalytic behaviour of modified PPL and CCL was greatly affected by the origin of the enzyme.

-With free PPL and CCL, the conversion at 72 h reached 12% and 14%, respectively.

-With Surfactant coated PPL and CCL, the conversion at 72 h reached 50% and 07%, respectively. Surfactants are insoluble in aqueous media and most likely the lipase is adsorbed to the surfactant that works as a carrier material. According to this hypothesis, surfactant binds to hydrophobic areas surrounding the active site of the lipase, causing displacement of peptide lid covering the active site and promoting the interfacial activation of the enzyme. This may be a likely reason for higher activity of coated PPL in comparison to uncoated lipase.

-With immobilized PPL and CCL, the conversion reached 20% and 45%, respectively. It was shown that the lipase from *Candida cylindracea* has a surface with a very high hydrophobicity and hydrophobic interactions have probably a significant role in the adsorption process. This enzyme appears to be adsorbed easily on the porous support. in order to restrict its mobility which makes it accessible to reagents in solution continuously.

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Thermogravimetric Analyses of Russian Biomasses

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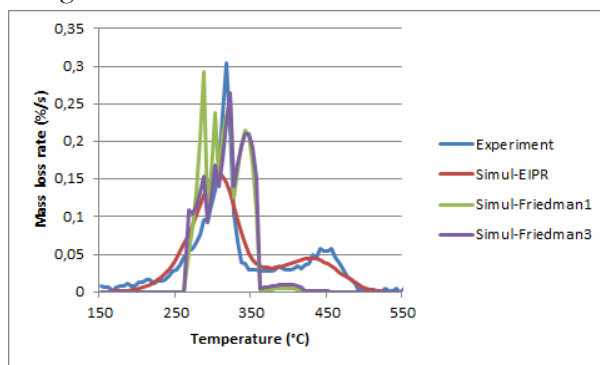
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The partial substitution of fossil fuels by carbon-neutral fuels such as biomasses is a promising way to reduce the environmental impact of fossil fuel utilization. Biomasses can supply around 14% of the world's energy consumption [1]. Co-firing coal and biomass is an option for converting biomass into power generation. In such a context, the operating parameters of the large size plants have to be optimized with models able to simulate biomass devolatilization and combustion which are the main thermochemical processes involved.

Many researchers throughout the world have already contributed to the determination of the kinetic parameters for different coals or biomasses, using different methods. The aim of the present contribution is twofold. First, we characterize the thermal degradation of biomasses and coals issued from Arkhangelsk region in the North-West of the Russian Federation. The thermal degradations of these biomasses or coals under inert atmosphere (pyrolysis stage) or under air (pyrolysis and combustion stages) are investigated in a thermogravimetric analyser. Modelling is performed using Friedman's isoconversional method [2], or an Extended Independent Parallel Reaction model [3]. Then we compare the values of the kinetic parameters obtained through these different tools.

Two functions have been tested in Friedman's method: Mampel's one $f(\alpha)=1-\alpha$ and the 3D diffusion one $f(\alpha)=1.5(1-\alpha)^{2/3}/(1-(1-\alpha)^{1/3})$. For the thermal degradation of pine trunk under air and for a temperature ramp of 10°C/min, we obtain the following mass loss rate curves



The values of the kinetic parameters obtained through the EIPR model are the following: $A_H=83717.3$ (s⁻¹), $E_{aH}=85000.0$ (J/mol), $A_C=5425548.9$ (s⁻¹), $E_{aC}=100000.0$ (J/mol), $A_L=11081.6$ (s⁻¹), $E_{aL}=92000.0$ (J/mol), $A_{char}=59999.977$ (s⁻¹), $E_{achar}=95000.0$ (J/mol). A measure of the errors between the experimental and simulated mass loss rate curves shows that the EIPR model is more performant than Friedman's method for the 3D diffusion function and for Mampel's function. Part of these results has already been exposed in [4].

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Biobased 3-hydroxypropionic acid through a new integrated process of glycerol bioconversion & membrane-assisted reactive extraction

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Within the actual transition from a fossil fuel-based to a bio-based economy, or bio-economy, the sustainable production at the industrial scale of bio-based polymer building blocks, such as 3-hydroxypropionic acid (3-HP, CAS number 503-66-2), is growing (1). 3-HP can be manufactured using petrochemical feedstock, but it is widely believed that biotechnology will provide a more sustainable route using renewable feedstocks (2). Nevertheless, to develop a robust biotechnological process, it is necessary to resolve technical issues, such as the inhibitory effect of the products. This can be obtained through integrated extractive bioconversion by which the product is continuously produced and recovered (3).

The integrated process targeted in this study includes 3-HP bioconversion from glycerol by *L. reuteri* and its reactive liquid-liquid extraction mediated by a hollow-fiber membrane contactor (HFMC). The HFMC aims to prevent the cells from direct contact with the organic phase while giving a high specific surface area without emulsifying. Moreover, a back-recovery step can be coupled to the extraction step with a second contactor to favor the mass transfer and get the product back in an aqueous phase.

First, a mechanistic study was performed to elucidate the inhibitory effects of 3-HP and of its metabolic intermediate 3-hydroxypropionaldehyde. Flow cytometry analyses highlighted the impact of these molecules on the cell physiological state: loss of membrane integrity and esterase activity. Regarding the extraction step, two extractants (trioctylamine and Aliquat 336) were used alone or in mixture, combined with three organic diluents (decanol, vegetable oil and oleyl alcohol). Mass transfer coefficients in the HFMC were determined in order to identify transfer limiting conditions. Results show interesting synergism for mixed extractants, giving high extraction performances over a wide range of pH, including the optimal range for bioconversion by *L. reuteri*. However, the performance of the whole process was shown to strongly depend on the coordination between the upstream and downstream operations in the quest for both extraction efficiency and biocompatibility.

To the best of our knowledge, this work reports for the first time a membrane based extractive bioconversion process for 3-HP production. These pioneering results represent a potential breakthrough towards the implementation of a robust and intensified biotechnological process at the industrial scale.

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Engineering cyanobacteria (microalgae) for the photoproduction of terpenes

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Thanks to their robust photosynthetic activity and powerful genetics, cyanobacteria (formerly termed blue-green algae) can be used for the production of commodity products (vitamins, food colorings, terpenes, etc) and biofuels (alcohols, alkanes, terpenes, etc) from nature's most plentiful resources: solar light, non-pure water, carbon dioxide (CO₂) and mineral salts ¹. We have a strong interest in terpenes because they are intensively used as flavoring agents and fragrances (many terpenes have a good smell), disinfectants (terpenes are cytotoxic) and nutraceuticals. Furthermore, in having a high energy density and a low-temperature-viscosity, terpenes can be blended with diesel to generate aircraft kerosene ².

Thanks to our long-standing expertise in cyanobacteria, we use a "synthetic biology" approach to engineer cyanobacteria for the carbon-recycling production of energy-dense terpenes. For this objective we are currently performing the following tasks

1) Introduction in cyanobacteria the (plant) genes encoding the missing terpene synthases enzymes. For this purpose we use our plasmid vectors that replicate autonomously in cyanobacteria, where they allow strong, constitutive or temperature-regulated, gene expression ^{3 4}. The temperature-control is advantageous, in allowing to decouple the production of biomass (at 30°C, the standard growth temperature) from the induction of terpene production (shift at 34-39°C where natural cells grow well). Such a separate production of biomass and biofuel should also limit the genome instability of biofuel producing strains, due to the positive selection of spontaneous mutations interfering with biofuel production to escape biofuel toxicity ⁵.

2) Increase the cyanobacterial tolerance to terpenes that are cytotoxic.

3) Combine terpene production and terpene tolerance in the same strain.

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Reactive extraction of bio-based 3-hydroxypropionic acid: towards an integrated process of a membrane-assisted extractive bioconversion

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3-hydroxypropionic (3-HP) is a promising building-block for renewable polymers and chemicals like acrylic acid, acrylates, acrylamides and bioplastics. As such, it has been referred by the DoE as one of the “Top 10” value-added chemicals to produce from biomass (1). A large variety of bio-sourced substrates to feed biotechnological processes have been investigated successfully to produce 3-HP like glycerol for wild strains or glucose, xylose and even CO₂ for genetically modified micro-organisms (2,3). However, rather low product concentration and productivity have been observed due to strong inhibitions from 3-HP and other metabolites, for example for glycerol bioconversion with *L. reuteri* (3). A solution to overcome this problem is called *in situ* product recovery. It consists in removing the product from the bioconversion broth while it is produced.

The process we chose is the reactive liquid-liquid extraction assisted by a hollow-fiber membrane contactor. Very hydrophilic acids such as 3-HP cannot be recovered efficiently through simple liquid-liquid extraction without using a huge amount of solvent. The aqueous phase containing 3-HP is then brought into contact with an organic phase containing a hydrophobic aliphatic amine. Both molecules can selectively interact with each other through acid-base interactions leading to the formation of a complex mainly soluble in the organic phase. The use of a micro-porous membrane between the two phases keeps the micro-organisms away from the organic phase potentially avoiding a high toxicity and stabilizes the interface preventing both phases from mixing and emulsifying while providing a high specific surface area when compared to traditional processes.

Several reactive liquid-liquid extraction assisted by a hollow fiber membrane contactor have been performed and parameters like the nature of the solvent and the concentrations of the aliphatic amine and 3-HP have been tested. We provide equilibrium and kinetics results and propose a chemical model taking into account the complex formation, the influence of the solvent, the acid dissociation, the acid partitioning between the two phases and the leak of amines in the aqueous phase to predict extraction yields. This is the first step for a deep understanding and the implementation of an integrated process of extractive bioconversion for 3-HP production from biomass.

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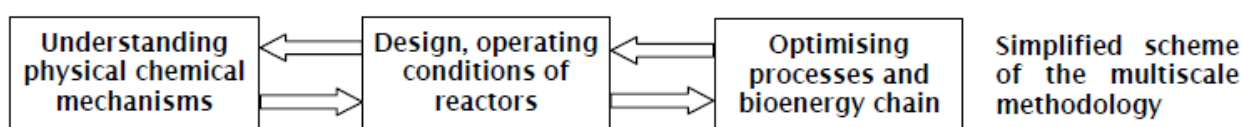
Current research on thermochemical conversion of biomass at the CNRS-Nancy

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This poster will give an overview of current research developed at CNRS-LRGP Nancy (France) on the thermochemical conversion of lignocellulosic biomass. The main studied processes are pyrolysis and gasification to produce electricity, biofuels intermediates or value-added chemicals such as aromatics. A multiscale methodology is developed ranging from molecular to bioenergy chain scales.



The studies at molecular and mesoscopic levels give insight into the mechanisms of biomass pyrolysis and are used to design reactors. Conversely, the detailed mass and energy balances of processes point out process units with low energy efficiency and/or high environmental impact and stress the improvement of reactors and the need of more fundamental knowledge.

The methodology will be highlighted by some examples:

1. At the molecular scale, the chemical mechanisms of biomass pyrolysis are studied by various complementary methods such as NMR [1], calorimetry and mass spectrometry [2, 3].
1. At the mesoscopic and particle scales, the mechanisms of biomass pyrolysis are studied by in-situ NMR and rheology [4]. The extent of softening during biomass pyrolysis and interactions in the polymer network are revealed by these in-situ analyses. Advanced mass spectrometry is also used to analyse tar/bio-oil on-line or after condensation [5, 6]. The conversion of particles of biomass is modelled with lumped kinetics coupled to mass and heat transfer models [7, 8].
2. The results from particle scales are used to improve the pyrolysis/gasification reactors [9, 10].
3. Models of pyrolysis and gasification processes are developed under Aspen Plus [11]. Detailed mass and energy balances are obtained including pollutant emissions (trace species such as tar, NO_x, minerals, etc.). The effect of catalysts and reactor operating conditions are modelled [12]. These models point out the key process units and parameters detrimental to the energy and environmental efficiency.

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Tandem Synthesis of Alternating Polyesters from Renewable Resources

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The vast majority of commodity materials are obtained from petrochemical feedstocks. These resources will plausibly be depleted within the next 100 years, and the peak in global oil production is estimated to occur within the next few decades.¹ In this regard, **biomass** represents an abundant carbon-neutral renewable resource for the production of polymers. Generally, aliphatic polyesters are obtained by either polycondensation or ring-opening polymerization of cyclic esters.² The latter route restricts the polymer architectures to those of the cyclic esters that are available. Although the nearly unlimited choice of diols and diacids gives access to a much larger range of polymer properties, their direct use in polycondensation reactions is energy intensive and requires drastic conditions to drive the reaction towards high conversion and very accurate comonomer stoichiometries to obtain high-molecular-weight products. In this overall context, organic acids have been suggested as important **renewable** building blocks because they are available in a minimum number of steps from biorefinery carbohydrate streams. We have initiated a research effort to synthesize aliphatic polyester via an auto-tandem catalytic transformation where ‘activated’ monomers (that is, cyclic anhydrides) are synthesized from dicarboxylic acids and subsequently copolymerized with epoxides (Figure 1).^{3,4}

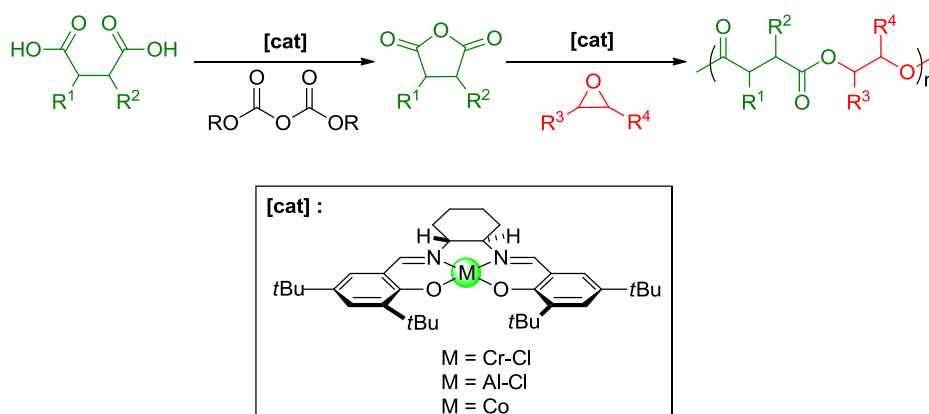


Figure 1 - Tandem synthesis of polyesters from epoxides and dicarboxylic acids.

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Synthesis of starch esters and ethers

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The observed decrease of the non-renewable resources and the environmental impact of the derived materials give a growing interest to the utilisation of biomass as raw materials for new materials. Starch is a naturally occurring polymer of D-glucose found in a large variety of vegetables. It is one of the most in-view biopolymers of interest for the replacement of the petrol based resources because of its low cost and its non-toxicity. In addition, it is renewable and can be modified. As native starch cannot be used because of its poor mechanical properties and its high hydrophilicity, it must be modified in order to give it thermoplastic properties.

To this end, researches have been conducted, for example, on the creation of starch esters and ethers. Several methods were studied, enhancing the utilisation of the reactants and eco-compatibility of the different synthetic routes. Hence, there is a significant state of the art concerning the synthesis of these derivatives.

In this context, we are studying starch derivatisation in order to create ethers and esters of this biopolymer. Ether-like and ester-like derivatives with different kinds of substituents and with various degrees of substitution were obtained.

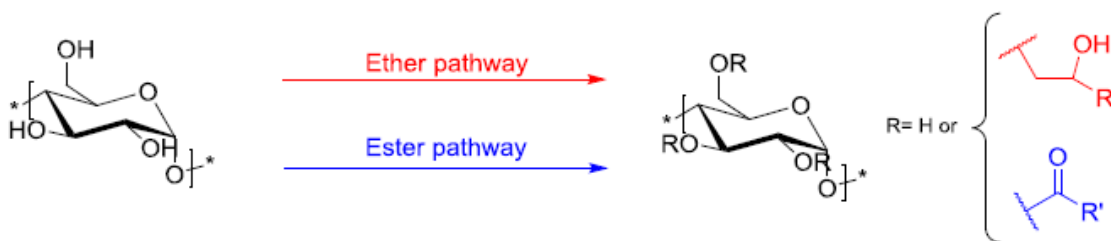


Figure 1: synthesis of starch ethers and esters

Subsequent physicochemical studies of the obtained derivatives allow us to apprehend their thermoplastic character.

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From biomass to functionalized terpyridines.

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Functionalized 2,2':6',2''-terpyridines (terpy) molecules (figure 1) are ligands which can form complexes with a broad range of metals. By varying the metal and the substituents onto the terpy scaffold, a huge number of different molecules can be prepared, with various possible applications ranging from catalysis to medicinal and polymer chemistry just to name a few [1,2].

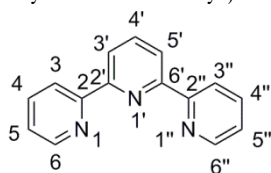


Figure 1 : molecular structure and atoms-numbering of the terpy motif.

Aldehydes are valuable starting materials for the preparation of terpy [3,4]. This communication will show how furfural derivatives (figure 2), which can be isolated from biomass, can be used for the fabrication of terpyridines with greener procedures [5,6].

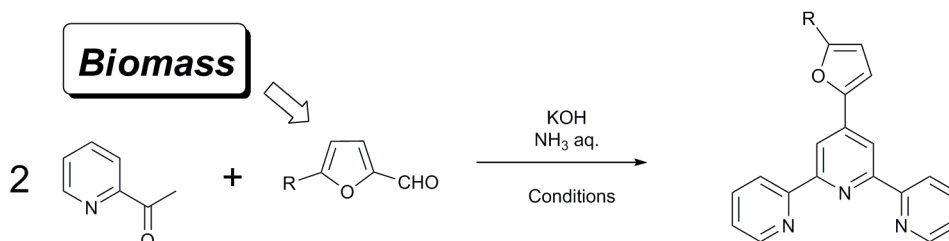


Figure 2: synthesis of terpyridines from furfural derivatives.

Some applications of these terpyridines in Dye-Sensitized Solar Cells, or in the preparation of new bioactive metal-complexes will be presented.

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Silica-supported biosorbents for sorption of metallic ions from aqueous solution

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Submicronic particles, functionalized by grafting or by encapsulation with bio-polyelectrolytes, open potential applications in applied sciences and diverse industrial sectors (use as composite coatings, as adsorbents, as water purification materials...).

Organo-mineral composites allow combining the properties of a mineral skeleton with the chemical reactivity of the organic functions present in abundant and low-cost biopolymers such as chitosan. The aims of this research are (i) to functionalize and characterize submicronic composites by grafting or encapsulating colloidal silica (Figure 1) and (ii) to study the capacities of these hybrid materials for the adsorption of divers divalent metal ions from aqueous solutions.

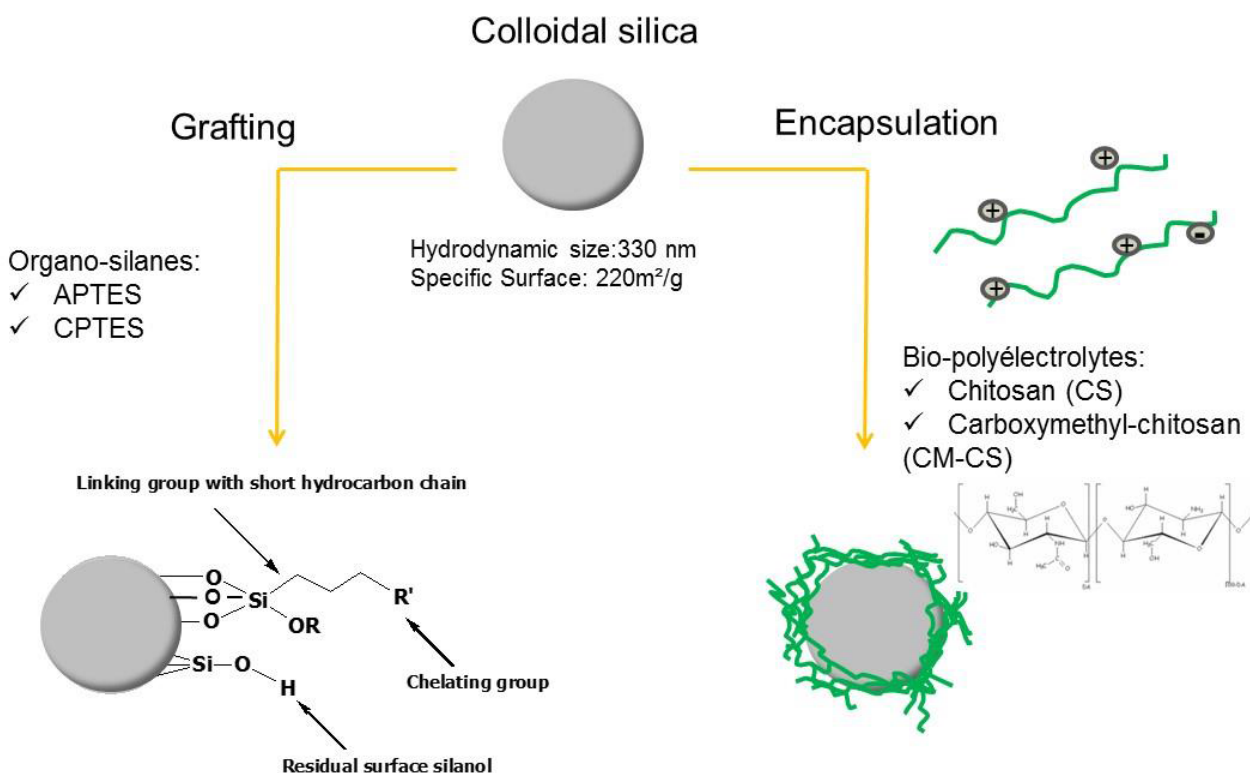


Figure 1: Functionalization of silica particles

The composition and physicochemical properties of these materials were characterized by means of elemental analysis, nitrogen adsorption-desorption and FT-IR spectroscopy. The analytical data confirm the successful grafting of the biopolymers CS and CM-CS on colloidal Aerosil 200 silica.

Nickel ion, Ni²⁺, was chosen as model for divalent metal ion to evaluate the effectiveness of the new sorbents for wastewater treatment. The influence of hybrid particles doses, buffer pH, contact time and nature of the counter ion was assessed through batch experiments. The results point out a high capacity of the hybrid particles to complex Nickel (> 200mg.g⁻¹ of sorbent). The best interpretation for the equilibrium data is given by the Sips and Redlich-Peterson isotherm models. The adsorption kinetics follow the mechanism of the pseudo-second-order equation for the systems studied.



Valorization of *Luffa Cylindrica* and *Phragmite Australis* biomass as adsorbents for removing Metal-Complexed dyes

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The effluents from different industries such as textile industries are generally highly colored and can be considered as an important source of water pollution [1,2]. Dyes usually have synthetic origin and complex aromatic molecular structures which make them more stable and resistant to light, water, soaps etc. and relatively non-biodegradable [3,4] Consequently, remove of textile dye effluent is becoming an obligation both environmentally and for water re-use. The main objective of this study is to evaluate the potential of cellulosic fibers of highly available and renewable Tunisian biomass *Phragmites australis* and *Luffa Cylindrica* for the biosorption of an anionic metal complexed dye: Alpacide blue.

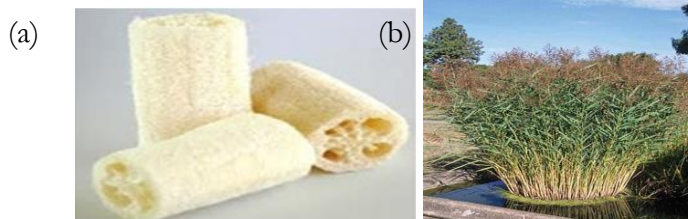


Figure 1: (a) *Luffa Cylindrica*; (b) *Phragmite Australis*

The present study shows that the *Phragmite Australis* and *Luffa cylindrica* fibers were applied successfully for the biosorption of Alpacide blue from aqueous solution. Optimal parameters for maximum quantity of absorption dye was achieved after 5 h for *Phragmite Australis* and 2 h for *Luffa cylindrica* fibers of treatment in batch system using an initial dye concentration of 20 mg/L, a mass of 0.5 g of *Phragmites australis* fibers, pH 2 and a granulometry size between 250 and 500 μm . In these conditions; the quantity of dye retained is 6.11 mg/g and the retention rate is 85.9 % for *Phragmite Australis* and 2 mg/g and the retention rate is 78 % for *Luffa cylindrica*.

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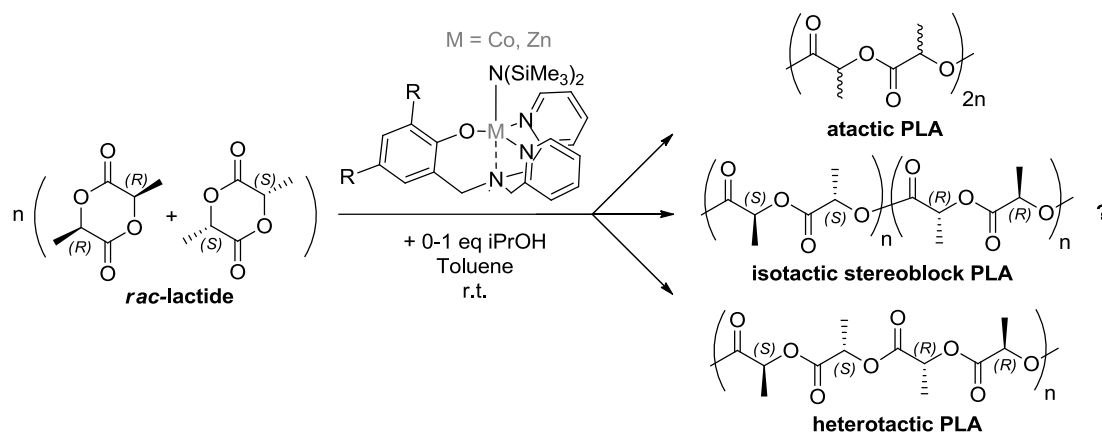
Synthesis and characterization of cobalt- and zinc-based catalysts for the selective Ring Opening Polymerization of *rac*-lactide

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Pioneered in 1932¹ and popularized during the 70's for medical applications, there has been a growing interest in the academic field for the synthesis of polyesters by Ring Opening Polymerization of dilactones², along with the development of new biodegradable and/or **bio-sourced** plastic materials in the industrial sector. Despite the discovery of well-described very efficient organometallic systems, new challenges need to be addressed: among them, new families of organometallic complexes and organocatalysts, utilization of less expensive/toxic metals³ or, recently, studies of stereoselectivity switch systems⁴. Beyond productivity or stereoselectivity aspects, the reactivity of catalytic systems toward different monomers is also extensively studied in order to achieve copolymers with unique properties. The work presented here will cover some properties of Co^{II} and Zn^{II} organometallic catalysts based on tripodal ligands⁶, for the selective Ring Opening Polymerization of *rac*-lactide.



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Photopolymerizable Synthons From Fatty Acids and Glycerol Derivatives

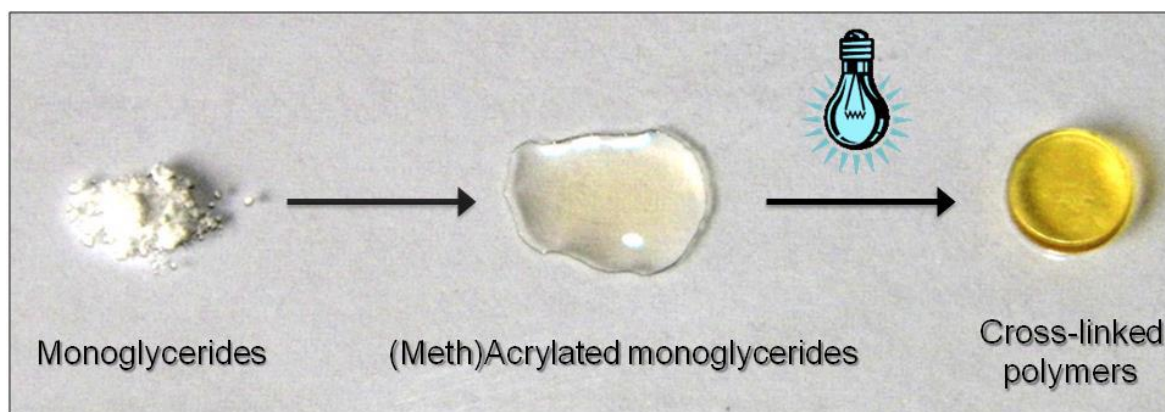
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The use of renewable resources for the synthesis of bio-based polymers is a current and growing challenge [1]. In this context and in the course of our ongoing studies in Glycerol Chemistry [2] and Green Polymerization [3], we report the synthesis of photopolymerizable bio-based monomers according to a two-steps procedure. The first one consists in the synthesis of monoglycerides of high purity, obtained by condensation of fatty acids with either glycerol carbonate or glycidol, in a solvent-free medium and in the presence of tetrabutylammonium iodide (TBAI) as organocatalyst. The obtained bio-based monoglycerides were modified in the second step by reaction with acryloyl and methacryloyl chloride leading to a series of new diacrylated and dimethacrylated monomers. Photopolymerization investigations monitored by infrared spectroscopy were achieved under ultraviolet radiation in the presence of a photoinitiator. The role played by the concentration of photoinitiator, the intensity of irradiation, and the nature of monomers were investigated. Thermal gravimetric analysis, gel content determination, tests of swelling and analysis of the pendulum hardness were also performed on the resulting bio-based photopolymers [4].



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Polysaccharide and lignin modification using reactive extrusion

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The presented project involves developing new chemical modification methodologies using the intensive and ecologically compatible characteristics of reactive extrusion [1-3] applied to polymers from biomass. With the prospect the exhaustion of worldwide oil supply, the use of renewable natural polymers as potential substitution candidates for oil based application polymers appear as a sustainable alternative. Natural polymers possess physicochemical properties in their native state, which limit their use in many industrial sectors. Even limited chemical modifications radically change the properties of these macromolecular entities. Chemical modifications commonly performed at industrial-level production in solution or in batches [4] are often laborious and difficult to monitor, and in addition, suffer from energy cost and environmental issues caused by co-products. The project aims at studying and developing the composition parameters (polymers, plasticizers, reagents and so on), and secondly, examining the operating conditions of the chemical modification carried out in an extruder: hydration rate, pressure and temperature kinetics and other parameters with reactions of specific modifications to meet the requirements of industrial applications. Three families of biopolymers of interest to large sectors of biorefineries are being studied: starch, lignin and cellulosic derivatives.

In a given example, carboxymethyl starches (CMS) with various degrees of substitution (DS) were synthesized in one step and with high levels of reaction efficiency (RE) using reactive extrusion processes. The influence of etherification reaction parameters and the extruder screw geometry on DS, RE, crystallinity as well as the viscosity of 1 wt.% of aqueous solution was determined. The kinetics of the reaction were studied using the loop mode of the laboratory extruder, which allow to vary the residence time of the melt. The distribution of the carboxymethyl functions on the different positions of the glucose monomer in the polymer were analyzed by high resolution NMR spectroscopy. Current results are being applied to larger machines in order to further transfer the reactive extrusion parameters to a scale closer to the industrial production requirements.

Key words: biomass, reactive extrusion, chemical modification, carboxymethyl starch

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Green Chemistry and Industrial Biotechnology for the Production of Biobased Chemicals

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To enable a paradigm shift from fossil- to biobased economy, biomass as industrial feedstock, there is a need to develop alternative “green”, energy- and cost-efficient technologies for transformation of biomass to chemicals, materials and fuels. Research at Lund University encompasses the development of sustainable and innovative processes based on green chemistry and industrial biotechnology for the production of biobased chemicals and polymers. Industrial biotechnology makes use of microorganisms and their enzymes as catalysts for the chemical transformations, and fulfills most of the green chemistry principles. We have developed efficient processes for the production of C3 platform chemicals, 3-hydroxypropionaldehyde (3HPA), 3-hydroxypropionic acid (3HP) and 1,3-propanediol (1,3PDO), from glycerol using *Lactobacillus reuteri* as the biocatalyst. 3HP has further been converted to acrylic acid by integrating catalytic dehydration using titanium dioxide as a green catalyst. We have further transformed the platform chemicals to useful products for the chemical- and allied industries, e.g. polyols to cyclic carbonates by lipase-catalyzed transesterification, and to hydroxyl-carboxylic acid by selective oxidation using *Gluconobactor oxydans* and *Corynebacterium* sp.

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Pd/C Catalysed Transfer Hydrogenolysis of Lignin

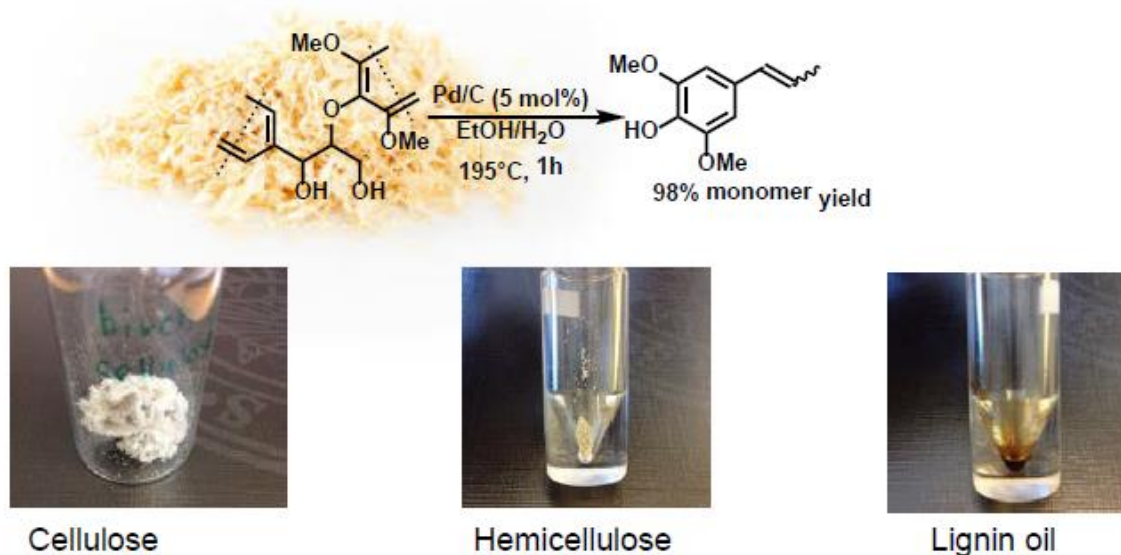
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A mild, heterogeneous Pd/C catalysed transfer hydrogenolysis of lignin models and organosolv lignin by formate to produce aryl ketones, alcohols, or alkyls is presented.¹ The reactions proceed under air in green solvents to give the products in excellent yields. Also, a transfer hydrogenolysis has been performed in tandem with an organosolv pulping process to generate propenyl aryls in which hemicelluloses in the wood acts as a hydrogen source (Scheme 1).²

A mechanistic study support that the reaction proceed through an initial dehydrogenation to generate a dimeric/polymeric ketone. The palladium with hydrogen inserts into the enol form of this ketone followed by a reductive cleavage.³

We have also started a company, RenFuel, that is valorizing precipitated lignin from the kraft pulping to a green diesel.



Scheme 1. Tandem organosolv pulping and transfer hydrogenolysis of wood to give propenyl aryls.

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High Pressure Rapid Heating Displacement Reactor; A novel tool for simulating innovative pretreatment schemes

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Conventional laboratory biomass pretreatment reactors in biochemical conversion are often limited by long heat-up times, low maximum temperature levels (<200°C) and no possibilities for displacing pretreatment liquors at high temperatures or pressures. As a consequence, these laboratory reactors are unsuitable for developing modern industrial pretreatment processes which involve rapid heating and displacement of dissolved substances at elevated temperatures and pressures.

As part of the Norwegian Biorefinery laboratory (NorBioLab) infrastructure, a novel laboratory pretreatment reactor has been designed by PFI aiming to overcome the obstacles of conventional laboratory pretreatment reactors. The reactor is termed *High Pressure Rapid Heating Displacement Pretreatment Reactor* and will be in operation at PFI during 2016.

Key characteristics for the reactor include:

- *Rapid heating:* Very rapid heating (approx. 30°C per min) using preheated oil as heating medium and preheating of cooking liquors in a heat exchanger before introduction into the reactor chamber.
- *Displacement of dissolved substances at elevated temperatures and pressures:* The reactor design allows exchange of cooking liquid at high pressure/high temperature.
- *High pressure system:* Maximum operating pressure is 50 bars.
- *Suitable for organic solvents:* ATEX approved.
- *Proper mixing:* Circulation of cooking liquid.

The High Pressure Rapid Heating Displacement Pretreatment Reactor will be a unique tool for developing new pretreatment and separation processes for biochemical conversion of biomass. In particular, innovative developments are foreseen with respect to the following novel pretreatment developments:

- Selective extraction of lignin by organic solvents or sulfite based pretreatment processes at high temperatures and/or pressures.
- Selective extraction of hemicelluloses by super critical extraction at high temperature/short retention times.

The High Pressure Rapid Heating Displacement Reactor is part of the Norwegian Biorefinery Laboratory (NorBioLab) Infrastructure, funded by the Norwegian Government through the Research Council of Norway. The reactor is owned and operated by PFI, located in Trondheim Norway.

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Chemical modification of lignocellulosic materials

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At the department of Chemistry and Chemical Engineering there is research on the valorisation of lignocellulosic materials. There are projects on the preparation and functionalization of nanocrystalline cellulose. Traditionally Nanocrystalline cellulose is prepared by acid hydrolysis of cellulose sources, we are looking at the use of acid catalysts reactions that would lower the acid content as well as reducing the volume of solvents used in the process. The formed nanocrystals are further developed towards specific material properties by chemical modification or addition of nano aggregates of ion clusters. These materials have been used for controlled drug release and currently their optical properties are investigated.

Other research field is to obtain high-value products from agricultural residues. In of the project we are extracting hemicellulose and cellulose from barley husk. The extraction method is optimized to get high yield of hemicellulose and also a cellulose fraction that is good enough to be used as source for the production of nano crystalline cellulose. The isolated hemicellulose is chemical modified to give it properties that make it possible to make foam by extrusion. A challenge in the project is to perform extraction and chemical modification on kilo-scale volumes. As complementary projects we are making model compounds of the lignocarbohydrate complexes, LCC and look at the dissolution and generation of cellulose. The model compounds are used as reference material for identifying LCC bonds in material from the extraction processes and as substrates for finding enzymes that cleaves LCC bonds. For the dissolution and generation of cellulose we are using ionic liquids and salts.

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Biomass valorization: Process Safety & Intensification

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LSPC (*Laboratoire de Sécurité des Procédés Chimiques*) is a chemical engineering laboratory located in Rouen with approximately 15 permanent members and 10 PhD students. The research activities of the laboratory are mainly focused on process safety, process intensification (essentially microwave technology) and biomass valorization.

Biomass valorization processes can be difficult to predict from a thermal and kinetic viewpoint due to presence of multiphase reactor system and multiple reactions. Furthermore, some exothermic reactions could occur and the process can present some thermal safety issues. For that reason, we have developed the following strategy:

1. Determine the **safety criteria** (adiabatic temperature rise, pressure rise and time-to-maximum rate) of a reaction system by using different calorimetry and microcalorimetry tools such as Accelerating Rate Calorimeter (ARC), Advanced Reactive System Screening Tool (ARSS), Tian-Calvet calorimeter (Setaram C80) and DSC. The goal is to obtain the safe operating conditions by using small sample amount.
2. Estimate the **kinetic and thermal parameters** of such processes by using numerical methods and the reaction calorimeters like RC1 Mettler Toledo.
3. When the safety criteria and kinetic and thermal parameters of a biomass valorization process is known, the process intensification stage and process simulation stage can start.

This approach has been done on different processes: epoxidation and carbonation of vegetable oils (1-5), levulinic acid valorization and continuous reactor (5-7) and biomass pyrolysis/gasification which has started this year.

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Norwegian Biorefinery Laboratory (NorBioLab); Establishing the Tools for Developing Tomorrow's Biobased Society

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The Norwegian Biorefinery Laboratory (NorBioLab) is a **national infrastructure for biorefining**, accessible to national and international stakeholders for the development of processes for the sustainable conversion of Norwegian land and marine based biomass to novel, environmentally benign biochemicals, biomaterials and bioenergy products.

Through the establishment of NorBioLab we aim to:

- Establish a unique laboratory infrastructure for biomass conversion
- Be the national fundament for developing environmentally friendly processes and products
- Position the research partners at an international level
- Stimulate both national and international industries, researchers and students to use the infrastructures
- Position Norway as an attractive R&D partner in international research projects

The NorBioLab project was established in 2014. The project is included in the Norwegian Roadmap of Research Infrastructures, listing prioritized national infrastructures that are considered the most strategically important investments in Norwegian research. The national research infrastructures are funded by the Norwegian Government through the Research Council of Norway.

NorBioLab gathers central Norwegian stakeholders in the biorefinery area, and unites existing and new research infrastructures and national competence, allowing for internationally leading research on new, innovative biorefinery processes. NorBioLab is headed by PFI, in close collaboration with The Norwegian University of Science and Technology (NTNU), The Norwegian University of Life Sciences (NMBU) and SINTEF.

Through NorBioLab a number of novel research tools are being established, complementing existing infrastructures. The aim is to establish flexible units that can be applied to different raw materials and that can address a large variety of processing schemes; both for biochemical and thermochemical biomass conversion (see Figure 1).

NorBioLab aims to have all research infrastructures installed by end of 2016. Some are already in use. The NorBioLab project, involving also the use of the installations, will last until 2021, but the intention is that the infrastructure user phase will last far beyond this.

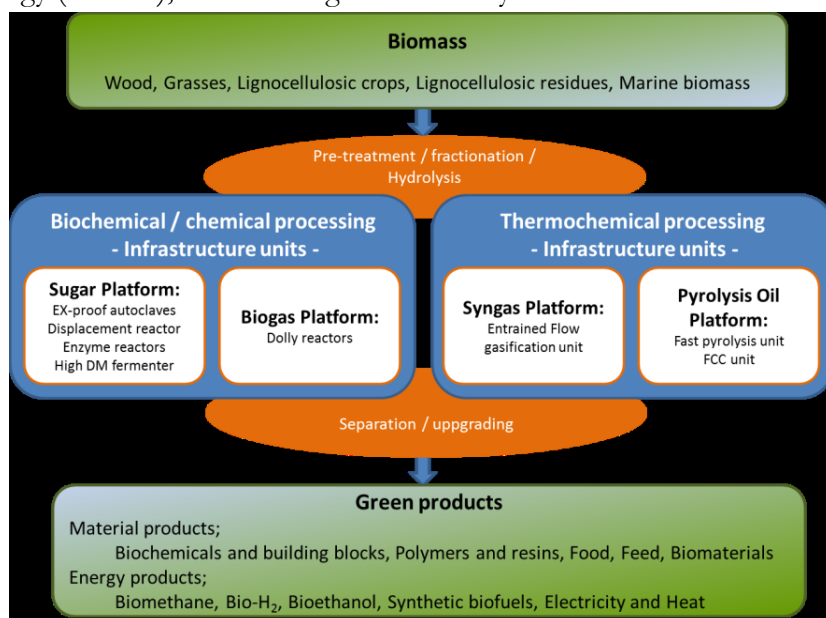


Figure 1. The NorBioLab Infrastructure Project layout.

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