ABSTRACTS

5th Latin American Congress on

Biorefineries

From laboratory to industrial practice

January 7-9, 2019 - Concepción, Chile

5th Latin American Congress on Biorefineries

From laboratory to industrial practice

January 7-9, 2019 - Concepción, Chile

ORGANIZED BY

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The mission of the Scientific and Technological Bioresources Nucleus BIOREN (University de La Frontera, Chile) is to strengthen multidisciplinary research and development in biological resources and bioprocesses associated with food production, environmental sustainability and human health; and further, to strengthen education, dissemination and outreach in the field of bioresources. BIOREN has a multidisciplinary research team including chemists and biochemists, molecular biologists, cellular biologists, microbiologists, agronomists, chemical and biochemical engineers, and medical and biomedical scientists to develop innovative products from biological resources and bioprocesses which can be introduced by industrial partners for the production of useful bio-compounds.

BIOTECHNOLOGY CENTER UDEC

The Biotechnology Center is a regional center for R+D+i focused on five main research areas: Forest Genomics; Second generation biofuels; Aquaculture Biotechnology; Environmental microbiology; Phytochemistry. Much of this research, particularly in forestry and biofuels, fits on the Bioeconomy concept, a sustainable approach seeking a better use of renewable resources.

UDT

UDT was inaugurated in 1996 as a specialized organization within the University of Concepción dedicated to science, technology and innovation. Since 2008 the UDT has been recognized by CONICYT, within the framework of its Basal Funding Program, as one of the thirteen centers of excellence in Chile.
The UDT approaches the development of knowledge in the field of forest biorefineries understood as a set of technological processes that generate valuable products from lignocellulosic raw materials. It has good analytical and laboratory facilities, as well as a wide range of pilot plants, whose combination can produce proof-of-concept results at demonstration scale.

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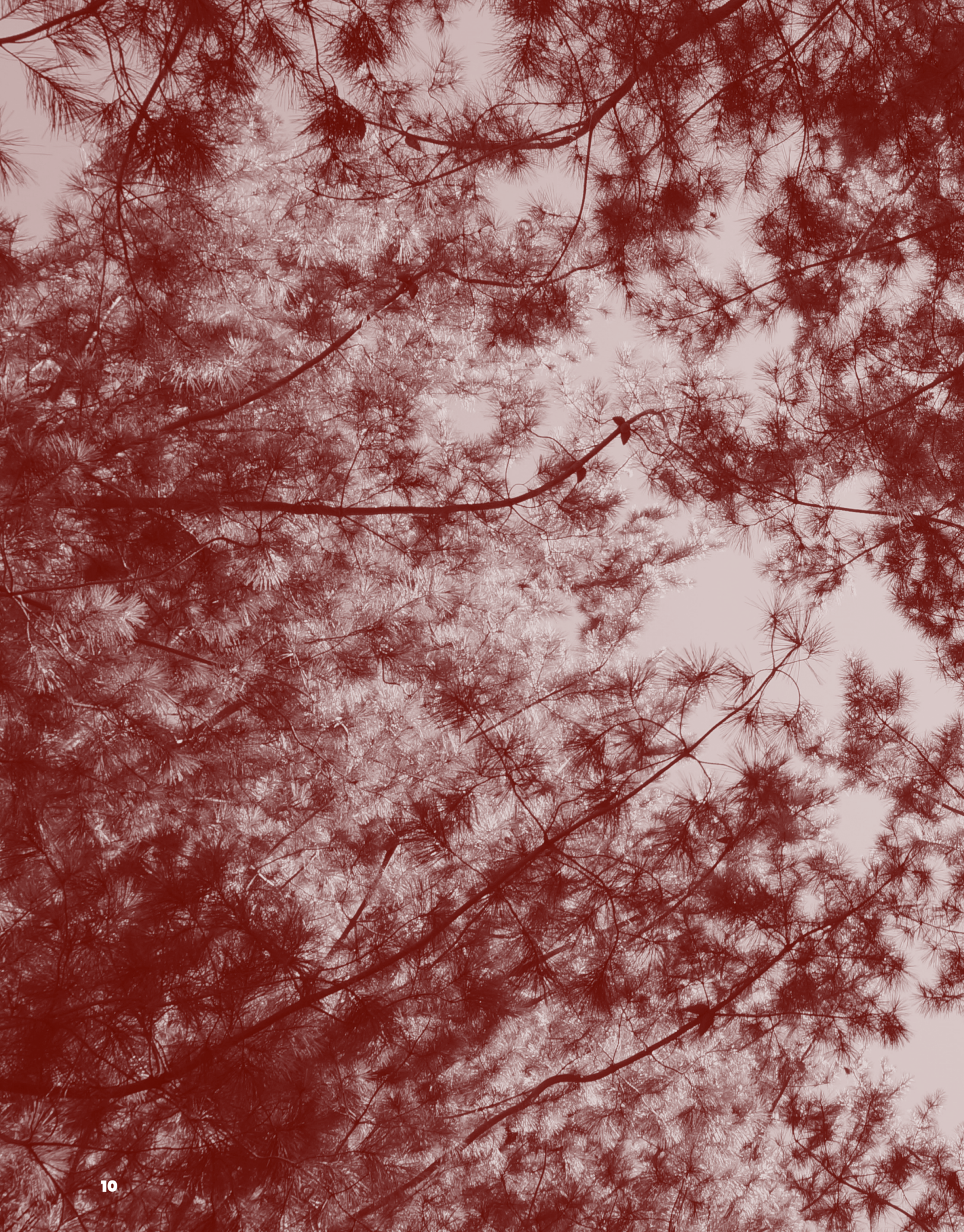

KEYNOTE SPEAKERS

PLENARY SESSIONS

EDUARDO FALABELLA SOUSA-AGUIAR
FEDERAL UNIVERSITY OF RIO DE JANEIRO, BRAZIL

Prof. Eduardo Falabella Sousa-Aguiar, Chemical Engineer, MSc, DSc, has 40 years experience in the field of catalysis and catalytic processes. He has worked in the Federal University of Rio de Janeiro for 38 years, where he is currently Full Professor of the Department of Organic Processes. He has also been a Senior Advisor in Petrobras Research Centre (CENPES), where he was the manager of the XTL cell, a group devoted to the development of XTL technologies in Petrobras.

He has been involved in many research projects and activities and spent quite some time as member of the team that has transferred the technology of cracking catalysts from AKZO Nobel to FCCSA. He has also worked some time as a research fellow in the AKZO Research Centre in Amsterdam, in the University of Brunel, UK, in the Technical University of Vienna and in the Texas Ketjen Plant in Houston, USA.

Prof. Falabella is a prolific writer and has authored over 300 scientific papers, two books and several patents. He has also advised over 40 MSc and PhD theses. He has been the focal point in Brazil for the international program CYTED, subprogram “Environmental Catalysis”. In 2011, as recognition of his contribution to the Catalysis Community, he was invited to become a member of the Scientific Committee of ICS-UNIDO. Also, in 2010, he was elected a member of the Council of the prestigious International Zeolite Association, being the first South American to occupy such position.

He has been awarded several times, deserving special attention the Plinio Cantanhede Award, in 1994 (the best scientific contribution to the Brazilian oil and Petrochemistry Industry), the Governador do Estado Award, in 1998 (the best international patent) and the Golden Retort, in 2000, for his contribution to Brazilian Catalytic Community and Life Achievement. Moreover, he was given in 2005 the award “Catalysis and Society”, for the creation of the Brazilian Network on Chemical Transformation of Natural Gas. In 2008, he was given the prestigious Brazilian National Technology Award for his developments in the field of dimethyl ether. In 2012, he was the recipient of the James Oldshue Award of the American Institute of Chemical Engineers for his contribution to the development of Chemical Engineering in Latin America. Finally, in 2014, he has received the FISOCAT Award, as senior investigator. In 2016, he has been nominated Honorary Professor of the China University of Petroleum. He is frequently invited as speaker in many congresses and seminars. Indeed, he has been plenary lecturer in international congresses in 21 countries.

ABSTRACT

BIOMASS CO-PROCESSING IN EXISTING REFINERIES: THE FUTURE OF REFINING

EDUARDO FALABELLA
FEDERAL UNIVERSITY OF RIO DE JANEIRO, BRAZIL

The survival of the oil industry will depend on many factors. Indeed, the refiner of the future will have to face multiple challenges. Among such challenges, the following ones deserve special attention.

- Increasing stringent environmental regulation
- Growing demand for cleaner fuels
- Globalisation
- Increase in the production of derivatives from declining quality oil
- Uncertainty about the consumer's choice
- Growing pressure of several segments of the society aiming at the reduction of GHG
- Maintenance of its profitability.

The refinery must search for intelligent alternative solutions to meet all those requirements. The search for alternative feedstock such as biomass has become a must in order to cope with more stringent regulations. Also, alternative refining routes such as synthetic fuels are striking back.

The concept of Integrated Biorefinery must be applied. An integrated biorefinery is capable of efficiently converting a broad range of biomass feedstocks into affordable biofuels, biopower, and other bioproducts. The integrated biorefinery must cope with the problem of residues.

Integrated biorefineries imply the use of innovation, or rather, new chemical routes must be developed in order to reduce costs, improve competitiveness and, above all, explore the potential of residues. Furthermore, aiming at having a better utilisation of the existing facilities, co-processing is often indicated.

In the present work, one discusses co-processing of different types of bio-oils, resulting from both catalytic and non-catalytic pyrolysis of lignocellulosic biomass. Bio-oils can undergo processing in different units of the refinery, hence different schemes of co-processing will be assessed. Since the problems of co-processing bio-oils are often related to the instability thereof, bio-oils stability will be also discussed.

PLENARY SESSIONS

LUDO DIELS
FLEMISH INSTITUTE FOR TECHNOLOGICAL RESEARCH (VITO), BELGIUM

Prof. Ludo Diels, Dr. in chemistry & biotechnology, works at the University of Antwerp, and is research manager Sustainable Chemistry for the Flemish Institute for Technological Research (VITO) in Mol, Belgium.

During 15 year he managed the Environment and Process Technology Business Unit and is now responsible for the transition toward sustainable chemistry and clean technology. He is responsible for the organisation of collaboration with the academic and industrial world and for co-financing projects. He coordinated and is involved in many international research projects. Ludo Diels is strongly involved in the set up of a biobased economy in Flanders.

He is also responsible for the collaboration between VITO and India and he is managing the creation of a road map and Strategic Research Agenda for R&D on biomass and biowaste between India and Europe. He is a founding father of the Shared Research Centre on Bio-aromatics (BIORIZON) between the Netherlands and Flanders. He is also founder and Flanders coordinator of the BIG-C trilateral alliance between Flanders, the Netherlands and NordRhein Westfalia (Germany), focusing on a border denying collaboration for the chemical industry with focus on waste gases and biomass as renewable resources. He is case leader for bio-aromatics in the Vanguard Initiative, pilot Bio-economy, leading to smart specialisation of interregional collaboration.

Process intensification and the partial replacement of fossil based resources by biomass-based and renewable resource form the basis for the Sustainable Chemistry Development. The integration of waste (including also waste gases as CO2 and H2) and wastewater management and technologies are key in the development of a sustainable World. In this way he also was on the basis of the ANDICOS™ concept, a combined waste and wastewater treatment system leading to reduced energy consumption in water treatment and production. He is the chairman of the working group FEED in the Energy and Resources (PPP-SPIRE between 8 industrial sectors and the European Commission) and member of the SPIRE-BBI working group.

ABSTRACT

BIOBASED AROMATICS – CHALLENGES, HURDLES AND OPPORTUNITIES

LUDO DIELS
VITO (FLEMISCH INSTITUTE FOR TECHNOLOGICAL RESEARCH) & ANTWERP UNIVERSITY, BELGIUM

Aromatics are among the most important resources for the chemical industry. Many materials are made from aromatics and lead to higher or better performance. Brand owners are on the search for more sustainable molecules (e.g. bio-based). But also the introduction of higher performance and safety issues can be seen as the most important driver for this development.

Currently virtually all aromatic building blocks are made from fossil oil. This presentation is anticipating the expected growing shortage of aromatics from the petrochemical industry and the widely shared ambition to green the chemical industry. On top of that one of the main drivers is to develop innovative molecules that are safer and more performing.
This lecture will give an overview of the problems linked to wood-based refineries and the availability of lignin sources. Next, it will give an overview of the different approaches worldwide to valorize lignin and to produce bio-based aromatic molecules. It will indicate the hurdles, challenges and needs for value chain approaches.

A nice example in integrated approach is the The Shared Research Center, Biorizon. Biorizon, an initiative of TNO, ECN, VITO and the Green Chemistry Campus, develops technologies to produce aromatics derived from plant-based (waste) streams. Biorizon brings together global leaders (large industry and SMEs) in the fields of feedstock, conversion, equipment, building blocks, materials and end-products. Biorizon aims to be a world leader in the development of biobased aromatics to provide the chemical megacluster around the Netherlands, Flanders (Belgium) and Nordrhein Westfalia (Germany) with innovative, sustainable building blocks leading to many different applications in the products marketed by brand owners and small companies. The objective is to make commercial production feasible for industrial partners by 2025 at the latest.

Biorizon utilizes plant-based streams such as wood or its fractions lignin and sugars to develop functionalized biobased aromatics for performance materials, chemicals & coatings.

Biorizon is based on the open innovation methodology, bringing together collective intelligence of various industries, companies and knowledge organizations. The multi-disciplined technological need, as well as the long term roadmaps based on thermochemical conversion, sugar chemistry for furanes and lignin depolymerisation-based chemicals for functionalized aromatics lead to a large network of applied research projects with more than 40 industrial partners, sharing research, intelligence, investments, risks and workload in different projects.

For partners and companies that are interested in the Shared Research Center, please join at: www.biorizon.eu/community

KEYNOTE SPEAKERS

ENVIRONMENTAL IMPACT OF CROPS AND AGRICULTURAL RESIDUES AS FEEDSTOCKS FOR BIO-BASED PRODUCT DEVELOPMENT

Marisol T. Berti[1], Dulan Samarappuli[1], and Ghasideh Pourhashem[2]

[1]Dept. of Plant Sciences, [2]Dept. of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND, 58108, USA.

Using crop biomass and agricultural residues to develop a variety of bio-based products may seem harmless to the environment. However, crop cultivation requires substantial amounts of nitrogen fertilizer which has negative impact on the environment. In addition, removing crop residues from the soil can have a negative impact on soil health and quality. Crop residues are not a waste, but a valuable resource to keep soil organic matter and fertility and removing only 66% of the residues is not a sustainable practice [1]. For example, removing corn residue reduces soil fertility, increases soil losses by wind erosion, and enhances nitrate leaching to water sources [1]. Studies have shown that production of biomass feedstock accounts for 80-90% of the GHG emissions of a finished biobased product whether is a composite, adhesive, or bioplastic especially if land use change (LUC) is involved [2, 3]. The objective of this study was to analyze and compare the intrinsic environmental impact of feedstock production stage for dedicated and industrial oilseed crops and their residues that are used in making a bio-based product. Two field studies including forage sorghum [*Sorghum bicolor* (L.) Moench] and corn (*Zea mays* L.) biomass and winter camelina [*Camelina sativa* (L.) Crantz.] seed were conducted in North Dakota, USA. Life cycle assessment (LCA) methods were used to assess the impact of a range of crop management systems on soil health, pollinators, and nitrate leaching throughout the biomass production stage. The results of these studies concluded that corn and sorghum biomass emissions are 63 and 54 kg CO_2 eq. Mg^{-1} of biomass [4], respectively, and camelina emissions are 0.84 kg CO_2 eq. kg^{-1} of seed [5]. Greenhouse gas emissions of crops being used as feedstock for biobased products such as kenaf (*Hibiscus cannabinus* L.), crambe (*Crambe abyssinica* L.), pennycress (*Thlaspi arvense* L.), and flax (*Linum usitatissimum* L.) will also be reported.

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NATURAL FUNCTIONAL INGREDIENT FROM SOUTH OF CHILE BIOMASS

Dra. Claudia Mardones

Departamento de Análisis Instrumental, Facultad de Farmacia, Universidad de Concepción.

Replacing fossil fuel with biomass is a current trending topic considering the well-known advantages of using renewable natural raw material. The same concept can be applied to new products creation for health care. Actually, our society much appreciates natural process for functional products than those conventionally produced by synthetic procedures (Zuin & Ramin, 2018). In this context, researches on secondary metabolites as nutritional components for promoting health benefits have triggered the interest to obtain them at industrial scale with ecofriendly process. The characterization and valorization of natural products and industrial waste (biomass) as a source of such bioactive compounds is a main goal of our scientific community (Muhlack et al., 2018). Dietary supplements have become the key to complement deficiencies in the western diet and therefore to reduce the incidence of oxidative stress related-diseases, especially supplementation with polyphenols. Our multidisciplinary research group have been focused on the study of two important polyphenols sources from southern regions of Chile, lignocellulosic residues of *Vitis vinifera* and Calafate (*Berberis microphylla G. Forst*). This research aimed to obtain enriched polyphenols products and to reveal their potential functionality for further applications.

Grape canes, obtained after annual pruning of vines, is a waste estimated in more than 120.000 tons per year only in Chile (Gorena et al., 2014). In this research we studied the wide diversity of polyphenolic compounds in waste product, especially focused on oligostilbenoids and procyanidins with potential health benefits (Sáez et al., 2018). Consequently, polyphenols can be used for development of additives in functional foods (Espín et al., 2007). Grape canes extract obtained at different scales (laboratory, bench, and pilot scales) has been characterized in order to determine their potential as stilbenoids and procyanidins natural source. Evaluation of purification and microencapsulation with β-cyclodextrins, and spray drying process has been also studied in order to produce a stable powder for nutraceutical and cosmetic products.

On the other hand, Calafate is a wild shrub with purple fruits endemic from Patagonia. We characterized the fruit and leaves of this plant as a source of polyphenols. Anthocyanin and hidroxycinnamic acid derivatives has been found in high concentration in berries, while the last class of metabolites were the main phenolics in leaves [Ruiz, et al., 2013; Ruiz, et al. 2013]. In other case, metabolites products of such phenolic compounds with increasing antioxidant capacity were found in plasma obtained after calafate consumption in an animal model [Bustamante, et al., 2018]. Metabolomics studies after consumption of the fruit and *in vivo* an *in vitro* assays to study effect of several calafate extracts is currently in process.

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ALGAE BASED BIOREFINERIES: BOON OR BANE? LESSONS LEARNT FROM A DECADE OF RESEARCH AND DEMONSTRATION UNITS WORLDWIDE

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Algae cultivation has raised high hopes for a sustainable production of various bio-based products such as biofuels, phytonutrients or bio-chemicals from seemingly abundant sunlight and CO_2. However, cultivation in sufficient concentrations, harvesting and conversion into products, especially via biorefineries, require technological solutions that can have considerable impacts on sustainability, namely environment, economy and society.

Development and diversity of algal biorefineries to produce several algae based commodities have increased tremendously in the last decade, especially in the research and demonstration levels as most of them are not yet economically viable. To optimize their sustainability, many sustainability assessments have been performed. To prove and/or increase their sustainability, integrated life cycle sustainability assessments (ILCSA) have been performed based on technological assessment (TA), life cycle assessments (LCA), life cycle environmental assessment (LC-EIA), life cycle costing (LCC), social life cycle assessment, and SWOT analysis on strengths, weaknesses, opportunities and threats.

From these studies and expertises, many lessons can be learned. Several measures to make algae production, conversion and use more sustainable will be highlighted in the talk. They include, next to many others:

- Site selection for algae cultivation is crucial.
- Solar power can make a big difference. Basically, the more renewable energy can be used, the better.
- CO_2 as an input with no or little impacts, e.g. from flue gas from a power plant, can improve the sustainability results significantly.
- Use of co-products can produce added value and enormously improve land use related environmental impacts.

Facts, data and figures will be displayed to underline their importance. Detailed discussion and presentation of the findings are complemented by conclusions and recommendations for policy, industry, science and society.

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DEEP EUTECTIC SOLVENT TREATMENTS IN A PRODUCTION OF NANOCELLULOSES

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Deep eutectic solvents (DES) are relatively new class of chemicals, which have been investigated as a green media in biomass processing. DESs are typically formed as mixtures of two or more components based on complexation of an halide salt of quaternary ammonium or phosphonium cation (as the hydrogen bond acceptor, HBA) along with a hydrogen bond donor (HBD) (e.g. urea, glycerol, or ethylene glycol) [1–3]. The DESs can be used as solvents, reactants, or even catalysts. They can often be prepared from green and bulk chemicals through the application of a straightforward heating and mixing procedure. Moreover, many DESs are biodegradable and have low vapor pressures and relatively low toxicities, which make DESs one of the most promising solvents for sustainable material production [4]. In our studies we have prepared several different DESs and used them in cellulose modification and production of nanocelluloses from different raw-materials and for different applications. The DES of choline chloride-urea, which is one of the most commonly known DES, was tested as a pre-treatment for nanofibrillation of bleached birch kraft pulp and secondary fiber sources, including waste board, fluting, and waste milk container board [5,6]. These nanofibrils were used as reinforcements in paper board and to produce highly porous superadsorbing aerogels for oils and several organic solvents [7]. In addition, we used DES of ammonium thiosyanate-urea and guanidine hydrochloride-urea as alternative, non-derivatizing pretreatments for nanofibrillation of cellulose fibers [8]. Chemical modification of cellulose fibers was conducted in DES of urea-LiCl to produce succinylated nanocelluloses [9]. Moreover, anionic nanofibers were produced from unbleached mechanical pulp with DES of imidazole-triethylmethylammonium chloride [10]. DES of sulfamic acid-urea was applied for direct sulfation of cellulose fibers [11]. Acidic DESs were used in a cellulose nanocrystal (CNC) production from dissolving pulp [12] as well as in a delignification and nanofibrillation of agricultural wastes wheat straw, corn stalk and rapeseed stem). Organic acids combined with choline chloride showed also to be potential hydrolytic solvents in a fabrication of CNCs. This method exhibits certain advantages over previously reported CNC production such as milder processing conditions and easily obtainable and relatively inexpensive biodegradable solvents with low toxicity. In addition, acidic DESs were shown to separate lignin selectively from agricultural waste material generating quite pure lignin and cellulosic fractions. In summary DESs are versatile solvents for cellulose modification and production of various nanocelluloses. By adjusting the components of DES, the reaction efficiency of cellulose modification can significantly be enhanced. Moreover, the DES solutions can potentially be recycled.

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DOMICILIARY WASTE: HOW MUCH HAVE WE ADVANCED IN ITS MANAGEMENT AND TREATMENT AND WHAT OPPORTUNITIES ARE THERE?

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For many years the materials, food, equipment and other elements that we use every day were produced with a linear logic (take, produce, discard) and did not think about what would be done with the waste generated at the end of its useful life, because “It was not my problem, it was someone else's problem”. Nowadays, due to a greater environmental awareness and the global world in which we live, it is clear that the local impact, it's not really so local, but may have global implications, as is the case of plastics, POPs and others. Concepts such as the circular economy (zero waste) come to reinforce the idea that the production and use of resources must be carried out in a sustainable manner, and that is why when a product reaches its useful life, it can be recycled until it has no value, in other words, make the most of resources.

The problem of municipal solid waste is not unique to Chile, all countries have faced it in different ways, the important thing is to learn from these experiences and move towards a solution that is consistent with the national reality. Two key aspects that coincide are: i) that the population and generators should be made aware of the impact of the waste, instruct them on how to recycle, on how to be empowered and informed consumers, and ii) that there should be a legislation that supports sustainable management. Chile is lagging behind about the management of its waste compared to other OECD countries, there is no updated data on waste generation per inhabitant, recycling rates, elimination rates; the latest data correspond to the National Solid Waste Register that UDT prepared for the Ministry of Environment in 2010. It established that in Chile 16.9 million tons of solid waste are generated per year, 38% municipal waste and 62 % industrial waste, which represents one of the highest rates in Latin America. The recycling rate does not exceed 10%, which is very far from the OECD countries that exceed 30%. We also have problems with the geographical distribution of landfills and waste treatment facilities, which are not available to manage all the waste generated, where they are generated.
A significant progress is the enactment of the "Law on Waste Management, Extended Producer Responsibility and Recycling Promotion", or REP Law, because it establishes the mechanism by which, according to the Ministry of the Environment, by the year 2030 we could reach the levels of a developed country. This Law will create a market around recycling and therefore the development and / or use of technologies for this purpose. In these instances, research can play an important role, either by designing new treatment processes, developing applications, optimizing already established technologies or adapting them to local needs.

In short, the problems are there, as well as the tools, you just have to face the challenge.

BIODEGRADABLE FILMS BASED ON BLENDS OF PVA AND BIO-OIL FROM LIGNIN

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Nowadays, the excessive use of plastics derived from fossil resources is causing an issue of catastrophic consequences on the environment. The reliance of the mankind of this type of commodities together the depletion of the fossil resources has led to search alternatives that replace the synthetic polymers. Face this scene, in the last decades, great efforts have been carried to find natural polymers that allow formulate adequate blends with similar or enhanced properties to the ones derived from the exhaustible sources. In fact, the use of renewable feedstocks to obtain biodegradable polymers is outlined as a rising option to substitute to the ones derived from fossil resources. Lignin is the more abundant aromatic biopolymer that exists in the nature and it is possible to extract it from lignocellulosic biomass [1]. Traditionally, the lignin is obtained as by-product in pulp and paper mills and it is used as energy source, but in the recent years new applications have been searched for it increasing its value. One of the explored fields is the conversion of lignin into a phenolic compound-rich bio-oil, which could be valuable for the replacement of fossil-derived aromatic ones. On the other hand, polyvinyl alcohol (PVA) has gained interest over the last years due to its biodegradability and non-toxicity despite the fact that it is synthetic [2]. The employment of the phenolic compound-rich bio-oil derived from the lignin and the PVA to synthesize biodegradable films can be an alternative to substitute the plastics for some applications. For all this, in this work the use of base depolymerisation products from organosolv lignin and PVA to formulate films is purposed. Several concentrations of bio-oil were blended with the PVA to assess its influence on the properties of the resulting films. Solubility in water and tensile tests were evaluated. The results obtained allowed to conclude that bio-oil could be a potential functional additive to blend with PVA for biodegradable films with specific applications.

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TOUGHENING OF PLLA BY VARIOUS POLY(CAPROLACTONE-CO-(D-LACTIC ACID)) COPOLYMERS

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Poly(lactic acid) (PLA) is a commercially available bio-based material with high strength and modulus. The major drawback of this polyester is its brittle nature. For applications such as thin films and foils, it is necessary to flexibilize PLA. Adding low molecular weight plasticizers can lead to increased elongation at break and impact strength of the resulting materials. However, this is linked to a decrease in thermal stability because of the lower glass transition temperature of the plasticized PLA. Additionally, complex (co-)crystallization (aging) and separation effects (migration) are observed for these systems. Another option for toughening PLA is blending it with more flexible polymeric components like PBS, PCL, PBAT, or other co-polyesters. Main drawback of this approach is that large fractions of the more expensive blend partners are needed which often makes these blends commercially unattractive.

Aim of the research performed at Fraunhofer UMSICHT was developing a non-migrating plasticizer for PLA. The idea is trapping low concentrations of plasticizing oligomers within the PLA matrix via crystallization in order to avoid migration and solubility problems. Block copolymers with a compatibilizing unit, poly(D-lactic acid) (PDLA), and a plasticizing unit, polycaprolactone (PCL), were synthesized and blended with poly(L-lactic acid) matrix (PLLA). Formation of the so-called stereocomplex between PDLA-blocks and PLLA-matrix traps the PCL-blocks within the PLLA (cf. Fig. 1).

It was found that stereocomplex bonding of the PCL-blocks not only reduces migration tendency but also improves the efficiency of the plasticizer. In comparison to polymer blends with the same amount of PCL-oligomers, block copolymers with PDLA and PCL shift the glass transition temperature to lower values. This effect can be explained by the suppressed crystallization of the PCL-blocks within the matrix. The mobility of the bound PCL-blocks is lower than that of neat PCL-oligomers. Hence, their ability to crystallize is lower and a higher effective amount of PCL can interact with the PLLA-matrix.

This effect is even more pronounced using branched PCL-blocks. The crystallinity of branched PCLs was significantly lower than of linear PCLs. Adding small amounts of DL-lactide units to these branched structures results in completely amorphous oligomers. PLLA blends with block copolymers containing 10 wt.% of such branched PCL-blocks show a tremendous increase in elongation at break from 1 % for neat PLLA up to 213 %.

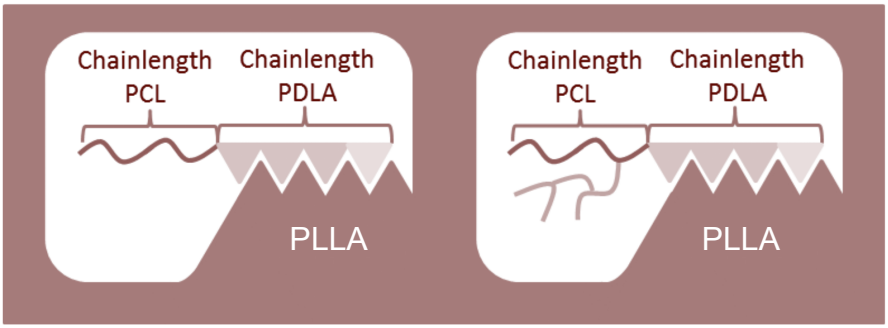

Fig.1 – Schematic representation of incorporating linear and branched PCL-blocks in PLA via stereocomplex bonding

CARBON-BASED PHOTOCATALYSTS TO PRODUCE SOLAR FUELS AND CHEMICALS FROM BIOMASS DERIVATIVE'S MOLECULES

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Solar fuels are a promising strategic pathway since they are produced from simple and abundant molecules using a renewable energy source such as sunlight (Figure 1). However, the efficiency is still low and far for the practical application. Highly active photocatalysts are required to produce solar fuels. This work will show the advances in the production of solar fuels using efficient carbon-based photocatalysts and results obtained in some model reactions will be shown. The efficiency for H_2 production by direct water splitting using TiO_2 is rather low, but it can be notably increased in presence of sacrificial agents [1] (electron donors). Aqueous pollutants can play the role of sacrificial agent and simultaneous H_2 production and pollutant removal can take place. The CO_2 reduction permits to obtain a wide variety of organic compounds such as formic acid, methanol and methane. Considering that noble metals have a high activity for C-O bond cleavage combined with flexible and highly tuneable chemistry of the carbon surface it can be postulated that noble metal/graphene-based catalysts should be suitable to achieve efficient hydrogenation of CO_2 in the aqueous phase [2]. Finally, the photo-assisted valorisation of furfuryl alcohol (FA) and 5-hydroximethyl furfural (5-HMF), two products from the biorefinery industry, and glycerol (Gly), the main by-product of the biodiesel industry, is an innovative approach to explore because these target molecules can be photo-converted into aldehydes or ketones or even more valuable compounds such as five- or six-member dioxane-based carbocycles by condensation reactions [3].

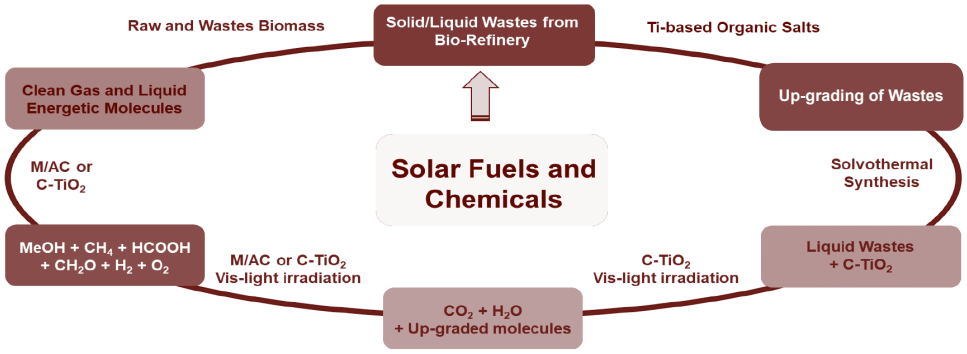

Figure 1. Strategic pathways for the production of solar fuels and chemicals.

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LIGNOCELLULOSIC BIOMASS AND RESIDUES AS POTENTIAL SUBSTRATES FOR THE INDUSTRIAL BIOTECHNOLOGY

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Objectives: Besides the quantity and availability of raw materials together with their properties the feedstock costs are crucial for the production of bulk chemicals like lactic acid. Especially for biotechnological processes, in which the carbon should be converted into microbial products, there is an increasing interest in the use of cheap raw materials.
Methodology: Renewable feedstocks (lignocellulosics, agri-food residues etc.) are already being used as raw materials for the production of bio-based products. However, these feedstocks cannot be used for fermentation directly because the fermentable sugars are bound in the structure especially as cellulose and hemicellulose. They have to undergo a pre-treatment to release these sugar components.
Results: Investigations dealt with the optimization of different process steps (e. g. disintegration and hydrolysis of biomass, fermentation, downstream processing etc.) and were performed subsequently in form of coupled process sequences. Different fermentation regimes were tested for the development of an innovative and environmental benign lactic acid production. Special detoxification steps can help to improve the fermentability and conversion efficiency of biomass hydrolysates. Depending on the further processing of the lactic acid the separation of impurities after fermentation is a major process cost too. Therefore an optimization is necessary to find a balance between the substitution of expensive nutrients and the limitation of interfering or undesirable components of natural raw materials.
Conclusion: The entire processing chain has been implemented: from the feedstock, the pretreatment/hydrolysis for releasing C5 and C6 sugars, the fermentation to lactic acid and the downstream processing of fermentation broth to generate marketable lactic acid of high enantiopurity and quality. Exploitation of L(+)- and D(-) lactic acid for the production of biopolymers is one of the recent applications.

Keywords: Lignocellulose, Feedstocks, Bioprocessing, Fermentation, Lactic acid

EXERGO-ENVIRONMENTAL AND EXERGO-ECONOMIC ANALYSES OF A FURFURYL ALCOHOL PRODUCTION PLANT

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Exergo-economic and environmental analyses are applied in energy conversion systems and any process that includes mass and energy balances because exergy represents the only rational basis for assigning environmental impacts and costs to the energy carriers and the inefficiencies within the system. In this work, the exergoeconomic methodology was used in the simulation of a commercial-scale furfuryl alcohol production plant to estimate the costs of final products as well as the costs of the exergy destroyed within each system component [1]. This information is essential to detect cost-ineffective processes and identify technical options, which could improve the cost-effectiveness of the overall plant.

The environmental consequences of commercial-scale plants must be predicted for sustainable development because potential environmental problems must be foreseen and addressed at an early stage in project planning and design. All production sectors have undertaken efforts to reduce their environmental impacts, in particular by introducing new technologies, which increase thermal efficiency, reduce toxic components in their process and decrease specific fuel consumption and related greenhouse gas emissions. These technical improvements may imply modifications of the design of plant components and result in less or more environmental damage. However, a traditional energy analysis cannot identify, for example, the extent of environmental damage, substances responsible for most of the emissions, the component or components of the system responsible for the environmental impacts, or the materials and energy needed for the fabrication, operation, and dismantling of the associated facilities.
Furfuryl alcohol (FOL) is produced from furfural (FUR), leading within 60 and 70% of its market. Hydrogenation of furfural toward FOL may occur in liquid or vapor phase, being the vapor one preferred due to their easy scaling up. FOL market has being grown because of its massive consumption in the production of furanic polymers used in thermoset polymer matrix composites, types of cement, adhesives, coatings, and casting/foundry resins. Furthermore, the most common historical usage of furan resin has been in the foundry industry as a semi-rigid chemical binder for sand casting due to its excellent resistance to thermal, chemical attack, and fire resistance when combined with glass fibers [2]. Furan resins have substantial market opportunities in Chile since furfural are produced from biomass raw material, and mine industry used it to produce cores and molds for the casting of metals.

The simulation of furfuryl alcohol plant (Fig. 1), life cycle analysis and assessment of environmental aspects used AspenPlus, SimaPro and Eco-indicator 99 respectively. Exegetic methods combined with the traditional economic analysis evaluating acquisition, operation and maintenance costs of each component of the process ended in the exergo-economic analysis. Similarly, exergo-environmental analysis resulted from the exergetic analysis and life cycle analysis.

The simulated plant produced 117.7 ton/day of furfuryl alcohol with an estimated efficiency of 96% due to high yield and low levels of exergy destruction in each component. The estimated economic production cost of FOL was USD 7,698 per hour, and the environmental impact was evaluated in 84,706 mPt/h (82,9%) including economic and environmental costs of equipment, fuel and exergy destruction.

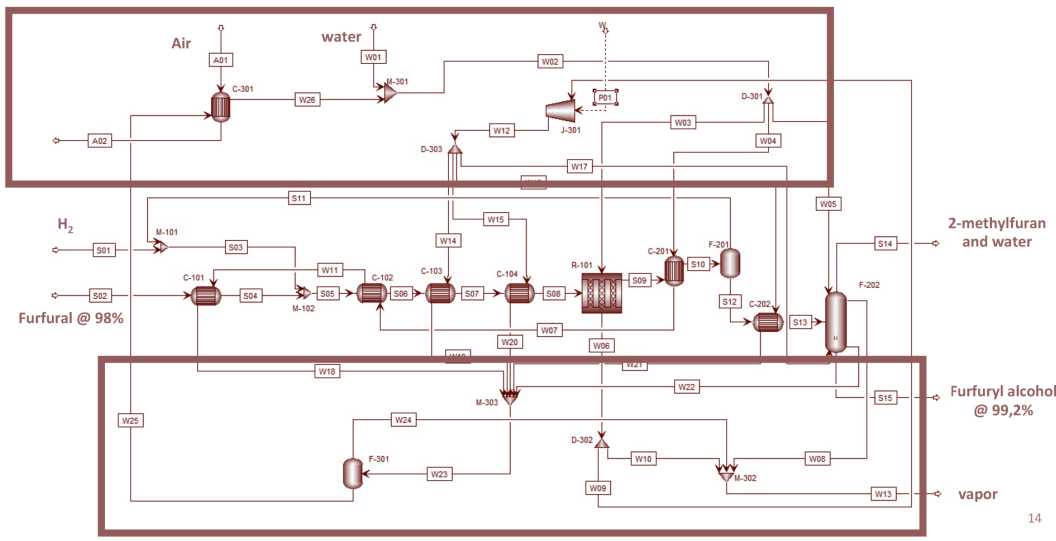

Fig.1 – Furfuryl alcohol plant simulation scheme.

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ORAL

EVALUATION OF BIOMASS-BASED VALUE CHAINS COMBINING GEOGRAPHICAL INFORMATION SYSTEMS (GIS) AND OPERATIONS RESEARCH TECHNIQUES

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The elaboration and implementation of successful biomass-based value chains requires a detailed evaluation of valorisation routes taking into account regional conditions and the multiplicity of biomass feedstocks, conversion technologies, and capacities, as well as output products. Mathematical optimization models in connection with GIS-based models can help identify ideal regional biomass valorisation routes. Thereby it is aim to make use of spatial information stored in the GIS while utilising operations research techniques to find good / optimal configurations of the value chain. We present a combination between a GIS model and an MILP formulation for optimizing regional decentralized bio-based value chains. This model combination has two central objectives, which are implemented iteratively with increasing level of geographical detail. First, the GIS model locates regional biomass volumes, identifies potential conversion sites, and determines actual transport distances on predefined geographical cluster layers from transparent open source data. Second, starting from the highest geographical cluster, the mathematical model plans locations of biomass conversion sites based on input data provided by the GIS model. Every cluster layer is optimized iteratively in terms of the most profitable biomass conversion site locations, integrating technological economies of scale, biomass feedstock and transport costs, as well as sales revenues. The optimal solution is returned to the GIS model, which updates the input data for the optimization on the next cluster layer. It is aim of this talk to present a model combination approach to evaluating decentralized bio-based value chains on the regional level through heuristic-based iterative optimization. The resulting insights support strategic decision making by determining conversion site locations and in tactical planning by allocating feedstock to conversion sites.

ACCEPTANCE OF BIOENERGY IN CHILE – AN EMPIRICAL ANALYSIS OF PUBLIC OPINION

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Practical experiences with renewable energy (RE) projects in Chile have shown that public acceptance is often a precarious issue. Lacking acceptance by the population has recently led to social conflict, especially with regard to hydropower projects, cf. e.g., Altomaipo [1], Hydroaysén [2], and Rio Cuervo [3], but also with regard to bioenery projects because of potential impacts on local residents and the environment, cf. e.g., biomass plant in Cabrero [4].

The present paper takes this observation as starting point for an empirical analysis of the public acceptance of bioenergy in Chile. The study is based on an online survey conducted in November 2017 which yielded a representative dataset [1] with 1,205 observations. The questionnaire consists of 77 questions covering personal attitudes and dispositions to act towards several RE technologies with a special focus on bioenergy.

Based on the data, we found that bioenergy is seen rather critically by the Chilean population compared to other REs. Solar and wind energy enjoy by far the highest support, whereas bioenergy, geothermal, and hydropower are much less popular. Fig. 1 shows the results with regard to appraisal and disposition to act towards different RE technologies: there is high approval of small PV (99%) and large PV (93%) as well as wind energy plants (87%). For bioenergy plants, however, the picture is quite different: the majority of respondents reject a local plant (71%) and thereof 18% are willing to actively oppose a local bioenergy plant in their neighborhood, only 24% of respondents would approve such a plant.

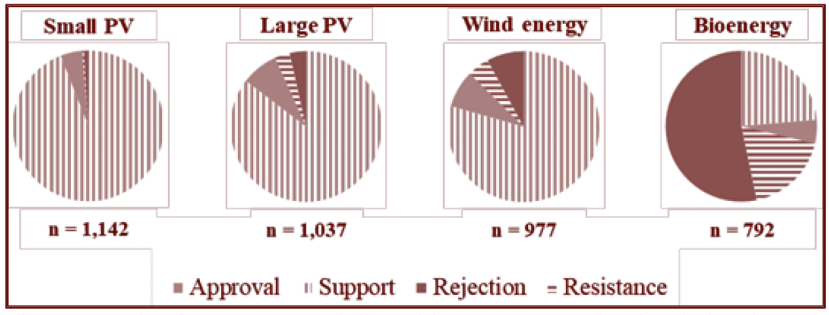

Fig. 1 - Levels of acceptance and disposition to act towards a local plant by technology
Notes:
Categories 'approval' and 'rejection' include the categories 'support' and 'resistance' respectively.
Respondents excluded who evaluated a local plant as "neutral" or "don't know".

Besides acceptance levels, we investigated the role of proximity of RE plants to the respondent's home by asking for the distance in kilometer (km) at which respondents would accept a RE plant in their vicinity. Figure 2 shows the cumulated relative frequencies of the desired distance. Again the low acceptance of bioenergy plants is confirmed by a substantially higher desired distance compared to the other REs.

[1] Representative with regard to sex, age, social status, and administrative regions.

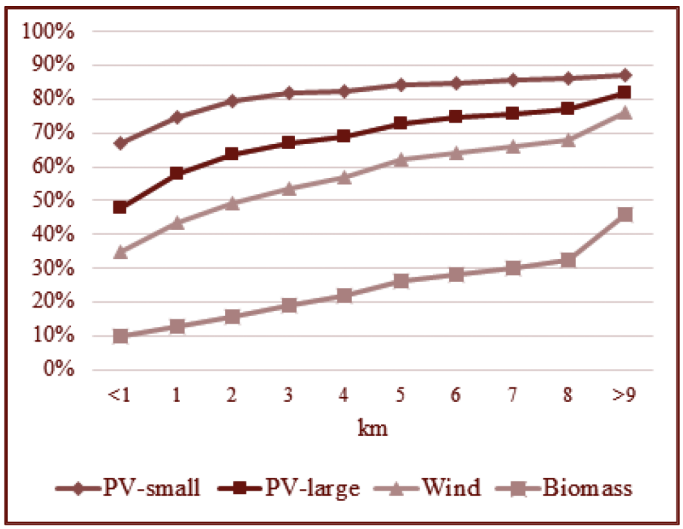

Fig. 2 - Cumulated relative frequencies of the desired minimum distance of RE plants in km
Notes:
Sample sizes: $n_{PV\ small} = 1{,}050$, $n_{PV\ large} = 986$, $n_{Wind} = 919$, $n_{Biogas} = 551$
Includes responses "The distance of the plant to my home is not relevant for me." as 0 km.
Answers of respondents excluded, who stated that they do not accept the plant at all or who stated that the visibility is more important than distance.

Using multiple linear regression analysis, we further identified three factors, which significantly influence public acceptance of bioenergy plants in Chile: the by far most important factor is "perceived benefit of biogas plants" with a highly significant positive effects on public acceptance ($\beta = 0.813$, $p < 0.001$), followed by "advocacy of renewable energies" ($\beta = 0.162$, $p < 0.001$) and "perceived costs of using energy plants" ($\beta = -0.164$, $p < 0.001$). The regression model explained 35% of the variance in the dependent variables.

The analysis of the empirical data revealed a low public acceptance of bioenergy in Chile and a strong influence of "perceived benefits of bioenergy plants". In the final article respective recommendations and implications for suitable framework conditions which stimulate social acceptance are derived.

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INTEGRATED LOGISTICS FOR IMPROVED FEEDSTOCK QUALITY AND CONSISTENCY

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The diverse portfolio of biomass sources that is available in the Southeastern U.S., including a significant supply of pine "residue", represents a valuable strategic position for the region. Through blends formulated based on critical properties, this project will take full advantage of the range in biomass properties afforded by the portfolio to produce a consistent, high-performance feedstock for the industry, while lowering cost. Key developments being targeted to enable this potential include whole-tree transport to a state-of-the-art merchandising depot that will further access biomass from ongoing, forest industry operations. The approach will more effectively utilize the tree and distribute cost, while minimizing in-woods contamination of the woody biomass component. To implement this vision, information on the chemical composition and changes that are induced during multiple preprocessing steps (size reduction, moisture removal, densification, etc.) is needed. New NIR sensor technology will be developed for online monitoring of important biomass properties. The data will be incorporated into a statistical process control platform to improve process efficiency and meet required specifications. Advanced process models are being developed to inform the techno-economic and life-cycle assessment of the program's impact. The new system will ultimately reduce operational risks from supply chain disruptions, and allow operation of larger-scale biorefineries.

A SUSTAINABLE SUPPLY CHAIN DESIGN FOR PHASE III BIOREFINERY: A COLOMBIAN CASE STUDY

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Bioeconomy has gained importance during the last decade as a frame of reference for the design and implementation of policies to foster sustainable development. Nowadays, given the urgent need of our society to move to forms of production in which the generation of waste and the use of fossil fuels are minimized or eliminated, biorefineries have emerged as a promising and central element in bioeconomy [1].

However, biorefinery development has been slower than expected, especially when non-food crops are employed as feedstock. According to the perception of investors, that type of projects are high technological risky and low profitable, because of their complexity and the lack of well-defined logistical models [2,3]. Therefore, trustable studies providing information related to project constraints and opportunities, technology to be used, structural and labor requirements, are needed in order to reasonably decide whether the project could be implemented or not. The traditional feasibility assessments are focused on the evaluation of the technical and economic performances of the project. Nevertheless, this type of evaluation alone is not always enough to estimate accurately the potential biorefinery project performance. For example, global biomass availability is heterogeneous and limited, which leads to the potential competition for biomass between different biomass consuming sectors. In addition, biomass sources can be used to exhaustion depending on the degree and type of exploitation [4]. The performance evaluation that integrates these aspects is known as sustainability assessment. Sustainability concept implies the management and conservation of natural resources, ensuring the attainment and continued satisfaction of human needs for present and future generations [5]. The challenge to integrate the sustainability assessment in the biorefinery design is addressed by the formulation and solution of a many-objective optimization model, where sustainability criteria are included in the formulation of twenty-four objective functions.

In addition, biorefineries can be classified according to integration degree depending on the variety of raw materials type used and the diversity of final products obtained [6]. A Phase I biorefinery uses a single raw material yielding one main product. A Phase II biorefinery also processes a single raw material type, but it is able to produce various end-products in response to market variations. Finally, a Phase III biorefinery uses several types of raw materials to produce a variety of chemical products, materials and energy [7] (A. Espinoza Pérez et al., 2017). Considering Phase III biorefineries are able to respond more rapidly to changes in the market and suppliers environment, but have not been implemented industrially, there are potential benefits and untoward effects that have not been borne out in practice.

In order to illustrate the proposed approach, a case study was developed for the Colombian context. Including the evaluation of palm oil and jatropha curcas oil as raw materials; and the production of biodiesel, aliphatic polymer and glycerol. The resulting Pareto fronts showed that

biorefineries integrating different types of raw materials, even non-food crops, are economically feasible in North Colombia under particular conditions of sustainability. Additionally, sensitivity analyses were conducted to provide further insights.

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NOVEL AND SUSTAINABLE BIOREFINERY CONCEPT BASED ON GREEN TECHNOLOGIES FOR CORN, WHEAT, AND RAPESEED RESIDUES

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Corn, wheat and rapeseed are three crops from which notable quantities of residual biomass are obtained worldwide every year, *e.g.*, corn stover is the most plentiful source of lignocellulosic biomass in the U.S., with only a portion removed from the field [1]. These residues are a potential unexploited biomass resource, and contain cellulose, hemicellulose, and lignin as major components, but also contain wax compounds, and bioactive compounds such as vitamin E, phenolics, and carotenoids. However, since the composition of these residues is complex the separation and fraction become a key issue for an efficient use of these materials. For this purpose, this work uses green techniques such as Supercritical Fluid Extraction (SFE) for extraction of valuable compounds [2]; hydrothermal treatment (i.e. the organosolv process) to obtain Lactic Acid (LA), and separate fractionations of cellulose, hemicellulose and lignin [3]; Deep Eutectic Solvents (DES) to selectively separate lignin form cellulose [4]; and HydroThermal Carbonisation (HTC) of lignin fractions to produce a polyaromatic/phenolic carbonaceous products [5]. In this work twenty-one genotypes of corn and fifteen of wheat were evaluated. There were significant differences (p-value <0.05) among genotypes for biomass dry weight, cellulose, hemicellulose and lignin yields. The best genotypes for further processing showed cellulose and hemicellulose yields of 2.4 ton/ha for corn stover, and 5.9 ton/ha for wheat, and low lignin yields of 0.43 ton/ha for corn, and 1.4 ton/ha for wheat. Optimal parameters for the SFE of wheat straw and germ, corn stover and rapeseed cake were determined. In all cases, it was possible to extract >88% of the extractable material. Through the organosolv process and DES it was possible to obtain separated fractions of sugars, cellulose and lignin. Further fermentation of the sugars fraction (83% xylose) showed high yield of lactic acid (90%). Strength properties of fibrillated Acid-DES-treated corn stover were measured and best results were obtained for LA-base DES treated samples with tensile strengths in the range of 92.0–99.2 MPa. The HTC at 240 ºC of the lignin fraction from the organosolv process yield 65% of solid material.

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ORGANOSOLV LIGNIN-ESTER DERIVATIVES AS UV PROTECTION AGENT FOR POLY(LACTIC ACID) (PLA)

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PLA is currently the most promising bioplastic in several sectors and especially for packaging applications. However, it has some shortcomings, such as brittle nature and high ultraviolet transmission properties[1,2], which limit its commercial use in food packaging sector. Therefore, the current work is focused on fabrication of eco-friendly poly(lactic acid)/lignin-ester derivatives based films with improved UV protection and ductility. Lignin, as natural broad-spectrum sun blocker, could be an interesting alternative to synthetic sunscreen additives for PLA materials maintaining thus the biobased content of the final product. Although lignin is considered as UV protective product, its sunscreen effect can disappear when forms agglomerated because of poor compatibility with the polymer matrix[3]. Therefore, it was interesting to modify chemically the isolated organosolv lignins from Eucalyptus and Spruce with dodecanoyl chloride in order to study the UV-vis protection properties of PLA/ lignin-esters blends, as lignin-esters present good compatibility with the PLA matrix. Figure 1 is a schematic representation of the most significant results of this research work. Modified lignins presented good compatibility with PLA matrix without the presence of aggregates. Furthermore, the results suggested that lignin-ester derivatives could substitute synthetic sunscreen additives, since both esterified lignins demostrated their capacity as UV light absorber product. In addition, a significant influence on mechanical properties was observed by the incorporation of lignin-esters into PLA, achieving an important enhancement in the ductility of PLA, essential requirement for packaging uses.

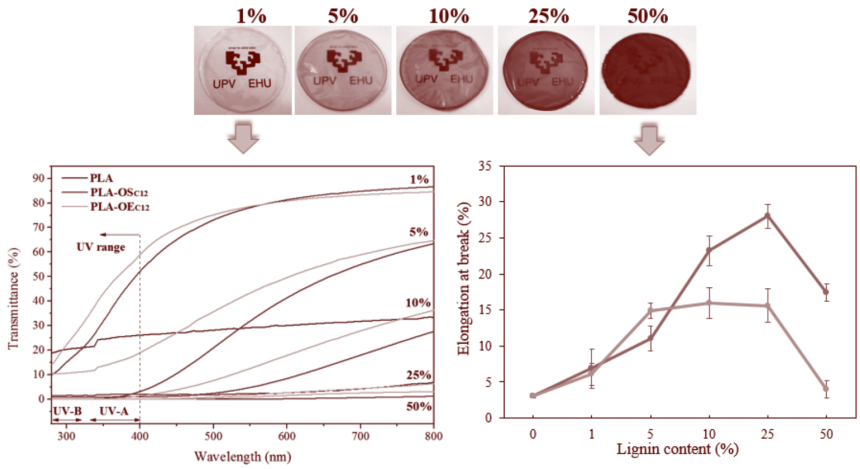

Fig. 1- PLA/lignin-esters films, UV-visible curves and elongation at break (%) of films.

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METABOLOMICS IN FOREST SPECIES TO IDENTIFY CHEMICAL RESPONSES TO BIOTIC STRESSORS: THE BEGINNING OF BIOACTIVE PHYTOCHEMICAL DISCOVERY AND APPLICATION

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Metabolomics is an analytical technique which has been successfully applied to the studies of biological systems behavior when facing biotic or abiotic stressors [1]. Through the simultaneous analysis of hundreds to thousands of metabolites, such technique provides with a global view of the metabolic status and biochemistry events taking place at a given moment in the organism under study. This is therefore a powerful tool in plant research, especially applied to identify biomarkers able to distinguish between genetically and morphologically related species [2], or for the study of plant-insect interactions [3].

In the present work we describe the LC-MS based metabolomics analysis on *Pinus radiata* aimed to determine biomarkers related to its defensive response against the insect *Sirex noctilio* F. This insect is currently considered by SAG (Servicio Agricola y Ganadero) as a quarantine pest under mandatory control in Chile.

With the purpose to reveal metabolites responsible for the different susceptibility showed to *Gonipterus scutellatus*, similar analytical strategy was also applied to *Eucalyptus globulus* and *E. nitens* leaves. This is a herbivore insect currently distributed in Chile among IV and IX regions, causing defoliation in trees that delays their rate of growing in between 18% and 33%.

The global analytical strategy followed in both cases aforementioned is shown in Fig.1. The obtained LC-MS data was processed by multivariate statistical analysis such as PCA and PLS-DA.

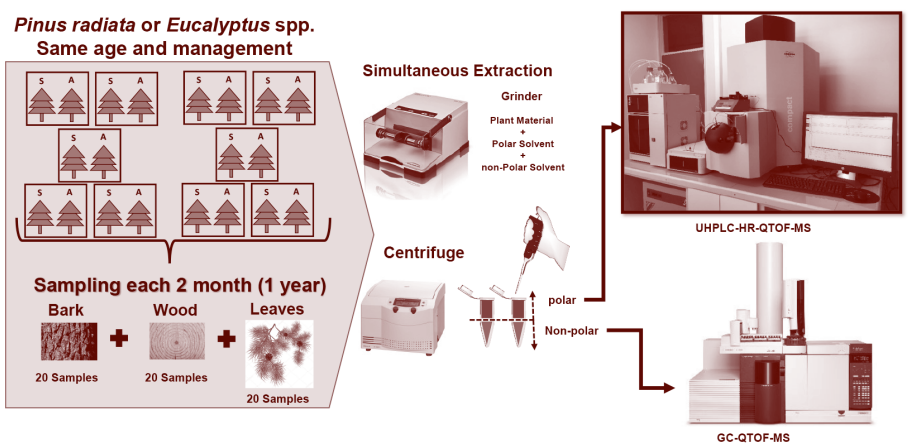

Fig.1 – General scheme of conducted experimental strategy for metabolomics studies in *P. radiata* and *Eucalyptus* spp. Healthy tree (S), attacked tree (A).

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Acknowledges

To CONICYT Fondecyt Regular N°1181915. To Forestal MININCO S.A., especially to Dr. Miguel Castillo, Head of Phytosanitary Protection Area. To Fondequip EQM170023.

SOUTH AMERICAN FRUITS, A SOURCE OF BIOACTIVE COMPOUNDS

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The early South American cultures developed economies based on fruits and seeds gathering and agriculture. In northern Chile, the algarrobo (*Prosopis* spp.) pods and chañar (*Geoffroea decorticans*) fruits supplied a kind of flour used for different preparations, including fermented beverages. The comparison of the bioactives in algarrobo [1-3] and chañar [4-5] from Chile and Argentina allowed the identification of constituents with inhibitory activity towards enzymes associated to metabolic syndrome (α-amilase, α-glucosidase, pancreatic lipase) and anti-inflammatory effect. The *Araucaria araucana* kernels and the native *Gevuina avellana* seeds are part of the pre-hispanic tradition incorporated into Chilean cuisine. The main diet supply of *Araucaria* kernels are carbohydrates while the Chilean avellana contain essential fatty acids.
Native berries are relevant sources of bioactive polyphenols [6-7] and were selected because of their pleasant taste and aroma. The phenolic-enriched extracts (PEEs) of Chilean currants (*Ribes* spp., Grossulariaceae) show good antioxidant activity and inhibitory effect on α-amilase, α-glucosidase and pancreatic lipase [8-10]. Simulated gastrointestinal digestion and colonic fermentation of *R. magellanicum* and *R. punctatum* PEEs [11-12] showed changes in composition and activity, related with antioxidant and enzyme inhibitory activity. The active compounds are metabolites from different structural groups and the mechanisms of action are different according to the composition of the PEE. The integral use of food resources requires studies on the waste products that are usually discarded and also new insights into known products. The information presented shows a glimpse on the potential of native food sources as future crops, taking into account the need of diversification in agriculture and the challenges of the global climatic changes.

Acknowledgements: FONDECYT Projects 1170090 and 1120096, PIEI-QUIM-BIO, Universidad de Talca.

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EFFECTS OF *Pinus radiata* PINE SEED OIL CONSUMPTION ON MURINE MODEL: EVIDENCE OF A NEW FUNCTIONAL ALIMENTARY ADDITIVE FOR THE CONTROL OF DIABETES

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Pines and other pinaceae, species of the pinaceae family, are classified within conifers that produce pine nuts contained in cone-shaped structures called strobilus, pineapples or cones. Worldwide there are about 30 species of pine that produce edible pine nuts, but only some have commercial relevance. The most important being *Pinus gerardiana*, which produces the so called Pakistani or Indian pine nut; *Pinus koraiensis*, the Chinese pine nut; *Pinus sibirica*, the Russian pine nut; and *Pinus pinea*, the Mediterranean pine nut. The rest of the edible pine nuts are relevant mainly at the local level, where they are in general a traditional food particularly used by aboriginal cultures or "First Nations" (GRAS-FDA, 2010).

The pine nuts, in comparison to other fruits or seeds, corresponds essentially to the significantly higher presence of C18 and C20 polyunsaturated fatty acid with unsaturations positioned in the form of omega-3, omega-4 and omega-6. Specifically, in this type of plant sources, a high content of linolenic acid, pinolenic acid (PNLA), taxoleic acid and sciadonic acid, among others, is usually found in a unique manner. Of these, one of the most studied corresponds to PNLA representing 14-19% of the total fatty acids present in the pine nuts. The consumption of PNLA has been associated with positive effects in the reduction of inflammation, immune function, appetite and body weight, blood lipids, insulin sensitivity and cancer metastasis (Xie et al 2016).

The present research proposes the use of a new formula based on *Pinus radiata* oil, pine specie widely present in Chile. The consumption of this product generated an appetite-modulating and insulin-sensitizing effect in a murine model based in female mice of strain C57BL/6. Likewise, the advantage of delivering results in times close to intake was found, which can be sustained both during the day and in longer periods of time. Its effectiveness can be demonstrated through the profile of weight evolution (Figure 1), which exhibits a 34% decrease in weight of the individuals consuming the optimized product (Formula D), compared to the control (Formula A). In addition, the tests of insulin response and glucose tolerance show positive effects on the *in vivo* systemic response to insulin in obesity.

These results suggest that said formula can be used as a functional food additive for individuals suffering from diabetes. It also allows the design of a new biorefinery concept that promotes community participation in the collection of *Pinus radiata* cones in Chile.

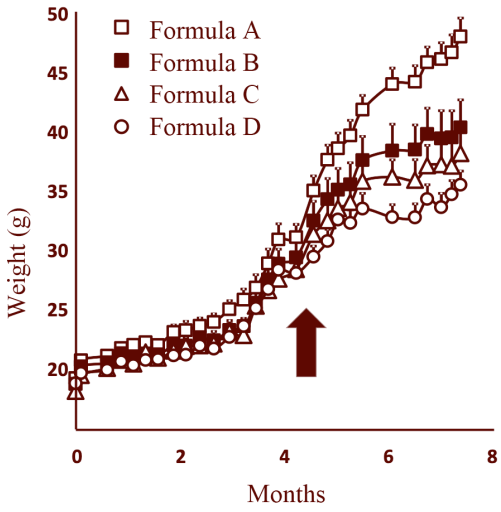

Fig.1 – Weight evolution profile.

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PHENOLIC RESINS DERIVED FROM MEDIUM BOILING FRACTION OF FAST PYROLYSIS OIL – APPLICATION AS WOOD GLUE FOR NON-LOAD-BEARING WOODEN MATERIALS

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Following orienting research [1] a systematic study was performed on the production and application of phenolic resins based on fast pyrolysis oil made from straw (mixture of wheat and barley). The primary vapors coming from a laboratory plant for ablative flash pyrolysis are condensed in three stages with falling cooling temperature. Each condensation stage is equipped with a double effect cooler followed by an electrostatic precipitator, which is kept at the same temperature as the cooler. The first stage is operated at temperatures around 120 °C to condense all high boiling components like anhydrous sugars and oligomeric lignin debris. The second stage is kept at temperatures around 80 °C to primarily condense phenolic monomers and the third stage collects the remaining condensables like water and acetic acid at 5 °C.

The medium boiling fraction, which is comparingly low in water (< 2 %) and acetic acid (< 6 %) on one hand and on the other hand high in phenolic compounds like guaiacols and syringols, is used to substitute pure, fossil based phenol in the production of resol resins. The classical recipe for the production of resol resin comprises phenol and formaldehyde (aqueous solution, 37 weight-%) as monomers and caustic soda as catalyst. The degree of phenol substitution is varied between 60 and 80 % on weight basis and the impact on resin quality is accessed. Additional caustic soda is added to neutralize the remaining acids in the pyrolysis oil. For comparison, samples were also produced using 0 and 100 % of pyrolysis condensate.

Kinematic viscosity, free formaldehyde content, and curing behavior were measured. Beech wood samples were glued with the resins and the tensile strength of these specimen was also measured. The majority of the 44 resins exceeded the minimum requirement of 10 N/mm^2 tensile strength following DIN EN 205 for non-load-bearing woody materials and nearly all samples broke within the wood and not in the glued joint. Fig.1 exemplifies the results. While the most important parameter tensile strength keeps constant more or less, the free formaldehyde concentration and the viscosity of the resol increase with the degree of substitution and the curing energy decreases. While the content of free formaldehyde is still below regulatory limits, the increased viscosity and especially the decreasing curing energy (equivalent to reduced reactivity) must be taken into consideration when applied to technical processes (e.g longer pressing times or higher pressure).

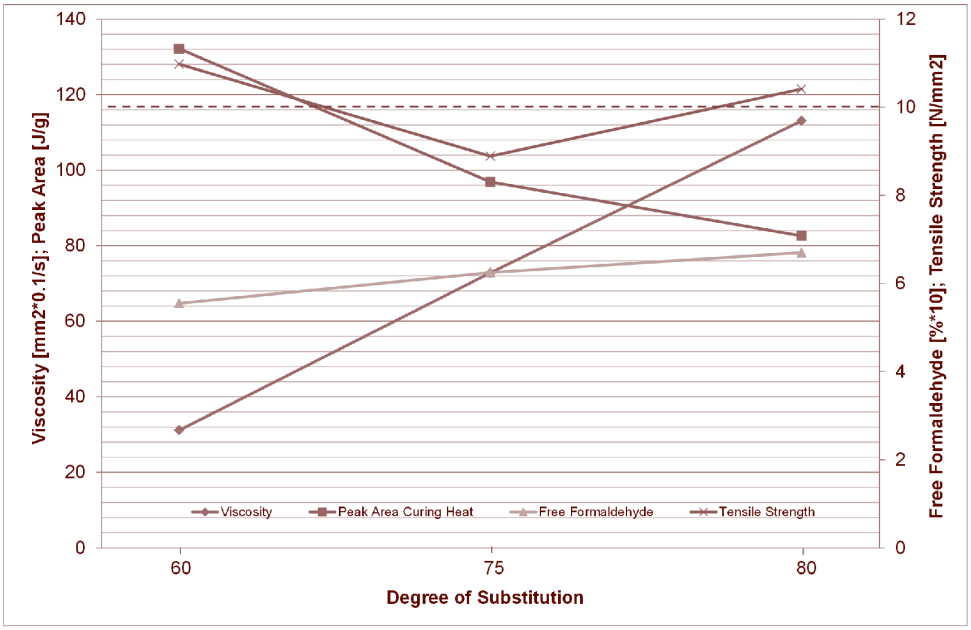

Fig.1 – kinematic viscosity, curing energy, free formaldehyde content and tensile strength as a function of degree of substitution

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SUSTAINABLE BIOMATERIALS FOR WOOD PANELS ADHESIVES

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There has been increasing international attention given to the production and use of sustainable adhesives, or also called renewable wood adhesives, for the manufacture and production of reconstituted and engineered wood products. This interest in these bio-based adhesives has arisen due to several drivers, the most important being recent government legislative changes to minimise the health effects relating to product emissions of volatile organic chemicals (VOCs), most notably formaldehyde, and the use of renewable materials as a cost-effective replacement for petrochemical components of adhesives. This has been coupled with an increasing environmental awareness of the consumer and drive for sustainability [1].

There is a significant challenge and even business risk associated with formaldehyde specially in developed countries. While the low levels of formaldehyde emitted from wood panels today have proven to be safe (CARB emission level), there are still some organizations that believe that any formaldehyde is unacceptable. Their views are not necessarily based in science, but a no formaldehyde solution is required. Obviously this solution must be cost effective. The actual replacement technology is MDI, but for PB and MDF in continuous presses and platen presses is very difficult due to the lack of tack, less reactivity and the use of release agent to avoid sticking.

Bio-based adhesives were defined as “materials of natural, non-mineral or non-petroleum based origin that can be used either in their natural state or after small modification, capable of reproducing the behaviour and performance of synthetic resins” [2].

Despite the great interest of sustainable adhesives, because they are environmentally friendly and renewable, they also present several disadvantages, with respect to synthetic adhesives such as amino resins and phenolic resins: They are more expensive, with natural variations and less reactivity, which means finally in lower production speeds and a higher production cost.
Tannins and nanocellulose are good candidates for sustainable materials, possible to use, for the manufacture of adhesives in the wood composite board industry. The radiata pine tannins have proven to be an excellent renewable material to replace phenol, in adhesives for plywood boards and nanocellulose also with great potential to reinforce synthetic resins, achieving a decrease in the consumption of adhesives. However, its use is not easy, and some difficulties must be solved, such as the high viscosity of adhesives and its high-water content, which limits its industrial applications.
This paper shows some results obtained at laboratory scale and industrial tests demonstrating the potential of using radiata pine tannin as options for sustainable adhesives as well as the use of nanocellulose to reinforce amino resins for wood panels.

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ECOFRIENDLY ADHESIVES BASED ON PINE BARK EXTRACTS

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The forest biorefinery concept is a strategic approach in line with present concerns relating to sustainability and the adverse ecological footprint of petroleum-based fuels and polymeric materials [1].

In Chile, *Pinus radiata* constitutes over 50% of forestry plantations, and it is majorly used in the pulp and paper industry. *Pinus radiata* bark is a major byproduct of such industrial activities, which is commonly burnt for energy production [2]. However, due to its rich chemical composition, this bark could also be exploited as a source of high-value chemicals. Therefore, we found an interesting opportunity in developing a bark biorefinery that first extracts valuable compounds such as extractives, tannins and non-cellulosic polysaccharides (NCP), and thereafter converts the residue into biofuels and energy.
As a first step in this direction, we at UDT are attempting to synthesize high-performance adhesives for engineered wood panels from water-soluble *Pinus radiata* bark extracts. For such purpose, we have developed a highly-effective continuous bark extraction process and are making our first attempts to prepare resin adhesive formulations based on the resulting extracts. Adhesion improving modifications of these bio-based raw materials as well as available and experimental crosslinkers have also been considered.

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FUNCTIONAL BIOMATERIALS FROM MACROALGAE: EXPERIENCES FROM THE LABORATORY TO THE FIELD

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In the last years, it has been frequent to hear about sustainable processes and biodegradable products. This has instigated reduction in the use of plastic bags and synthetic chemical products used in agriculture. However, the industry requires plastic containers and chemicals in order to prevent infections triggered by phytopathogens. In this context. Macroalgae's versatility is useful when producing biomaterials, due to their chemical characteristics that offer wide protective capabilities against oxidative agents, as well as bacteria and fungi. Their physico-mechanical properties and their capabilities to form matrix with natural fibers ensure fluidity and molding at high temperatures for thermoplastic production, and fiber interactions, for paper production. In this context, The Interdisciplinary Group of Marine Biotecnology (CB-UdeC), in cooperation with the Biomaterials Area at UDT (UdeC) and the Laboratory of Forest Resources (Engineering Faculty) have executed R+D projects with the aim of developing biodegradable thermoplastics [1] for the farming industries [3,4], and bioactive paper-based products for phytopathogen control in the fruit industry [2]. The macroalgae were collected at different sites in the Biobío province and later selected according to their chemical and structural characteristics, antifungal capabilities and physico-mechanical properties for paper and plastic production. The production of thermoplastics was performed under ASTM and SCAN standards [1,2,3]. On the other hand, bioactive paper was produced under TAPPI standards [2]. All processes related to production are protected by 4 invention patents. Mechanical properties of thermoplastics were characterized by TGA and rheological testing, as well as in vitro and in situ biodegradation and bioactivity testing. Regarding paper products, burst, tear and breaking length indexes, as well as bioactive capability, were assessed. Fruit containers, bags, fruit sleeves and graft holders presented mechanical properties capable of resisting thermal processes concerning extrusion and injection, along with proper biodegradability within 90 and 180 days under simulated compost conditions and outstanding antifungy capabilities [1,3]. Additionally, fruit containers (fig.1) and seedbed bags (fig.2) were assayed under real industrial conditions, successfully completing a one-year production cycle [4]. On the other hand, alga-based bioactive papers presented mechanical properties similar to those conventionally used in the fruit industry, with additional antioxidant, antibacterial and antifungal capabilities [2]. This last characteristic was tested under laboratory and industrial fruit-packing conditions (Fig.3) inhibiting the growth of B. cinerea in 50 to 70% in exportation apples (Fig.4) The optimal results obtained from these tests reinforce and expand the development of these functional materials from macroalgae, contributing to their valuation, used and cultivation as a main raw material.

Fig. 1 – From left to right, biodegradable containers after 2 months of use under real conditions, after 4 months of use and after 6 months of use with blueberry plants

Fig. 2 – Holder biodegradable seedlings with blueberry plants in a commercial nursery

Fig.3 - Assembly of the experiment in packing. A) Selection of apples, B) Inoculation with pathogen B cinerea, C) Generation of standard wounds and D) Formation of the experimental pallet.

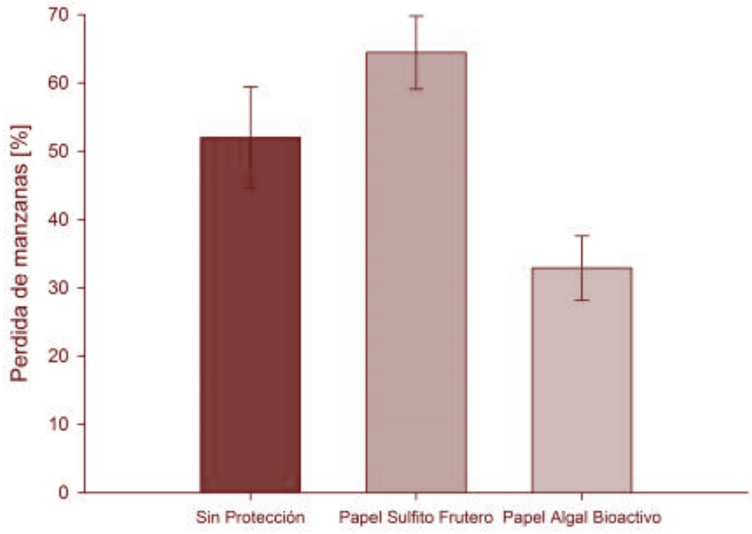

Fig.4 – Experience under real use conditions. Protective capacity of apples against the phytopathogenic fungus *B. cinerea*. The bioactive algal paper managed to reduce the loss of apples by 37% compared to the losses occurred in the control group (without protection). In relation to the loss achieved by the treatment with the conventional product (fruit sulphite paper), a reduction of 49% was achieved.

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MODELLING THE EFFECT OF ENVIRONMENTAL CONDITIONS ON MICROALGAE'S GROWTH DURING CONTINUED CULTURE

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The growth of microalgae has awakened a growing interest in the last years, due to its potential as an alternative to cropland. Within its advantages, we can highlight the efficient use of solar energy to produce biomass, making it possible to annually obtain a higher performance and under certain conditions. Many strains can build up high concentrations of compounds of commercial interest, such as proteins, lipids, carbohydrates, glycerol, pigments or biopolymers [1].

Microalga biomass has a wide variety of uses and applications, that go from its use as food for animal or human consumption, to its use for biofuel production. Some of the biofuels that can be produce from microalgae are methane, hydrogen, ethanol, biodiesel, among others. Moreover, microalgae can be use to obtain biotechnological products for medical purposes, and for cosmetics and adhesives production.

Modelling of microbial growth is normally based on models that were published between 1940 and 1950. The study of these models is crucial to understand and describe many phenomena involved in biotechnological processes. Models are nowadays used to predict growth rates, production of pigments and metabolic products, response to changes in light, effect of temperature and available substrates. The study of these responses can lead to a better comprehension of the environmental variables that define the conditions of microalgae culture, contributing to the improvement of bioprocess.

The study proposes to evaluate the effect of disturbance different environmental conditions on the response of growth rate. Assessing the time response to adapt the growth rate that these photosynthetic microorganisms have, using as methodology the evolution of the oxygen production rate (OPR) as a response indicator, analysing its representation through traditional culture kinetics models. Given that, time response is some not many studied and that can alter the prediction based on traditional models. Making the models inaccurate in a transient state. Hence, it is necessary to study this, given the potential biotechnology applications of microalga culture.

Figure 1 represents the OPR volution when it is submitted to an absence of light. At the moment of the disturbance there is a change in the photochemical activity, moving from an initial OPR state with a 0.4456 mg/L min to a dark phase where OPR changes for a short period to a 0.1039 mg/L min of oxygen consume rate. When the light returns to its initial condition so does the OPR. The OPR come back to the first state. These experiments allow to estimate that the microorganisms' response doesn't show a delay to light source disturbance. The study will continue to evaluate the effects of other disturbances in substrates as carbon and inhibiting compounds.

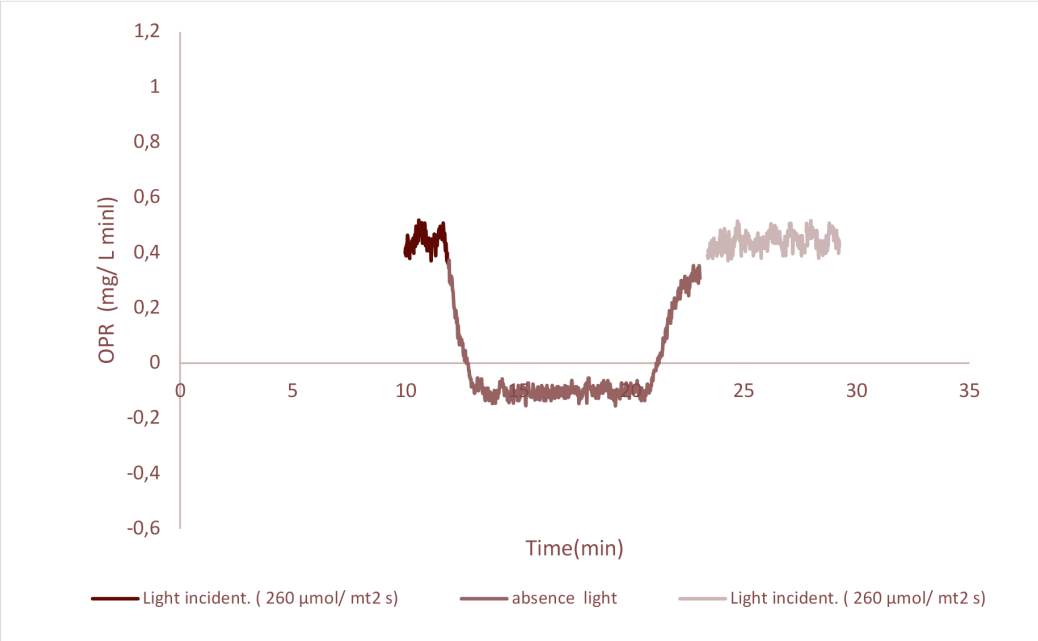

Figure 1: An evolution of the OPR during the incidental light intensity disturbance for a cellular concentration of 0.63 g_{DCW}/L.

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COMPARISON BETWEEN TWO METHODS OF PRETREATMENT OF AGRICULTURE WASTE FOR THE PRODUCTION OF CELLULOSE NANOFIBRILS

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Over the past few years, research on nanocellulose has extremely increased because this material has many potential applications thanks to its attractive properties. It can be used to produce porous materials, functional surfaces, coatings.
In this study, agriculture residues as wheat straw were used like starting material to produce cellulose nanofibrils (CNFs). A preliminary delignification step is necessary to enhance following nanofibrillation process (1).

Previous studies have shown that organosolv (OS) pretreatment catalyzed by H_2SO_4 easily allows deconstruction of lignocellulosic biomass in its three main components: cellulose, hemicellulose and lignin (2), making then the process suitable for CNFs preparation.

Starting from these results we made a comparison between OS pretreatment and that based on eutectic mixtures (Deep Eutectic Solvents - DES -).

OS pretreatments were done using a solids loading of 10% (w/v) and 2.5 % (w/w) of H_2SO_4. The severity of the process has been taken into account to maximize the deconstruction of the biomass and preserve the integrity of the cellulose fraction. By composition analysis has been possible to determine the percentage of each component (glucans, xylans, lignin) after the pretreatment, achieving a glucans recovery of 70%.
DES mixtures were prepared by mixing choline chloride with different carboxylic acids. Multiple tests were performed using different ratio of two components and changing temperature and reaction time. The best DES treatment gave a glucans recovery of 73%. Results of delignification of two pretreatments were comparable in term of composition analysis of the biomass.

The nanofibrillation process was realized with both biomass (OS and DES). Mechanical properties of suspensions and films produced were investigated.

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CURRENT RESEARCH ON NANOCELLULOSE APPLICATIONS IN FOOD AND PHARMACY FIELDS AT WEST VIRGINIA UNIVERSITY

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Currently in the US Appalachian region there is a vast amount of low-value, low quality hardwood that can be potentially used as feedstock for novel bio-products. Only West Virginia generates 2.41 million dry tones of underutilized wood per year that represents a great source for nanocellulose production. Today the technology to separate and obtain wood polymers at nanoscale exists and it has been demonstrated with success; however, specific applications for these novel raw materials are still a challenge. At West Virginia University, we have been developing the scientific and technological basis to utilize lignocellulosic sources as a novel template for organic and inorganic chemical compounds and promote their utilization in applications related to the packaging, catalyst and medical/pharmaceutical fields [1, 2]. We have developed a simple but novel methodology to synthesize copper nanoparticles (CuNPs) on cellulosic-based materials with effective antimicrobial properties when applied on polyvinyl alcohol thermoplastic films [3, 4]. Cellulose based materials were specifically chosen as nanoreactors in the synthesis of CuNPs to facilitate the metal antimicrobial availability within/atop thermoplastic resins. The cellulosic-CuNPs were effectively incorporated in a thermoplastic resin, polyvinyl alcohol (PVA), and the antimicrobial analysis demonstrated that one-week exposure of nonpathogenic *Escherichia coli* DH5α to the nanocomposite films resulted in up to a 5-log reduction in *E. coli* survival [3, 4]. Moreover, PVA films with the hybrid c-CuNPs were also effective against the genetically diverse model of eukaryotic organism *S. cerevisiae* [5]. To move beyond these promising preliminary results and optimize the nanocomposites for the flexible packaging industry, we have started a systematic evaluation of the release and antimicrobial activity of metal nanoparticles synthesized on improved raw cellulosic-based materials [6]. We have also explored the application of the hybrid lignocellulosic material and copper nanoparticles as catalyst in important chemical transformations. Copper was synthesized onto carboxymethyl cellulose, nanofibrillated cellulose, TEMPO-nanofibrillated cellulose, and lignin. The lignocellulosic frames were used with the aim of providing an effective support for catalyst copper and allowing its further reutilization. Each organic support was successful and effective in the coupling of copper with the exception of lignin. These complexes were used as heterogeneous catalysts to produce 1-benzyl-4-phenyl-1H-[*1,2,3*]-triazole from the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) between benzyl azide and phenylacetylene. Each reaction was carried out in water and acetonitrile. Those performed in water were completed in 15 minutes while those done in acetonitrile were allowed to react overnight, reaching completion in about 20 hours.The yields for Cu-CMC resulted in over 90% for those reactions performed in acetonitrile. All catalysts were easy to recover except Cu-lignin which could not be filtered or extracted from the reaction effluent [7]. Finally, we have been using nanocellulose in combination with polyvinyl alcohol and polyethylene glycol matrices for drug delivery purposes. Acetaminophen has served as an initial model drug in the formulations. Preliminary release studies produced release profiles specific to each formulation.

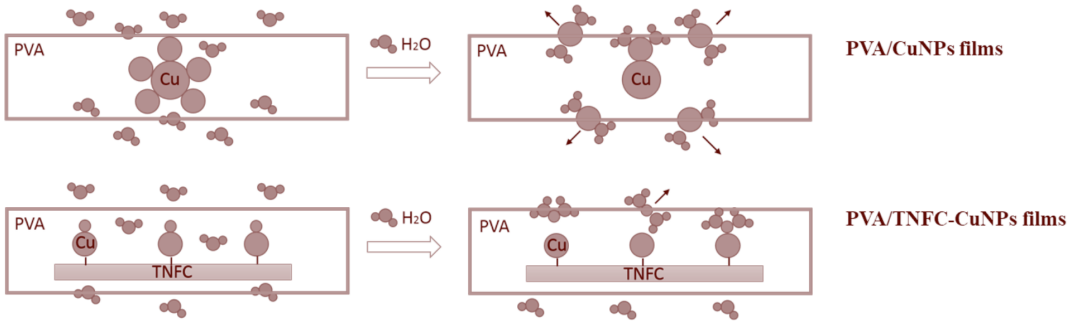

Fig.1 – Proposed release mechanism of copper ions from a polyvinyl alcohol (PVA) matrix. a) without a cellulosic material; b) copper synthesized on a cellulosic matrix (TNFC: TEMPO nanofibrillated cellulose). CuNPs: Copper nanoparticles.

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BIOREFINERY: MACRO, MICRO AND NANOCELLULOSE FIBERS FROM FOREST AND AGRO-INDUSTRIAL WASTES

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Globally, the industry has an increasing need to replace fossil raw materials with renewable ones. On the other hand, the generation of by-products in large volumes in agroindustries causes environmental problems. These two factors have led to the development of integrated biorefinery, with multiple processes and products that plays a central role in sustainable development and in the bioeconomy. Residual biomass, (by-products) generated in the brewing, oil, banana, cacao, coffee, rice, export of roses, etc .; both in the field during the harvest and in the industrial plant during its processing, it is constituted as a renewable raw material that contains valuable chemical components, which are potential sources of bioenergy, biomaterials and bioproducts. Countries such as Ecuador must stop exporting raw materials and export products with high added value, for this reason research and development of new processes and products is essential. Universities, research institutes and private companies must form multidisciplinary work teams that promote innovation and development of new technologies that are friendly to the environment and have their own markets. Biomass is a complex material due to its structure and chemical composition and requires physical, chemical, physical-chemical and biotechnological processes that facilitate the fractionation of the plant cell wall, the isolation and characterization of its biopolymers for potential industrial applications. Fig. 1 schematizes the deconstruction of the cell wall to access cellulose, isolate and purify it to obtain macro, micro or nano fibers or depolymerize it in glucose and then ferment it to obtain bioethanol. In general, biorefinery facilitates the procurement of bioenergy and bioproducts.

Fig. 1 Deconstruction of the plant cell wall in its components: cellulose, hemicellulose and lignin. [1]

During the last 20 years organosolv technology was developed using organic solvents and solubilizes or extracts one or two of the biopolymers that make up the plant cell wall; These solvents are volatile, toxic and require careful handling. In the previous decade, ionic liquids were developed as solvents of cellulose, these have advantages

over traditional organic solvents such as not being volatile and being less toxic; Its disadvantage is the cost and its difficult handling. The last generation of solvents used in the conversion of biomass are deep eutectic solvents, which are non-volatile, selective, more environmentally friendly, more economical and easier to handle. Agribusiness, the forestry industry and industry in general could incorporate biorefinery into their facilities and obtain greater added value, making them more profitable and more competitive. Three case studies are presented: 1) Nanocellulose fibers from agroindustrial waste of apples and peas [2]; 2) Obtaining cellulose nanocrystals from by-products of African palm oil extraction [3]; and 3) Extraction of lignin and hemicellulose from the lignocellulosic matrix and obtaining better quality cellulose fibers [1]; as examples of biorefinery for obtaining macro, micro and nanocellulose fibers with potential applications in the textile industry, pulp and paper, packaging, cosmetics; and for an integral use of the biomass, valorization of the by-products of the agroindustry and industry and improve its profitability. All this will improve the trade balance of imports and exports and allow sustainable development within the concept of bioeconomy.

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PREPARATION AND CHARACTERIZACIÓN OF β-CHITIN MICROFIBERS (CHMF) FROM SQUID FISHERY WASTES

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Chitin or poly (β-(1→4)-N-acetyl-d-glucosamine) is a natural polysaccharide synthesized by large numbers of living organisms. It is considered as the most abundant natural biopolymer after cellulose. In the native state, chitin occurs as ordered crystalline microfibrils, which are structural components in the exoskeleton of arthropods or fungal cell wall[1]. Depending on its source, chitin exists as two crystalline allomorphs, namely in α- and β- forms. The α-chitin isomorph is by far the most abundant, whereas β-chitin is found in association with proteins in squid pens and in the tubes of some worms. Both chitin allomorphs are biodegradable, biocompatible and nontoxic but highly insoluble in aqueous or common organic solvents, which limit their applications. It is known that β-chitin is less crystalline allomorph and it shows higher water swelling capacity. In Chile, near 46,000 ton/month of Humboldt squids (*Dosidicus gigas* Wild) are caught for human consumption. As a consequence, large amount of squid pen byproduct is generated, which is currently used as fish flour extender. However, it could be used as source of value-added source of β-chitin and protein, respectively.

Recently, the use of chitin micro and nanofibers as natural reinforced fillers for bioplastics has been studied, but novel and larger applications for this material are still needed. Various methods have been investigated to obtain chitin microfibers from different species, most of them including application of high mechanical force. The goal of the present work is to prepare and characterize β-chitin microfibers (ChMF) from squid pen residues for agronomical applications. Squid pen containing 75-80% of proteins, 20-25 wt% of chitin and 1.8 wt% of ashes on dry bases was used to extract chitin. Extraction was carried out by repeated (2x) deproteinization (NaOH 1M) and demineralization (HCl 1M) treatments. Obtained chitin macrofibers were dried and grinded to a 1 mm size. Afterwards, 2 wt% of chitin fibers was suspended in water and the suspension was passed throughout a massive collider equipment (Mazuko) for 3 cycles until a gel was obtained. Isolated squid pen chitin and its gel were characterized by ^{13}C CP-MAS NMR, FTIR, TG-DTG, SEM, TEM and AFM. ChMF structure was confirmed in gel after 10 cycles in the massive collider equipment (Figure 1). The chemical structure of ChMF was similar to the original chitin source. The radish seed germination assay shows that ChMF display phytostimulant properties, suggesting its application in organic and traditional agriculture.

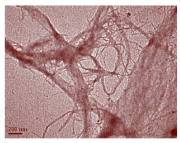

Fig.1. TEM image of β-chitin microfibers.

Acknowledge. Author thanks financial support of CONICYT PIA/APOYO CCTE FB170007.

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THE ROLE OF THE DEGREE OF POLYMERIZATION OF CELLULOSE IN THE DECONSTRUCTION OF THE CELL WALL FOR OBTAINING CELLULOSE NANOFIBRILS (NFC)

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Cellulose nanoparticles comprise a broad spectrum of materials obtained by the destructuration of the cell wall. Due to the surprising intrinsic properties of these nano cellulose particles, such as a Young's modulus similar to that of steel but 5 times lighter in weight, low density, surface area 7 times greater than that of carbon nanotubes, and its natural, renewable and biodegradable origin, is that in the last decade several research centers have focused their efforts on the industrial scale production of this nanomaterial. However, the processes of deconstruction of the cell wall by mechanical methods require large amounts of energy, which is why the process of producing CNFs (cellulose Nanofibers) is expensive. To overcome this obstacle, several chemical and enzymatic processes have been proposed as pretreatment of the pulps prior to the mechanical process of obtaining CNFs. The use of cellulase enzymes as pretreatment for the production of CNFs has been one of the most studied and promising, since it favors the process of deconstruction of the cell wall and can decrease the specific energy consumption up to values close to 90%. The effect of the enzymes during the fibrillation process has been widely reported, however, the available information does not allow to clearly establish the relationship between the degree of enzymatic hydrolysis and both the ease of fibrillation achieved for a certain amount of energy applied and the morphological and resistance of the CNFs produced. In this work, CNFs pretreated enzymatically with different loads of enzyme and different numbers of passes through the homogenizer were produced. It was determined that the decrease in the degree of polymerization (DP) plays an important role in the processes of fibrillation of the cell wall for CNF production. Moreover there is a direct relationship between the degree of polymerization and the length of the CNF (transverse rupture of the macro/nano-particles) (Figure 1) and a polynomial relationship between their degree of polymerization and diameter (longitudinal rupture of the macro fibrils). On the other hand, it was observed that the CNF that were produced from pulps treated enzymatically with a lower degree of polymerization have the lowest intrinsic mechanical strengths.

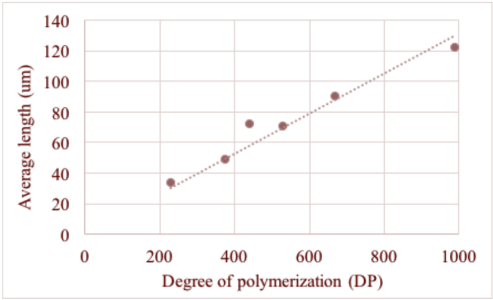

Figure 1. Relationship between the degree of polymerization (DP) and the average length of suspensions of cellulose nanofibers

COMBUSTION OF REFINED RENEWABLE BIOMASS FUEL (RRBF) IN A FLUIDIZED BED

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Within the framework of EU-Life+ research project MARSS (Material Advanced Recovery Sustainable Systems) the outlet stream of a mechanical-biological treatment plant for the processing of mixed municipal solid waste is further processed to produce RRBF (Refined Renewable Biomass Fuel). The material is dry and has (very) small particle sizes below 40 mm, which makes it impossible to be burnt in standard grate firing systems. Fraunhofer UMSICHT operates a bubbling fluidized bed combustion plant with a nominal fuel input of 100 kW suitable for combustion test campaigns. Three test campaigns with RRBF derived from different seasons and therefore differing composition and moisture content were performed with combustion temperatures between 850 and 925 °C.

The received RRBF as well as the fly ash from the cyclone were analyzed. Proximate and ultimate analyses were performed as well as additional elemental analysis for sodium, potassium, chlorine, sulfur and phosphorous. The fuel and ash melting behaviour was examined, too.

The first test with RRBF revealed, that with the original preparation method there were several oversized particles in the material, so that the feeding system of the combustion plant was blocked. After secondary milling in a single shaft shredder no more blockage was observed and the material flow inside the plant was quite steady and reproducible. The following two batches delivered to Fraunhofer UMSICHT were directly treated with secondary milling and no dosing problems occurred during combustion test campaigns.

Table I gives the results of fuel analyses, while Table II shows the ash melting behaviour of the fly ash taken from the primary cyclone. The fuel analysis showed high ash contents between 27 and 37 weight-% on dry basis, while the lower heating value lay in the range of 10.5 – 13 MJ/kg for the original substance. The ash softening temperature was above 1,150 °C and therefore no bed agglomeration was observed. Although the heat loss of the combustion reactor due to its relatively large surface area for the small reactor volume was very high, combustion at above 900 °C could be maintained even without preheating of the combustion air. The carbon content of the fly ash was below 0.8 % for the first two combustion campaigns and below 2 % for the third, which indicates nearly complete combustion in the bubbling fluidized bed with sufficient residence time. The content of phosphorous in the fly ash was above 1.1 % and therefore this is an interesting material for prospective phosphorous recovery, potentially together with sewage sludge or ash from sewage sludge combustion.

From the combustion tests it became clear that the RRBF produced from the outlet of mechanical-biological treatment of mixed municipal solid waste is a potential fuel for bubbling fluidized bed combustion for the production of either process heat or steam for a power plant without the necessity of additional fuel, as the lower heating value is high enough for self-sustained combustion. The fly ash is an interesting source for future phosphorous recovery, as its content is greatly enriched in comparison to the original material. [1]

Table I: Fuel Analysis

	Original Substance			Dry Basis			Dry Ash Free		
	1. Batch	2. Batch	3. Batch	1. Batch	2. Batch	3. Batch	1. Batch	2. Batch	3. Batch
Water [%]	13.2	14.99	24.5	-	-	-	-	-	-
Ash [%]	23.3	31.88	21.74	26.84	37.5	28.8	-	-	-
C [%]	33.18	29.58	29.07	38.23	34.8	38.5	52.26	55.68	54.07
H [%]	5.55	5.58	5.89	4.7	4.6	4.2	6.42	7.36	5.90
N [%]	1.56	1.19	1.43	1.8	1.4	1.9	2.46	2.24	2.67
O [%]	35.23	29.39	41.86	27.08	18.9	26.6	37.01	30.24	37.36
S [%]	0.38	0.48	0.3	0.43	0.56	0.4	0.59	0.90	0.56
Cl [%]	0.8	0.71	0.91	0.92	0.84	1.2	1.26	1.34	1.69
Na [ppm]	6,290	5,326	5,616	7,250	6,265	7,439	-	-	-
K [ppm]	864	5,728	4,938	996	6,738	6,541	-	-	-
P [ppm]	2,150	1,471	2,103	2,480	1,730	2,786	-	-	-
LHV [MJ/kg]	12.882	10.451	11.104	15.212	12.7	15.5	20.79	20.32	21.77

Table II: Fuel and Fly Ash Melting Behaviour

	RRBF			Fly Ash		
	1. Batch	2. Batch	3. Batch	1. Batch	2. Batch	3. Batch
Shrinkage Start Temperature (SST) [°C]	1,151	1,150	1,148	1,168	1,159	1,152
Deformation Temperature (DT) [°C]	1,180	1,172	1,172	1,180	1,170	1,196
Hemisphere Temperature (HT) [°C]	1,187	1,175	1,175	1,183	1,177	1,197
Flow Temperature (FT) [°C]	1,214	1,190	1,190	1,192	1,186	1,215

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UPDRAFT GASIFICATION OF MUNICIPAL SOLID WASTE WITH POLLUTANT EMISSIONS REDUCTION

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Nowadays, solid waste treatment and disposal is one of the main problems faced by the Chilean society. After Turkey, Chile is the country that most disposed MSW in landfills among the 34 countries of the Organization for Economic Cooperation and Development (OECD). Currently, 77% of the almost 7 million tons of urban waste generated in Chile are disposed in one of the 38 sanitary landfills distributed across the country, fronting a close opposition from neighbors and environmentalists, and without any potential valorization of these residues. The main route for MSW deposition in the world, instead landfill or composting, is through the incineration, due to its advantages of energy recovery and reducing the waste volume and weight. However, some inherent properties of MSW such as high moisture content and low calorific value are the main drawbacks associated the process and as a result, MSW combustion has low thermal efficiency and high pollutant emissions, principally arsenic (As), volatile chlorides, heavy metals, dioxins, furans, polycyclic aromatic hydrocarbons (PAHs) and particulate material (PM). These components are carcinogenic, teratogenic and mutagenic elements and requiring expensive cleaning systems in the incineration plants. Updraft gasification combined with producer gas combustion, as MSW thermal treatment, appear to be an alternative to the incineration with environmental advantages, mainly in relation to the emissions reduction, considering that updraft gasifiers are capable of process feedstocks with a wide range of sizes, compositions and water contents. The main drawback of this technology is that, notwithstanding there are significantly lower pollutant emissions when compare to incineration treatment, the presence of PAHs in the producer gas still remain as an unsolved problem.
This study assessed the technical economic and ecologic-energetic feasibility of a new two-stage thermochemical technology for MSW treatment, consisting of updraft gasification and plasma converter system for producer gas cleaning (G–Pl), assessing mixtures of waste with different composition, water contents and heating values. The comparison results and the characteristics and particularities of each process were presented. In the environmental analysis the pollutants emissions of the conventional incineration plant are much larger than the emissions when applied the proposed technology, demonstrating the ecological viability of the implementation of this technology for MSW treatment.

Keywords: Updraft Gasification, Plasma, emission, incineration, Municipal Solid Waste, Ecologic-Energetic analyze

PYROLYSIS OF MUNICIPAL SOLID WASTE IN CHILE: AN ECONOMIC AND ENVIRONMENTAL ASSESSMENT

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Chile's waste volumes have increased steadily in recent years as its population and prosperity have grown. Per capita waste production is now the highest in Latin America, while recycling rates are still low. About a quarter of municipal waste is currently stored on improper or open landfills. Moreover, the generation of municipal waste is expected to double by 2025 compared to 2012. As a result, there is a need for the reduction of waste volumes as well as for efficient technologies to valorize municipal solid waste (MSW).

Various technologies for the utilization of MSW exist, but they all have specific disadvantages. Anaerobic digestion of the organic fraction of MSW has been increasingly applied in Europe and California. However, anaerobic digestion requires source separated waste fractions since non-organic components such as plastic waste cannot be degraded by microorganisms. Apart from individual pilot projects, waste separation is not yet widespread in Chile. Since domestic waste often has a high moisture content, it is also not an ideal feedstock for incineration or other thermal processes such as gasification. These problems could be overcome via intermediate pyrolysis, a thermo-chemical process to convert MSW into different energy-dense products (gas, char and oil). Compared to direct incineration, the combustion of pyrolysis gas in an engine generator is more efficient at smaller capacities and therefore better suited for a decentralized implementation. In comparison to anaerobic digestion, intermediate pyrolysis accepts a broader range of feedstock materials. For instance, food waste and packaging can be processed together without further separation. Moreover, the pyrolysis pathway allows for the production of fuels and other value-added products in addition to electricity. With regard to the predicted cost reductions for solar and wind power in Chile, alternative sources of income besides power generation could be advantageous for a waste-to-energy project.

In this article, an economic and environmental assessment of the intermediate pyrolysis of MSW in Chile is carried out. To this end, a simulation model is developed which represents the mass and energy balances of the pyrolysis plant, the required capital investments and the resulting operating costs. Carbon dioxide emissions along the value chain are compared to fossil-based reference processes to analyze the ecological benefit of utilizing MSW via pyrolysis. The model is applied to evaluate the profitability of a potential pyrolysis plant with respect to the income from gate fees, electricity and fuel production, metals recovery and potential carbon credits. A Monte-Carlo-Simulation is carried out to explore the impact of uncertain framework conditions, such as the electricity price. In particular, economies of scale, minimum plant capacities and the associated financial risk are examined. The results indicate that intermediate pyrolysis could offer economic and ecological advantages over the incineration of MSW in Chile.

ADVANCED THERMOCONVERSION PROCESS FOR MUNICIPAL AND HAZARDOUS SOLID WASTES TREATMENT

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Since the end of World War II, the human society generate more and more domiciliary and industrial wastes per capita at a level that is becoming unmanageable, causing permanent damages to the environment. Particularly in Chile the disposal of MSW is a major and urgent problem, 77% of the almost 7 million tons of municipal solid waste generated are disposed in one of the 38 sanitary landfills of the country, fronting a close opposition from neighbors and environmentalists, and without any potential valorization of these residues. Plasma gasification combined with producer gas combustion, as MSW thermal treatment, appear to be an alternative to landfills and incineration with environmental advantages, mainly in relation to the emissions reduction, considering that plasma gasifiers are capable of process feedstocks with a wide range of sizes, compositions and water contents. High temperature thermal plasma has as major drawback the high energy consumes. Therefore the non-thermal plasma induced by microwave is more attractive technology to be applied in MSW treatment due to a comparatively lower energy consumes knowing that AC and DC arc torch processes, consume almost 80% of the energy they generate, instead the microwave-induced plasma (MIP) process consumes only 20% of the recovered energy. MIP gasification also carries the advantages in terms of simplicity, compactness, lightweight, uniform heating and the ability to operate under atmospheric pressure. The present paper assessed the current knowledge available for MIP gasification of solid fuels and waste and the technical economic and ecologic-energetic feasibility of the implementation of this technology for municipal and hazardous solid wastes valorization in Chile.

Keywords: Microwave-induced plasma, emission, Municipal Solid Waste, Ecologic-Energetic analyze

PYROLYSIS OF POST-CONSUMER PLASTICS WASTE

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The consumption of plastic worldwide has increased from 1.5 MM ton in 1950 to 335 MM ton in 2016 [1]. The recycling rate of developed countries such as Switzerland, Norway or Germany amounts to 30%. The remaining 70% corresponds to energy recovered by incineration [2]. It is estimated that 8300 MM tons of plastic have been produced worldwide since beginning of plastic industrialization. From this quantity, 9% has been recycled, 12% has been used in energy recovery processes and 79% has been disposed in landfills, waterbodies or vacant lands [3].

Chile is far away from this reality, the plastic consumption per capita is 51 kg per inhabitant [4]. The reported recycling rate do not exceed 10%, mainly mechanical recycling of PET. Therefore, the magnitude of this environmental problem is enormous, but also the opportunity, since there is almost 90% of waste plastic capable of being valued.

There are proven industrial recycling alternatives, such as mechanical recycling, that uses post-consumer plastics in extrusion/injection or extrusion/blow molding processes to reinsert these plastics into the production chain. The processing standards of this type of process require plastics with very low level of impurities or with certain mechanical characteristics, limiting the application of this technology. On the other hand, waste to energy (incineration) processes are presented as a more far-reaching alternative, in terms of the variety of waste treated. However, high environmental standards mean that these technologies have high investment costs, which limits its application range.

Plastic pyrolysis is an incipient technology at industrial level and corresponds to a complement to the existing recycling processes. By means of degradation in absence of oxygen allows to obtain value-added products from plastic waste by manipulating processes variables such as temperature and pressure. An advantage of this process is that pyrolysis allows treatment of waste plastic with less restrictions in terms of raw materials quality in comparison with mechanical recycling.

The Unit of Technological Development has more than 6 years of experience in this area and is pioneer at country and global level with the development of a plastic pyrolysis demonstration plant, which allows to obtain value added products, such as paraffin waxes and oils, from industrial and household plastics waste streams. The plant has been successfully developed and designed to treat 150 kg/h of waste plastics. Currently, UDT possess plastic pyrolysis know-how and capabilities in: (i) Laboratory characterizations facilities (Py GC-MS), (ii) Laboratory scale plants and (iii) Engineering design and construction of a demonstration scale plant.

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NOVEL STRATEGIES FOR THE DEVELOPING "SUPERABSORBENT POLYMERS" BASED ON PINE BARK POLYFLAVONOIDS FOR ENVIRONMENTAL APPLICATIONS

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Novel strategies based on co-polymerization of pine bark polyflavonoids (PF) derivatives with acrylic acid (AA) at different temperatures (20, 40, 60, 80 °C), and PF:AA molar ratio (0.25:1; 0.5:1; 1:1; 2:1) was performed in order to develop bio-based polymers with super swelling capacity. Polyflavonoids were functionalized with unsaturated cycle anhydrides (maleic, itaconic, and citraconic) in order to enhance reactivity toward free-radical polymerization [1]. Polyflavonoids based macro-polymer were characterized by using several methods (gelation, monomer conversion, *sol/gel* fraction yield, and swelling capacity in deionized-, and sea-water). Results reveal high feasibility of maleic-based polyflavonoid derivatives as a convenient co-monomer for acrylic acid polymerization. Temperature and PF:AA molar ratio affected the network properties to a high extent. However, regarless temperature and molar ratio the synthetized polymers show superabsorbent properties (weight gain: 5.000-8.000 %) in a wide range of experimental conditions.

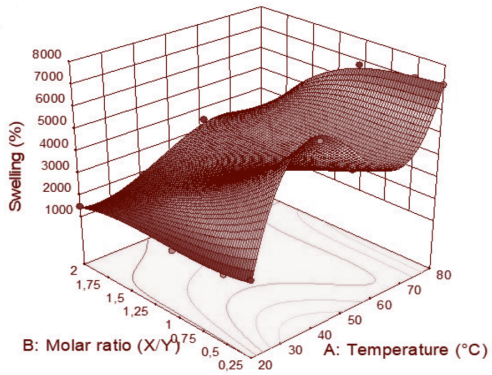

Fig.1 – Swelling capacity of maleic/polyflavonoid-based superabsorbent polymer in function of temperature and molar ratio.

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A NOVEL PHA SYNTHETIZATION TECHNIQUE AND ITS ENVIRONMENTAL ADVANTAGE IN TERMS OF MICROPLASTIC IMPACTS

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Public awareness of plastic contamination has lead to political action and grass-root movements, such as the proposal for a European Directive [1] which bans various single-use plastic items, and the Medellin Declaration on Marine Litter in Life Cycle Assessment and Management [2]. Emerging technologies aiming to alleviate plastic related problems should be thoroughly assessed to prove their benefits. Thus, the aim of present study is two-fold. 1) To assess the environmental and economic life cycle of an innovative biorefinery technology, producing an environmentally-biodegradable plastic and 2) To quantify the benefits of producing such a product, in terms of saved microplastic impacts on humans.

To accomplish these two goals, a techno-economic process flow sheet was developed under Innoven's supervision, using SuperPro Designer [3]. The results from this model were used to populate a detailed LCA inventory, which was analysed using OpenLCA [4] and the Ecoinvent database [5]. Process hot-spots and optimization options were elucidated in this step.

The technology in question takes commonly used feedstock, such as winery wastes and animal manure, and converts these into biogas, digestate and polyhydroxyalkanoates (PHAs) through a

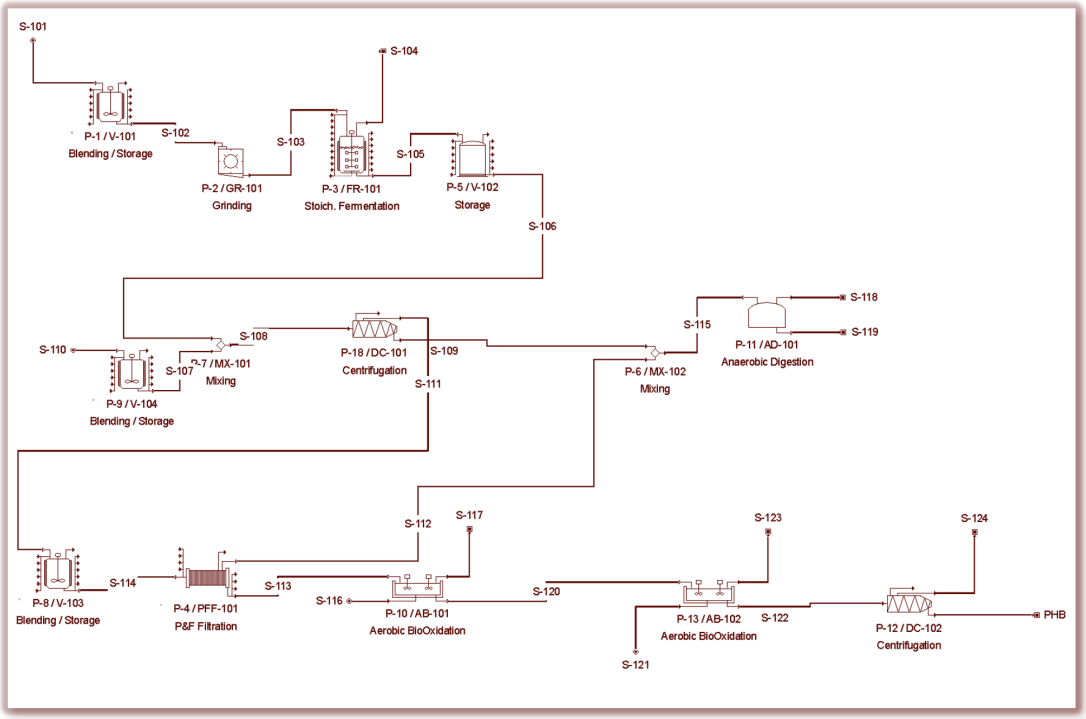

Fig.1 – Process flow diagram developed with the SuperPro Designer Software

modified anaerobic digestion (AD) process. PHAs degrade safely on soil and marine environment [6] thereby it is important to account for saved marine litter, but even more for saved microplastics impacts, which have been shown to cause adverse effects on various animals as well as on humans [7] and have not been quantified so far in any LCA. A novel approach was used to quantify exposure (or the lack of exposure) and final impact of replacing agricultural tunnels generally made of polyethylene with PHA. Though results are preliminary at this point, a case study was made for Northern Italy, where data were available from a waste water treatment plant removing microplastics into waste sludge. Impacts were assessed at endpoints in disability-adjusted life years (DALY).

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PHYSICOCHEMICAL CHARACTERIZATION OF POLY-3-HYDROXYBUTYRATE PRODUCED BY *Bulkholderia xenovorans* LB400

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Poly-3-hydroxybutyrate (PHB) is a hydrophobic polyester produced by a wide variety of bacterial under nutrient limiting conditions and an excess of carbon source. *Burkholderia xenovorans* LB400 has been described as a PHB producer under nitrogen limiting conditions using glucose, xylose and mannitol as sole carbon source. The objective was to characterize the PHB produced by *B. xenovorans* LB400 grown in medium supplied glucose, xylose, or mannitol as the sole carbon source.

The LB400 strain was grown in M9 minimal medium using xylose (PHB_x), mannitol (PHB_m) or glucose (PHB_g) (10 $g \cdot L^{-1}$) as the sole carbon sources, and 1 $g \cdot L^{-1}$ of NH_4Cl as the sole nitrogen source at 30°C. The polymer was extracted with chloroform at 30°C. The solvent was evaporated to a small volume with a rotary evaporator. Finally, the solution was transferred to a Petri dish and dried at room temperature to obtain a PHB film. The polymers were characterized by FT-IR, TGA-DSC and their molecular weight (M_W) was calculated by gel permeation chromatography using chloroform as the mobile phase and a polystyrene curve. All polymers were compared with the commercial PHB (PHB_c).

The FT-IR spectrum showed that the PHB produced from the strain LB400 possesses the same characteristic bands as the PHB_c. However, the intensity of bands was different, proving that crystallinity is different in each polymer, which could be associated with the drying environmental conditions. The thermogravimetric analysis showed a two-step degradation process. The PHB_m showed a previous loss of mass as high as 10%, which could be associated with impurities or higher content of volatile compounds compared with other polymers produced by the strain LB400 [1]. The PHB_c lost 50% of mass (TD_{50}) at 293.40°C, while PHB_g, PHB_x, and PHB_m reached TD_{50} at 292.70, 295.70, and 297.42°C. Between 300 and 380°C, it is possible to observe a decrease of the degradation rate for the three PHBs produced by the strain LB400. The melting temperature (T_m) and the degradation temperature (T_d) were calculated from the maximum of the first and the second endothermic peak in the DSC, respectively. The T_m was 174.18°C for the PHB_c and 175.34, 179.82, and 171.37°C for PHB_g, PHB_m and PHB_x, respectively. The molecular weight of each polymer was 694, 800, 1,724 and 262 g/mol for PHB_g, PHB_m, and PHB_x, respectively. A linear correlation was observed between the polymers molecular weight and the T_m with a R-value of 0.9930.

The use of different carbon sources to produce PHB from *B. xenovorans* LB400 showed to affect on the molecular weight changing slightly their physicochemical properties.

This study was partially supported by Dirección de Investigación, Universidad de La Frontera, Conicyt Scholarship N° 21160515, and Anillo de Investigación en Ciencia y Tecnología GAMBIO (Project No. ACT172128)-CONICYT, Chile

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SYNTHESIS AND PROCESS ENGINEERING OF GLYCEROL BASED POLYESTERS AS TOUGHNESS ENHANCERS FOR COMMERCIAL BIOPLASTICS

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Glycerol is an abundant and cheap biobased molecule, mainly obtained as a co-product of biodiesel production at industrial level. This biobased molecule, which worldwide production from biodiesel industry reached over 30 million cubic meters in 2016 [1], needs the development of new alternatives for its industrial usage to support the growth of the biodiesel sector. An emerging field of application for glycerol is the synthesis of poly(glycerol-*co*-diacids), which can be synthesized through simple and industrially feasible polycondensation routes [2]. The synthesis of glycerol based polyesters has been proposed mainly as biobased and biocompatible materials for biomedical applications. This work explored the utilization of glycerol based polyesters as toughness enhancers for commercial biobased and biodegradable polymers, namely poly(lactic acid) (PLA) and poly(butylene succinate) (PBS). Increasing the toughness of these commercial biobased materials through industrially applicable melt blending strategies could contribute in widening their suitability for applications where higher tensile and impact toughness is required.

In a first section, synthesis conditions for the glycerol based polyesters were explored and a tensile toughness increment for PLA was achieved using a reactive extrusion technique [3]. In a second stage, the addition of PBS to the system was studied and statistical linear regression models were used for modelling tensile and notched Izod properties of the ternary system. Through this approach, biobased materials displaying a tensile strength of 33.8 MPa, tensile modulus of 1.47 GPa and notched Izod impact of 159 J/m were obtained, being comparable to some commercially available non-biobased polypropylene products [4].

Acknowledgements: The authors are thankful to the Chilean National Scholarship Program for Graduate Studies from CONICYT-Chile; the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), Canada/University of Guelph-Bioeconomy for Industrial Uses Research Program Theme (Project # 200001 and 200283); OMAFRA, Canada New Directions Project #050155; the Ontario Ministry of Economic Development and Innovation (MEDI), Canada, Ontario Research Fund, Research Excellence Round 4 Program (ORF-RE04) (Project # 050231 and 050289); the Natural Sciences and Engineering Research Council (NSERC), Canada - Discovery Grants (Project # 401111) for the financial support to carry out this research work.

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DEVELOPMENT AND CHARACTERIZATION OF NOVEL ACTIVE BIOMATERIALS INTENDED FOR FOOD PACKAGING APPLICATION

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Active packaging represents a large and diverse group of materials that are used to prolong the shelf-life of food products, by acting as emitters (antimicrobial agents, antioxidant agents) and/or absorbers (bind ethylene, moisture, CO2 and O2). Due to depletion of fossil resources and harmful effect of petroleum-derived materials on environment, there is an urge need for development of eco-sustainable materials obtained from natural and renewable resources. Starch is renewable, biodegradable, easily modified both physically and chemically, and available in bulk in all parts of the world at low cost, making it as a very attractive raw material for manufacturing of "green" thermoplastics. It is a natural polysaccharide mainly composed of amylose, a linear polymer of D-glucose units attached α-1,4-, and amylopectin, a highly branched polymer of D-glucose units attached α-1,4- with branch points attached α-1,6. On the other hand, pruning is one of the most important cultural operations in grape production. As a consequence of such activity a large amount of grape cane, rich in stilbene, are generate as viticulture waste material. Those compounds were extracted using organic solvent, dried and its chemical composition was determined by chromatographic techniques [1].

In this work, active biomaterials of thermoplastic starch that contain different content of grape cane extract were prepared using compression molding technique. The thermal, structural, mechanical, antimicrobial and antifungal properties of obtained films were evaluated. The obtained results showed that addition of grape cane extract, led to changes in thermal and mechanical stability of films. The formulated thermoplastic starch films showed antifungal activity toward *Botrytis cinerea* and antimicrobial activity toward *Staphylococcus aureus*, suggesting potential application in food packaging as an active biomaterial layer.

Acknowledge. The authors gratefully acknowledge the project CONICYT PIA/APOYO CCTE FB170007 for the financial support.

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GRAPHITIZATION OF LOBLOLLY PINE WOOD AND BIO-CHOICE LIGNIN INVESTIGATED BY *in-situ* X-ray DIFFRACTION AND ELECTRON ENERGY LOSS SPECTROSCOPY

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Graphitization behavior of biomass has long been veiled due to the complex structure of both the precursor biomass and product graphite. X-ray Diffraction (XRD) is a common tool used to study the structure of graphitic carbon, and also the processes used to create graphite. Biomass has been classified as a 'non-graphitizing' carbon source because it produces a 'disordered' graphitic structure after the thermal treatment. However, recent developments in analytical techniques and better insights into the graphitization process have reopened the possibility of utilizing biomass to produce graphite. Although the biomass derived graphite has a disordered structure, locally crystalline graphitic structures can be identified with XRD and transmission electron microscopy (TEM) [1]. In this work, *in situ* high temperature XRD and differential scanning calorimetry (DSC) were used to examine the phase transition occurring between 1,000 and 1,500 °C in loblolly pine wood and Bio-Choice Lignin (BCL). Formation kinetics of two materials were further systematically calculated by interpreting XRD patterns collected from three different graphitization temperatures. Electron energy loss spectroscopy (EELS) was also used to study these wood-derived carbon materials. XRD data of loblolly pine wood showed the disappearance of a disordered carbon phase between 1,300 and 1,400 °C, followed by the formation of a crystalline graphitic phase between 1,400 and 1,450 °C. Lattice parameters and the crystal structure of the loblolly pine wood-derived graphite were systematically calculated from the empirical data. The presence of a large endothermic peak at 1,500 °C in the DSC thermogram supported this observation. Selected area electron diffraction patterns showed the growth of graphitic crystallites after heat treatment. EELS spectra also supported the presence of a well-developed graphite structure. Graphite formation kinetics were studied with, loblolly pine wood was heated to 1,400, 1,438, and 1,450 °C and held for 2 hours while monitoring development of the graphitic (002) reflection. As the treatment temperature increases, the graphitic (002) reflection developed quickly. BCL was also heated to 1,438, 1,475, and 1,500 °C and a similar phenomenon as loblolly was observed. Our analysis confirmed that the graphite formation is more influenced by the thermodynamics because the graphite formation threshold temperature exists. Furthermore, graphite formation temperatures variated depending on precursor materials; physical and chemical structures of biomass also influence the final structure of graphite

Yoo, S. Kelley, S.S., Tilotta, D. C., Pary, S., (2018), Structural Characterization of Loblolly Pine Derived Biochar by X-ray Diffraction and Electron Energy Loss Spectroscopy, *ACS Sustainable Chem. Eng.*, 2018, *6* (2), pp 2621–2629, DOI: 10.1021/acssuschemeng.7b04119

PREPARATION OF PHOTOLUMINESCENCE CARBON DOTS FROM RENEWABLE LIQUID SOURCES BY HYDROTHERMAL SYNTHESIS

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In last few decades, renewable biomass sources were accepted as effective raw materials for the preparation of numerous bio-based products due to their plenty availability and eco-friendly nature [1]. Apart from fuels production, utilization of biomass sources for the making of materials is an interesting re-search area. Carbon dots (CDs) are under the category of carbon materials that are fluorescent in nature and have sizes below 10 nm [2]. In recent years, CDs have received immense attention due to their exciting structural, morphological and physicochemical properties as well as flexibility in the synthesis towards various applications. Here we aimed to synthesize CDs and/or their composites from various renewable sources by simple hydrothermal treatment in water medium.

In detail, a known amount of bio-oil (renewable source) and deionized water were taken. Then the mixture was transferred into a teflon lined autoclave reactor and heated at different temperatures for different times. After the reaction was completed, the auto-clave was cooled down to room temperature. The collected reaction medium was centrifuged and the CDs were obtained as supernatant and showed green emission under UV light. TEM analysis confirmed the formation of carbon dots. Further, the prepared CDs were analyzed by UV-vis absorption as well as photoluminescence (PL) technique. From UV-vis spectrum it was found that the peak at 272 nm attributes to π-π^* transition that corresponds to aromatic sp^2 domains. Also, the study was extended for the preparation of CDs from different renewable liquid sources. Furthermore, a detailed characterization as well as application of the prepared CDs are under study.

Authors acknowledge FONDECYT-CONICYT (Postdoctoral Project No. 3160392), Anillo de Investigación en Ciencia y Tecnología GAMBIO (Project No. ACT172128)-CONICYT, Chile and MRP/UGC-SERO (Proposal No. 1593), India.

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MICROWAVE ASSISTED HYDROTHERMAL CARBONIZATION: A NEW OPTION TO OBTAIN CARBON NANOSTRUCTURES FROM BEET MOLASSES

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Molasses is defined as dark brown and viscous liquid with high content of carbohydrates (40%-70%) and the final product of sugar factories. On the other hand, hydrothermal carbonization of carbohydrates includes several reactions to obtain nanostructures such as carbon foams, graphene sheets or carbon spheres [1]. Moreover if microwave irradiation is used, the decomposition of different biomass can be carried out at low temperatures and short residence time [2]. Considering this information, the main objective of this work was to produce carbon nanostructures from beet molasses derived from Chilean sugar industry using microwaves assisted hydrothermal carbonization (MHC). The first stage of this work contemplates the use of model molecules (Sucrose, glucose and fructose) to evaluate the effect of time, power irradiation, temperature and water content for the microwave assisted hydrothermal carbonization process. Temperature, residence time, moisture, power supply were the parameters evaluated. Obtained products were characterized by morphology (SEM-EDX), elemental composition (Eurovector EA 3000), proximal composition (TGA), functional groups (FTIR) and surface area and porosity (NOVA 1000e). Preliminary results shown that hydroximethylfurfural (HMF) formed is the main precursor of the nanostructures which is in accordance to the described by Titirici (2012)[1]. The HMF concentration increases until the first five minutes, reaching a maximum value and, the decrease within the reaction time leading to the formation of Hydrochar. Morphology of hydrochar can be observed in Fig. 1. B. Furthermore, liquid phase presents micro and nano carbon spheres (Fig. 1. A). Carbon spheres yield decrease while increase residence time from 20% at 1 minute to 4% at 60 minutes. FTIR spectrum shown typical vibrations of carbon spheres. In particular, a vibration band between 1450 - 1750 cm^{-1} due to the C=C bonds, which refers to cyclic aromatic hydrocarbon-like structure. For other hand, higher power irradiation (300 W), decrease particle size.

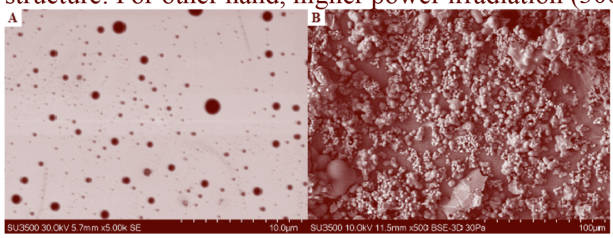

Fig.1 – MHC at 5 minutes, 200°C and 200 W of power irradiation. A) Carbon spheres, B) Hydrochar.

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CARBONIZATION AS RECYCLING STRATEGY FOR CARBON AND NUTRIENTS

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Maintaining our limited soil resources fertile for the feed and food production for a rapidly growing global population is an important issue. Therefore, sustainable soil management is crucial and limited sources of nutrients leads to the necessity to recover plant nutrients such as phosphorus, nitrogen, potassium, and silicon from residues and waste materials. Thermo-chemical conversion techniques (pyrolysis, gasification, hydrothermal carbonisation, combustion) offer opportunities to convert waste into marketable fertilizers and soil amendments targeting multiple functionalities: carbon stabilization for mid to long-term storage in the soil, nutrient recycling, dewatering, logistic of storage and distribution, and tailoring products for diverse applications and markets. Raw materials considered include sewage sludge, green waste, residual wood, food processing residues, cellulosic fiber pulp, landfill material and others.

Utilizing a carbon based product with recovery of phosphorus and silicion as additional benefit is investigated. Data on pyrolysis and hydrothermal carbonization process engineering by varying feedstocks and process parameters (temperature, pressure, time, water content, additives etc.) are presented. The development of fertilizer and soil amendment products optimized for multiple purposes is aimed. The feedstock materials as well as the products are analysed regarding C, H, O, N, S, P composition, moisture, heating value, plant availability of the nutrients, etc. A mass balance on the char constituents as well as on the storage in the soil is given.

The presented, innovative strategies primarily aim at recovering carbon from residues and waste materials. Additionally, closing nutrient cycles and protecting the diminishing phosphate resources are ensured. Moreover, negative emissions apply due to storage of stabilized carbon in the soil. This multiple purpose approach will increase the value of the products and thus facilitate the carbonization of feedstock materials in industrial scale.

CARBON AEROGEL-SUPPORTED Ni FOR UPGRADING BIOMASS-DERIVED VAPORS: A Py-GC/MS APPROACH

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A comprehensive study of carbon aerogel-supported nickel (Ni/CAG) on the catalytic fast pyrolysis (CFP) of torrefied *Eucalyptus globulus* was performed in a micropyrolysis unit (py-GCMS). Effects of torrefaction pretreatment, pyrolysis temperatures (450 – 600°C), catalyst-to-biomass ratio (1:1<C-to-B<1:10) and metal cluster sizes (9.6<D_{pi}<21) on upgrading reactions were analyzed. Torrefaction reduced the selectivity to carboxylic acids to ca. 7%, while furanics, phenols and ketones were increased by almost 50%. Despite the proportional increment on those functional groups, their internal composition was rather different owing to the operation parameters. Ni/CAG was active for hydrogenation under H_2-depleted atmosphere, presumably by a synergic effect between water gas shift and reforming with the phenolics and furanics conversion routes. Catalytic parameters such as C-to-B and cluster sizes influenced the reaction routes by favoring hydrogenation on metal facets and deoxygenation on step/corners sites, as demonstrated by the upgrading parameters (ξ_{L-T} and ξ_{k-A}).

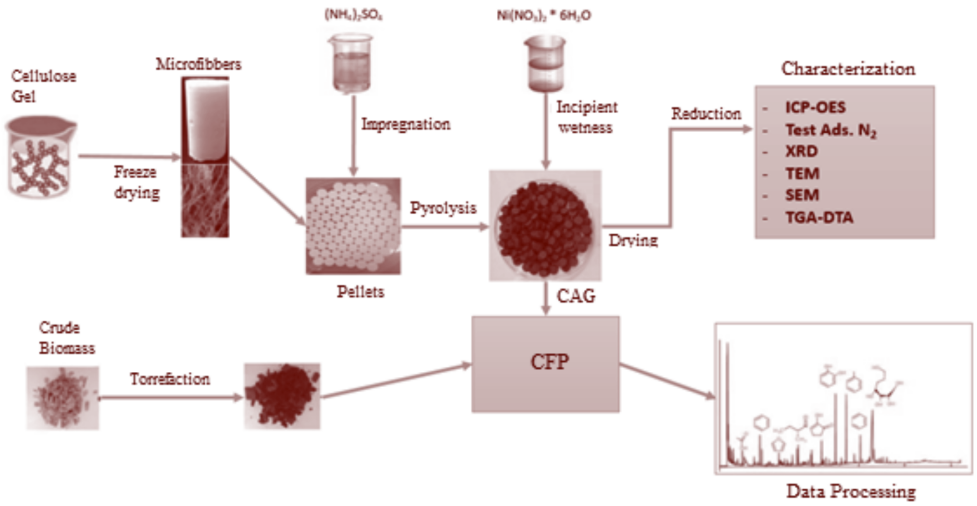

Fig.1 – Graphical abstract

FROM WHEAT STRAW TO LACTIC ACID: ORGANOSOLV PRETREATMENT OF AGRICULTURE WASTE FOLLOWED BY HOMOLACTIC FERMENTATION

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This study is placed in a green path based on pretreatment of agriculture residue, as wheat straw, to produce cellulose nanofibrils (CNFs). The aim of the work is to improve the total process by valorization of the main components of lignocellulosic biomass, specially the C5 fraction for the production of lactic acid. This monomer serves as building block for the synthesis of the biodegradable polymer polylactic acid (PLA).

Previous studies in our laboratory have shown that organosolv (OS) pretreatment, using H_2SO_4 like catalyst, looks functional because it easily allows deconstruction of lignocellulosic biomass in its three main components: cellulose, hemicellulose and lignin (1).
In this general project we decided to valorize the C5 — fraction by the addition of a fermentation step to obtain lactic acid (Fig.1)

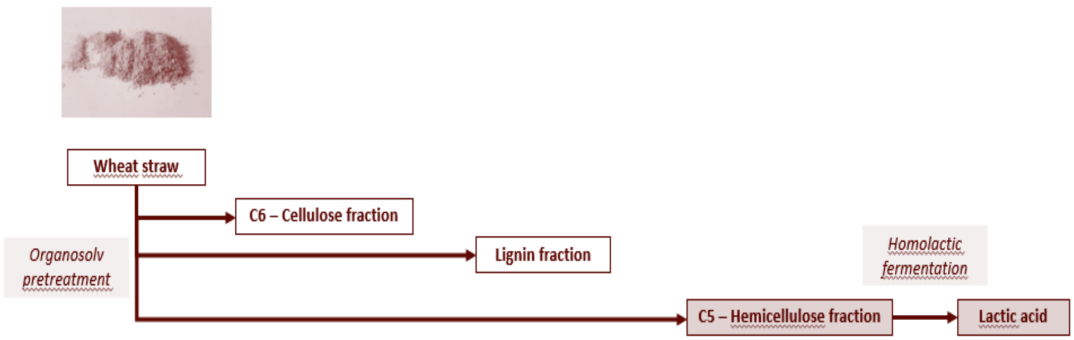

Fig.1 Schematic representation of the general project

OS pretreatments were done using a solids loading of 10% (w/v) and 2.5 % (w/w) of H_2SO_4. The process was evaluated to maximize the recovery of C6 — cellulose fraction (used for cellulose nanofibrils production) and the optimal severity was found at ~1 CSF with a glucans recovery of ~70%. The C5 — fraction has reached an high xylose concentration with a recovery of ~40%.

After OS pretreatment, obtained sugars monomers were used as carbon source in fermentation by *Bacillus coagulans*. Two different strains were investigated in this fermentative process: *Bacillus* sp. strain XZL4 and sp. strain 2314. Both strains were able to produce lactic acid by homolactic fermentation. Firstly, to investigate the utilization of glucose and xylose, we maximized the ability of microorganisms using different initial concentrations of both sugars. After, we used the C5 fraction obtained after OS pretreatment as substrate for fermentation step. Lactic acid recovery was evaluated by HPLC analysis.

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ORGANOSOLV RE-USE LIQUOR STRATEGY APPLIED TO ENZYMATIC SACCHARIFICATION OF LIGNOCELLULOSIC BIOMASS

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Cellulose is the most abundant and valuable component of lignocellulosic biomass but its transformation into glucose by cellulolytic enzymes is inhibited by the hemicelluloses-lignin matrix, which surrounds the cellulose microfibrils, and by the crystalline regions of the cellulose [1]. Therefore, a pretreatment is necessary to make the cellulose accessible to the enzymes. The ethanol-water fractionation of lignocellulosic biomass is an effective pretreatment for enzymatic cellulose hydrolysis to produce sugars and lignin within a biorefinery scheme [2-3]. However, in an environmentally sustainable process, the use of fresh water, the amount of wastewater and energy consumption should be minimized, which could be achieved by recirculating the process streams [4].

The pre-treatments were carried out in a 6 L tank reactor provided with liquor recirculation, temperature control and sampling. The reactor was loaded with 100 g of WS (dry basis) and the solvent at a liquid/solid ratio (L/S) of 20 L/kg. The fractionation was performed at 160 ºC for 60 min, with an EW mixture with 33.3 % (v/v) of ethanol and a 1 % (w/w) of sulfuric acid, and reusing the liquor obtained after each pretreatment, up to a total of six times. Solid fractions were removed at the end of the experiments, washed and weighed and enzymatic hydrolized with a mixture of commercial cellulases. The sugars in the liquefied fraction were analyzed by HPLC.

The results obtained showed that as the liquor obtained from the pre-treatment stage was recirculated, solids with different chemical compositions were generated and a better enzymatic digestibility was achieved. The yield of EH (%) obtained for S2 (first reuse) was 82.30%, which results in a 6.0-fold improvement over raw material without pretreatment (WS) and 7.31% over S1 (first pretreatment, with liquor new). This behavior is repeated in all reuses made, achieving a maximum of 95.30% of EH for S6.

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RECOVERY OF RESOURCES FROM LANDFILL LEACHATE THROUGH THE USE OF AN *Opuntia ficus* (L.) MILL POLYMER

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Currently in Chile, the management of household solid waste is limited to waste collection and final disposal, with a recorded 38 landfills that receive 7 million tons of municipal waste (Relagres, 2016).

In landfills, solid waste is deposited, compacted, and covered to minimize exposure to air (Baird et al., 2014). However, water in contact with this waste forms leachate that contains elevated contaminant concentrations due to the liquid extraction of dissolved or suspended materials, such as heavy metals, among others.

Internationally, numerous leachate treatment options exist that range from physiochemical, biological, or mixed systems. Yet, the national reality is recirculation of the leachate in the landfill, storage in evaporation pools, or biological treatments within the landfill.

An alternative treatment proposal for this environmental liability involves the use of a series of processes that combine biological and physicochemical processes, which have been demonstrated to be efficient and effective. Accordingly, Nharingo (2016) established that polymers from vegetable species could be utilized to treat contaminants in wastewater treatment plant effluents using a species belonging to the family Cactaceae through a mechanism of BIOSORPTION. This mechanism removes organic and inorganic contaminants through a surface phenomenon in which the contaminant goes from a soluble phase to a solid that is then fixed (Barakat, 2011). This method has the advantage of being low-cost, efficiently removing contaminants with minimal waste, is reversible and can be reclaimed after use, is easily adaptable to plant processes, and can be used at a wide range of pHs (Farooq et al., 2010). We propose the treatment of landfill leachate and the reclaiming of water and heavy metals by utilizing a polymer originating from *Opuntia* sp. that is capable of fixing them.

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Seminario Internacional RELAGRES. Santiago de Chile Junio 2016

BIOHYDROGEN PRODUCTION FROM OPUNTIA CO-SUBSTRATES WITH AN ALKALINE PRETREATMENT

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Fossil fuels cover 85% of global energy demand [1]. However, the disadvantages of their use have encouraged the search for renewable and sustainable alternative energy sources. Hydrogen (H_2) is a promising alternative; it is a clean fuel with high energetic power [2]. Its production through dark fermentation is interesting because several low-cost organic substrates can be used, which make the process economically viable and sustainable. The general goal of this work was to evaluate the effect of the co-substrates ratio (using mixtures of Nopal, rabbit excreta and rancid fats), in the production of hydrogen by kinetics in reactors per batch.

Four feeding mixtures were tested: 1) cactus and water, 2) cactus cladodes, rabbit manure, and water, 3) cactus cladodes, rabbit manure, rancid fats and water and 4) cactus cladodes, rabbit manure, rancid fats and anaerobic digestate. Each mixture was tested in triplicate in bach reactors Oxitop® that were incubated for 60 days. The pH of the co-substrate mixtures was 7.5 and was adjusted at the start of the fermentation to 9.9 ± 1 with $Ca(OH)_2$ to inhibit methanogenesis. In each reactor, the production of biogas was measured indirectly through the pressure recorded in the head, and a biogas sample was also taken to quantify the hydrogen content. Also, the following parameters were monitored in the reactors: pH, COD, TOC, NT, Fe, Ca, Mg and P.
The hydrogen production with the mixtures of co-substrates was as follows: with mixtures 1 and 2, 27 and 31% of hydrogen were obtained, respectively, with the mixture 3, 39% and with 4, 22%.
The COD removal in the mixtures varied from 44.2% to 50.5% and was from highest to lowest in the following order 3, 2, 4 1, which coincided with that of H_2 production. Total nitrogen behaved very similarly in all mixtures: in the first 30 days it significantly decreased from 2353 mg/L to 1379 mg/L on average and finally increased slightly (1507 mg/L on average).

According to the results, the addition of rancid fats in the mixtures increased the production of H_2, while the substitution of water by leachate had the opposite effect. The addition of $Ca(OH)_2$ to adjust the pH was sufficient to inhibit methanogenesis and favor H_2 production.

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USE OF WASTEWATER SLUDGE AS A POTENTIAL RAW MATERIAL FOR THE PRODUCTION OF BIODIESEL USING MICROWAVE TECHNOLOGY

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Global energy demand has been increasing as a result of the growing trend of modernization and industrialization, leading to increased consumption of fossil fuels and the depletion of global oil reserves. For this reason, most of the resources are spent on the purchase of petroleum products, so the development of alternative fuels with low emissions and economically sustainable for the environment is essential. The main objective of this research was to compare different methods of cell disruption and the performance of biodiesel obtained through the transesterification of oil lipids from sludge from the wastewater treatment plant (WWTP).
The disruption methods used were mechanical, by abrasion with agitation at 360 rpm and room temperature; cavitation using ultrasound (at 120, 240 and 360 W power and 20 kHz) and microwaves (at 30 and 60ºC and 200W power), using a 1:2 chloroform/methanol mixture. In addition, each disruption method was applied for periods of 5, 10 and 15 minutes to evaluate the performance of extracted lipids, where controls were also carried out without being exposed to any treatment and at room temperature. Once the treatment and the most efficient time for the extraction of lipids was obtained, we proceeded to make mixtures of chloroform, heptane and petroleum ether, all in combination with methanol at different proportions to achieve a higher lipid yield. For the production of biodiesel, oil extracted from greasy sludge was transesterified, using concentrated sulphuric acid (96%), functionalized biochar (acid) and DOWEX (industrial acid catalyst), at a mass ratio of 10% catalyst and methanol at a molar ratio of 1:10 was used as the solvent for the reaction. The transesterification reaction was carried out with a time of 1, 5, 10, 20 and 30 minutes in a microwave reactor at a temperature of 100ºC.
The most effective extraction of lipids was achieved by means of microwave treatment at 30ºC and 5 minutes of exposure, in which 37 % of lipids were obtained. As for the different mixtures of solvents, the one that obtained the highest content of extracted lipids was 1:1 chloroform/methanol solution (v/v ratio), with 56% extraction at 30ºC and only when exposed to agitation. To obtain biodiesel, the maximum yields of FAME from the degreasing sludge lipids achieved with the different catalysts were: sulphonated biochar (9.6% to 5 min.), resin (33% to 20 min.) and H_2SO_4 (69% to 10 min.).
The amount of obtained biodiesel (69%) is very close to that perceived by means of dry biomass of residual sludge (71%), indicating the feasibility of the lipid extraction method and the potential of wet sludge as a raw material for the manufacture of biodiesel.

Acknowledgements: This work was supported by CONICYT Project Nº ACT172128, RING GAMBIO.

PECTIN OPTIMIZATION EXTRACTION FROM WATERMELLON WASTE

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Pectin is a commonly used in the food industry as gelling and thickening agent, and consists in a heteropolysaccharide, mostly composed of galacturoric acid-based units, present as free acids, methyl esters or acid amides[1]. Brazil stands out as the largest producer and exporter of watermelon (*Citrullus lanatus*), producing more than two million tons of watermelon per year, where Goiás, Ceará, São Paulo and Minas Gerais regions being the largest producers of the Brazilian domestic and foreign market[2]. Even with a high productivity, large amounts of agroindustrial waste are generated by the watermelon crop, largely due to inadequate procedures in the production chain. But also from the fact that Brazilian producers do not use the fruit rinds[3].

So, this paper refers to the use of watermelon waste, namely watermelon rind, as a raw material for pectin production by acid extraction. A Box-Behenken Design was conducted to optimize extraction variables citric acid concentration, time and temperature. Extracted rind watermelon pectin was subjected to physico-chemical analysis, as well as degree of esterification. Watermelon waste were obtained at local markets at Rio Verde city, watermelon rind was separeted and sanitized in sodium hipochloride solution (1% w/v), dried till constant weight and milled through a 32 mesh seive, producing a flour, which was kept in plastic sealed bags at -8 ^{o}C, until used for the pectin extraction.

Physico-chemical analysis of the watermelon rind flour indicated a 6.70% dry weight umidity content, 8.87 % ashes, 0.67% lipidic content, total protein content of 4.49%, and 1.8 Brix soluble solids. All of them in good agreement with reported results in the literature.

Carotenoids content analysis indicated 0.0031 mg 100mL^{-1} of β-carotene and 0.0048 mg 100mL^{-1} for licopene. Chlorophyll results were 0.0142 mg 100mL^{-1} for chlorophyll a and 0.0022 mg 100mL^{-1} for chlorophyll b.

Color analysis by CIELab system indicated 79.06 (L*), 3.50 (a*) and 18.00 (b*).

Higher calorific value of watermelon rind flour analyzed by an Ika C200 bomb calorimeter indicated a 14,987 KJ Kg^{-1} energetic content.

Optimization experiments indicated citric acid concentration and temperature as significant variables for extraction yield, while time was not significant. Total error and lack-of-fit were low. S value for the model used was 3.29, squared R was 91.08%, adj R2 was 87.06% and predicted R2 indicated a value of 78.42%. All of which indicates that the model used fits well the data and can be used to generalizations. Normality plot of the residuals analysis which confirms its normal distribution.

Optimization procedures presented two possible solutions. Solution 1 indicates citric acid concentration at 1 M, time of 78.6 minutes and temperature at 40 ^{o}C with a 44.3% yield extraction. Solutions 2 uses same values for citric acid concentration and temperature, but a slightly longer time of 89.8 minutes, with a 44.2% yield.

Extracted Pectin obtained from watermelon rind waste displayed a DE of 3.76% and a pH 2.53.

Acknowledgments
The authors wish to thank FINEP, CAPES, CNPq, FAPEG and IFGoiano for their financial support to this research.

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PRELIMINARY EVALUATION OF THE USE OF LEES GENERATED IN THE REFINING OF THE VEGETABLE OIL MIXTURE AS A SUBSTRATE FOR THE PRODUCTION OF BIOSURFACTANT

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The biosurfactants are active compounds, produced by microorganisms, with capacity to reduce the surface tension, possessing low toxicity and high biodegradability. These substances can be produced from renewable and low cost carbon sources, and vegetable oil sludge is a potential source for the production of the same. In this sense, the objective of this work is to make a preliminary evaluation of the use of sludge generated in the refining of a mixture of soybean and cotton oil as a low cost substrate for the production of biosurfactant.

In the industrialization of vegetable oils generates three sub-products: the gums, the lees from the neutralization step and the condensate [1].

The methodology consists of: collection of information from a vegetable oil production industry located in Bahia, covering the technical visit and data collection on residue availability and sample collection for qualitative and quantitative analytical evaluation.

The industry works on refining the soybean and cottonseed oil blend in a ratio of 1: 1 by mass and produces about 8 tons per day of this waste. The material contains fatty acids, sodium salts, water, triglycerides, saponifiable material and oil degradation products [1].

The lees, separated in the centrifugation, leaves at a temperature of 75 ^{0}C, figure 1, has viscous consistency, color ranging from amber to dark and average of 38.0% total fatty acid and 38.2% moisture and pH 11. In tank where it is stored at ambient temperature, between 25 ^{0}C to 30 ^{0}C, water is added to maintain a viscosity that allows pumping. Under these conditions the total fatty acid is 35.9% and humidity 43.8%.

Studies of the production of a type of biosurfactant, the rhamnolipids, by bacteria Pseudomonas sp. using oleaginous residues from the food industry, pointed the soybean oil sludge as a good substrate [2]. Based on this reference and the preliminary evaluation made of this sludge, there is potential to use this residue as a substrate in the production of biosurfactant.

Figure.1 – centrifuge sludge outlet

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PRODUCTION OF ANTIOXIDANT ADDITIVES FROM RESIDUES WITH HIGH LIGNIN CONTENT

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There are a significant number of industrial processes where high-lignin streams are obtained as by-product or waste: paper industry, bioethanol production, etc. Due to its chemical nature, the lignin contained in these materials is a very interesting source of phenolic compounds. Many of these compounds have previously shown to be excellent antioxidant additives for biofuels[1], which can replace the antioxidants used at this moment, obtained mostly from fossil materials, without a negative effect on the emissions of a diesel engine[2].

The use of lignin with this purpose is complex due to its great stability, so it is necessary to use high temperature processes for its depolymerization, and often the presence of catalysts or solvents. The processing of those materials does not have a high selectivity so it is necessary to study the most suitable conditions to obtain important quantities of additives with high antioxidant capacity.

In this work, a lignin obtained in the semi-chemical soda pulping of barley straw, has been tested for the production of antioxidant additives for biodiesel.

Depolymerization has been carried out in a 300 mL batch reactor, under autogenous pressure, at temperatures ranging from 250 to 325 °C along 1 hour. Additionally, the effect of adding formic acid to the reactant mixture has been studied.

The liquid obtained from the reactor was collected, centrifuged and filtered. Subsequently, it was extracted with isopropyl acetate. The upper (organic) phase was separated and filtered, before being evaporated in a rotary evaporator at 40° C. The solid obtained was weighed and collected with a small amount of isopropyl acetate and stored. This product constitutes the biodiesel additive.

The additives obtained in the different conditions tested have been characterized and blended with biodiesel in a percentage of 1%. Oxidation stability, both before and after the mixing, was measured using a PetroOxy oxidation stability tester.

The incorporation of additives prepared significantly improved the oxidation stability of biodiesel, in percentages between 200% and 500%.

For the additives obtained without using formic acid, a clear positive effect of the temperature was observed, so the antioxidant activity of the products obtained enhances as increasing the processing temperature. As regards the incorporation of formic acid in the reactive mixture, while its effect is small and negative at high temperatures, its

presence significantly improve the oxidation stability of the additives obtained by processing the lignin at the lower temperatures (250 and 275ºC).

The main conclusion obtained in this work is that is possible to produce additives, from carbon based wastes and residues to improve the oxidation stability of biofuels.

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EFFICIENT STRATEGY BASED ON CENTRIFUGAL PARTITION CHROMATOGRAPHY TO RECOVER BIOACTIVE COMPONENTS FROM CHILEAN PLANTS AND AGROFOOD BY-PRODUCTS

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Chilean plants have biased and incomplete chemical and pharmacological studies. The main reason for this situation has been the low availability of sufficient quantities to make biological tests and structural elucidation. Therefore, it is necessary to have more rapid and scalable methodologies, aimed to obtain large amounts of high-value molecules. In this work is presented the application of efficient strategies for the extraction of polyphenols from Chilean plants and some cheap agro-wastes. As starting approach we used liquid-liquid methodology with different Centrifugal Partition Chromatography (CPC) configurations to perform bio-guided fractionation of proanthocyanidins (PACs) from *Peumus boldus*, apple and avocado peels with the aim to test and refine their biological properties. PACs also were used as starting material to prepare semi-synthetic derivatives of epicatechin/catechin by well-known nucleophilic attack reaction. One-step isolation of these semi-synthetic derivatives was achieved through CPC-250L and identified by TLC and LC-MS/MS. The semi-synthetic adducts prepared from avocado and Boldo PACs reduce significantly cell injury in *H. pylori*-infected AGS cells. To confirm the protective properties of PACS and semi-synthetic derivatives in an animal model, PACs were obtained in high amounts using a continuous liquid-liquid separation by True Moving Bed system (TMB-500) and combined with semi-synthetic adducts. Hence, a dose of 100 mg PACs + 50 mg adducts /kgxd was able to prevent *H. pylori* SS1 infection in Mongolian gerbils.

POSTER

AGGREGATION PATHS OF POLY-3-(HEXYL THIOPHENE) IN THE PRESENCE OF EITHER PCBM OR POLY(ε-CAPROLACTONE)

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Poly-3-(hexyl thiophene) (P3HT) is currently the benchmark semiconducting polymer for organic photovoltaics. Its physical, electrical, photophysical properties are strongly dependent on its morphology in the solid state. However, several issues remain unclear, regarding the forces that drive the assembly/crystallization of P3HT to form fibrillar nanocrystals (NCs) in marginal solvent conditions (anisole) [1,2].
This work reports the results of a systematic study on the aggregation/crystallization behavior of P3HT to NCs under different solution conditions and in the presence of different relative contents of either PCBM [3] or poly(ε-caprolactone) PCL. PCBM and PCL confined the aggregation/crystallization process of P3HT NCs allowing the formation of extended crystallites, on the other hand at high concentrations in solution it hindered the formation of NCs slowing down their assembly. The results obtained in this work offer a promising perspective for the obtainment of functional all-polymeric NCs.

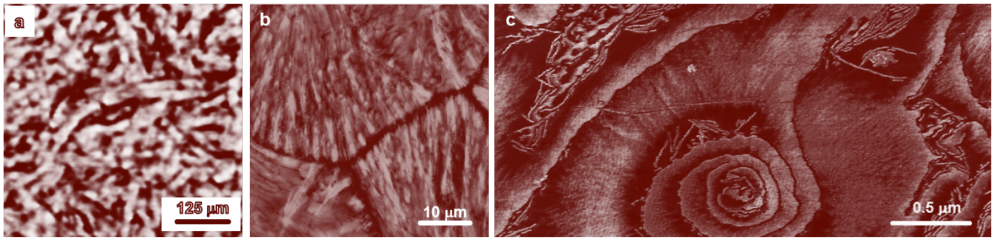

Figure 1: AFM phase micrograph of P3HT NCs mixture obtained from a) P3HT:PCBM 1:1, b) and c) P3HT:PCL 160:1 relative concentrations (w/w).

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ANAEROBIC DEGRADATION OF AGROINDUSTRIAL AND DOMESTIC WASTE FOR METHANE PRODUCTION

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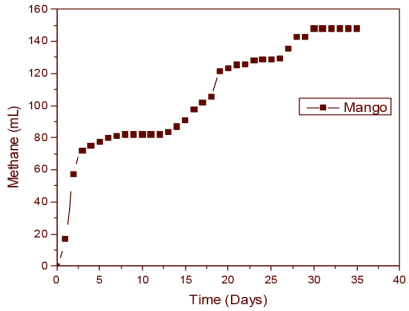
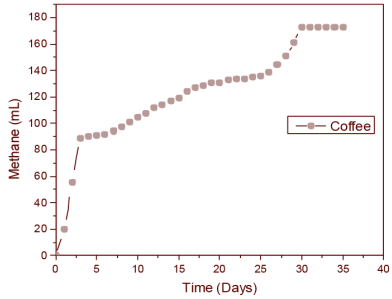
Agroindustrial, domestic waste and agricultural by-products are viable raw material and use for a certain purpose is considered advantageous, since it is available in large quantities, characterized as renewable and low-cost resources[1].
For the processes of digestion and anaerobic co-digestion are known as effective technologies of digestion of waste and have been used to treat various types of waste such as: domestic, agricultural and agroindustrial, municipal solid waste, effluent pigs and cattle, and sludge of wastewater [2].
Anaerobic digestion is a biological process where organic matter is degraded in the presence of a large consortium of microorganisms under anaerobic conditions [3, 4]. The main product of the process obtained is biogas rich in methane and an excellent alternative to fossil fuels. [5].
For the technology of biogas production, it is necessary to determine certain operational parameters (temperature, pH, biodegradability, characterization of substrates and C/N etc.).
The substrates used in anaerobic digestion were residues of Ataulfo mango pulp, coffee pulp and as inoculum sludge from wastewater.
The substrates were characterized physicochemically and bromatologically in accordance with Mexican Standards for pH (NMX-AA-008-SCFI-2000A), Chemical Demand for Oxygen (NMX-AA-030-SCFI-2001), Total Solids (NMX-AA-034-SCFI-2001)), Volatile Total Solids (NMX-AA-034-SCFI-2001), Moisture (NMX-FF-109-SCFI-2007), Ash (NMX-F-066-S1978), Total Nitrogen and Total Carbon were determined by the FLASH equipment 2000 Organic Elemental Analyzer.
As results (Fig. 1), accumulated methane from a single substrate and substrates in different mixing proportions during anaerobic digestion is shown. The digestion of mango had a higher production of 172.766 mL, compared to the coffee pulp that had a low value of 148.033 mL and the mixture of both residues with an average value of 151.433 mL.





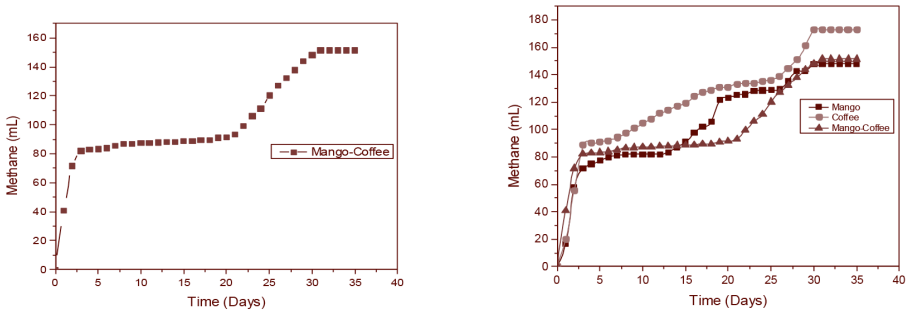


Fig.1 Production of methane with the domestic and agroindustrial residues of mango and coffee pulp and the mixture of both, the experiments were carried out in triplicate.

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BIOAGREGADO DE CAÑA DE COLZA COMO AISLANTE TÉRMICO INSUFLADO

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El uso de materiales de aislamiento biobasados en los edificios presenta dos ventajas. Por un lado, mejoran el rendimiento térmico de los edificios, reduciendo los impactos ambientales en la etapa de uso. Por otro lado, contribuyen a la valorización local de los subproductos de los cultivos que son materias primas renovables anualmente y compostables al final de su vida útil. En Chile, la estructuración de una cadena de suministro basada en estos materiales puede ser una estrategia territorial para hacer frente a la nueva situación derivada de los recientes aumentos de exigencias relacionados con al conservación de la energía en la edificación residencial . En las zonas rurales, después de la reciente aprobación de la ley que restringe las quemas en el campo, los agricultores están exigiendo soluciones innovadoras para deshacerse de los rastrojos a un costo razonable. En el presente trabajo se estudiaron las propiedades físicas y térmicas de un bioagregado a base de colza. El material se insufló en un prototipo de pared hueca a escala real, hecha de madera, con el objetivo de probar la viabilidad técnica para su uso como aislamiento térmico insuflado. Durante el proceso de instalación, se optimizó la fluidez y el tiempo necesario para la implementación mediante el control de los parámetros del soplador. Se probaron la densidad resultante, la conductividad térmica y la sedimentación. Los costos de producción y los impactos ambientales fueron comparados con los de la celulosa utilizando un enfoque de análisis del ciclo de vida para un estudio de caso en la Araucanía, al sur de Chile. Los resultados muestran que el agregado de colza tiene una conductividad térmica ligeramente mayor que la celulosa soplada (0.045 W/mK vs 0.042 W/mK). Sin embargo, se encontró que era competitivo con la celulosa, lo que fomenta su uso como aislante para aplicaciones en la construcción.

Se necesitan más investigaciones para separar mecánicamente la médula de los tejidos vegetales fibrosos, ya que la caracterización física muestra que la médula tiene propiedades mejores en términos de densidad y conductividad térmica en comparación con la fracción fibrosa.

CELLULOSE AND CHITIN NANOFIBER FILMS WELDING VIA IONIC LIQUIDS

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Cellulose based nanomaterials synthesis, demands the production of high mechanical performance fibers and films used extensively as textiles, support for particles and composites materials in kinetic and electrochemical applications, among other applications [1]. On welding process natural fibers are transformed to create a congealed network using an Ionic Liquid (IL´s) solvent. This process is intended mainly for cellulosic and proteins based fibers with the purpose to improve mechanical properties, synthesized composite and functionalized materials [2]. In the present work Cellulose Nanofibers Films (CNF), Cellulose Nanofibers Films Tempo Oxidized (CNF-TO) and Chitin Nanofiber Films (ChNF) are synthesized through filtration and hot pressing process. The films are welded individually using six Ionic Liquids (ILs): 1-Ethyl-3- methylimidazolium chloride [emim][Cl], 1-Ethyl-3-methylimidazolium acetate [emim][OAc], 1,1,3,3-tetramethylguanidinium acetate [TMGH][OAc], 1,1,3,3-tetramethylguanidinium propionate [TMGH][CO2Et], 1,5 Diazabicyclo[4.3.0]non-5-enium propianate [DBNH][CO2Et], 1,5 Diazabicyclo[4.3.0]non-5-enium acetate [DBNH][OAc]. These six ionic liquids have shown an impressive potential on cellulose partial dissolution process [3].
The impregnation and diffusion dynamical behavior of Ils into individual CNF, CNF-TO and ChNF films was characterized using: Contact Angle (CA), Scanning Electron Microscopy (SEM) and X-ray diffraction measurements (XRD). The mechanical performance of individual impregnated films was tested using a vertical tensile tester (MTS 400/M, MTS System, USA) and dynamical mechanical analysis equipment(Q800 instrument, TA Instruments, USA).
Previous results display a substantial effect on mechanical properties, increasing young modulus and tensile strength of the individual films. X-ray diffraction patterns shown that individual yarns are quenched without losing the fiber nature, and molten parts include a change of cellulose from cellulose I to type II.

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CHARACTERIZATION OF BLUEBERRY PRUNING RESIDUES (BPRs): A POTENTIAL SOURCE OF NANOCELLULOSE

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Blueberries (Vaccinium corymbosum) are round fruits that are typically dark in color and grown from medium-sized shrubs with deciduous leaves [1]. Regular consumption of blueberries is associated with health benefits [2], [3], [4]. Chile has become a main producer and exporter of blueberries, second to the United States [5], [6]. The location of Chile in the southern hemisphere makes it possible to ship high quality, fresh blueberries to countries in the northern hemisphere during winter [7], [8]. The management of the pruning of bushes influences the quality of the blueberries. The average fruit size can be increased if shrub pruning is applied systematically to allow for a balance between the annual growth of shoots and fruit production [9], [7], [10], [11]. Accordingly, between 3000 kg and 7500 kg (dry weight) of pruning waste are generated in a planted hectare [12]. Given the threats of reproduction and growth of pests and pathogens from residues that are left on fields after compaction, the only currently viable solution is to burn this lignocellulosic biomass [13]. While this is the easiest and least expensive practice related to agricultural activities, the impact on the air quality cannot be ignored. It contributes to 40% of carbon dioxide, 32% of carbon monoxide, 20% of particulate matter, and 50% of polycyclic aromatic hydrocarbons emissions released into the environment globally [14]. Currently, approximately 10,000 ha are planted in the regions of Maule and Bío-Bío, which corresponds to 56% of the total Chilean production [15], generating a large amount of underutilized lignocellulosic waste, which in the vast majority of cases is burned, increasing CO_2 emissions in these regions. As an alternative to the current incineration practices and their negative air pollution effects, this study proposed value-added utilization of these agroindustry residues. The chemical compositions (cellulose, hemicellulose, lignin, extractives, and ash) of the pruning residues from blueberry branches and trunks were analyzed. The cellulose contents from the branches and trunks were similar at 52% and 51%, respectively. The characterization of the obtained cellulose was carried out, the results are shown in fig.1. The X-ray diffraction analysis indicated important differences in their crystallinity index, with 52% and 84%, respectively. Due to the higher crystallinity, the isolation of nanocellulose was carried out from this residue, obtaining cellulose nanocrystals (CNC) by means of hydrolysis with ionic liquid. According to the results, it is expected that the agroindustrial waste from the pruning of the Chilean blueberry bushes can be used as a potential platform for bioproducts, with the economic and environmental advantages that this implies due to its low cost, high regional availability and its capacity to replace some polymers synthetic (non-biodegradable) from fossil sources.

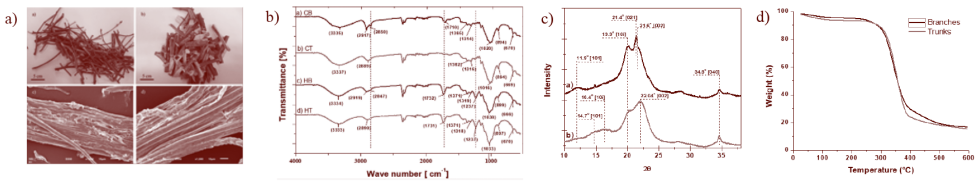

Figure 1. Blueberry pruning residues (BPRs). a) Images photograph and SEM micrograph of the cellulose; b) FTIR spectra of the alpha-cellulose and holocellulose; c) XRD diffraction patterns of the alpha-cellulose; d) Thermal analysis of weight loss vs. temperature.

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CO_2 ADSORPTION ON FUNCTIONALIZED CELLULOSE NANOFIBRILS (CNF) FILMS- AGRICULTURAL WASTE

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The capture, storage and possibly the exploitation of emitted greenhouse gases is facing nowadays as major challenge from an environmental point of view. A particular attention has been drawn to carbon dioxide (CO_2) as it is the largest produced gas on earth, has a huge impact on environment and due to its toxicity. However, CO_2 has also potential to be used as building block for many applications. The development of efficient and low-cost technologies for the capture and recovery of CO_2 is therefore of high importance.[1,2]

The present work demonstrates a simple and straightforward chemical modification of cellulose nanofibrils (CNF) films in order to produce CO_2 adsorbent materials. The CNF films were obtained from two agricultural residues, *i.e.* corn husks and oat hulls. CNF from kraft pulp was used for comparison purposes. Controlled surface silylation was conducted on the preformed CNF films in aqueous media under mild conditions using three aminosilanes bearing mono, di and triamine groups. The success of the grafting of the aminosilanes on the CNF films was demonstrated by FTIR and XPS analyses. The results of the contact angle measurements and FE-SEM coupled with EDS showed homogenous coverage by the amino-groups on the surface of the modified CNF films, particularly with the diaminosilane N-[3-(Trimethoxysilyl)propyl]ethylenediamine (DAMO). The adsorption of CO_2 in CNF films was measured through CO_2 adsorption isotherms at 273 and 298 K respectively. The isotherm data were analyzed by fitting them to various isotherm models. In this work, the different isotherm models such as Langmuir, Freundlich and Dubinin-Radushkevich models were employed for testing the experimental equilibrium adsorption data. The produced films were thermally stable and when subjected to 99.9% CO_2 flow at 25°C, these modified films showed good adsorption of CO_2. Indeed, after 3h of exposure the adsorbed concentration of CO_2 of the CNF films modified with DAMO was 0.90, 1.27 and 2.11 mmol CO_2 /g polymer for CNF films from corn husks, oat hulls and kraft pulp, respectively.

Fig.1 Graphical abstract

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COMPUTATIONAL MODELING OF DYNAMIC SYSTEM RHEOLOGY FOR ALGINATE PRODUCTION

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Alginate is a polysaccharide that can be secreted by bacteria such as *Azotobacter vinelandii*. Due its viscosity and gelling properties, alginate is used as stabilizer and gelling agent in food, beverage and pharmaceutical industries [1,2]. This biopolymer can also be used in the production of bioplastics, for example, films for food packaging, paper coating, fibers for wound dressing and other medical textiles. These bioplastics show advantages with respect to the traditional alternatives because of the alginate mechanical properties [2]. However, the production of this compound has some difficulties because the apparent viscosity of the culture medium change gradually as the alginate is secreted, which impairs the mass transfer of substrate and oxygen inside the reactor medium [1].

Computational Fluid Dynamic (CFD) is an advanced computational modeling technique that allows the numerical resolution of the governing equations of fluid flow, mass transfer and heat transfer [3]. This modeling approach is a promising tool to study, predict and optimize bioprocesses. CFD modeling can allow the evaluation of different operating conditions of a bioprocess without the expense that an experimental procedure requires. Moreover, CFD can couple the biochemical reaction dynamic with the fluid dynamics to gain an integral representation of the bioreactor [4,5]

CFD modeling has been applied to study different bioprocesses, such as the baker´s yeast production in a bubble column [6], biohydrogen formation in a completed stirring tank reactor (CSTR) [7], synthesis of cellulose in a CSTR [8] and the anaerobic digestion in different reactor configurations [9], but none CFD model has been implemented to study the alginate production so far. Also, despite these studies have enhanced the knowledge about different relevant issues for a bioprocess, its results have a limited scope due to key phenomena have been neglected. For instance, the rheological changes caused by the bioproduct formation and the biomass proliferation have been neglected.

Based on these findings, this study shows the implemention of a CFD model of the alginate production that includes the rheological changes caused by the alginate accumulation in a batch culture, enabling an integral analysis, prediction and optimization tool of this bioprocess. A three-dimensional domain of a 20 L active volume tank with two Rushton impellers on a central axis, an air-sparger and four baffles is used (Fig.1). The apparent viscosity of the non-Newtonian culture medium is modeled as a dynamic function of the alginate concentration which in turn is included as a function of the bacteria kinetics. A simulation of the transient dynamic of the system was obtained using the Sliding Mesh technique to simulate the mechanical agitation of the reactor. The results show how the oxygen mass transfer and alginate production is affected as the alginate accumulate in the medium. Cavitation and dead zones can be identified. This first CFD model of alginate production is a useful design tool to improve the reactor geometry and study agitation patterns which allows the maximization of the alginate production with a low power consumption at different scales.

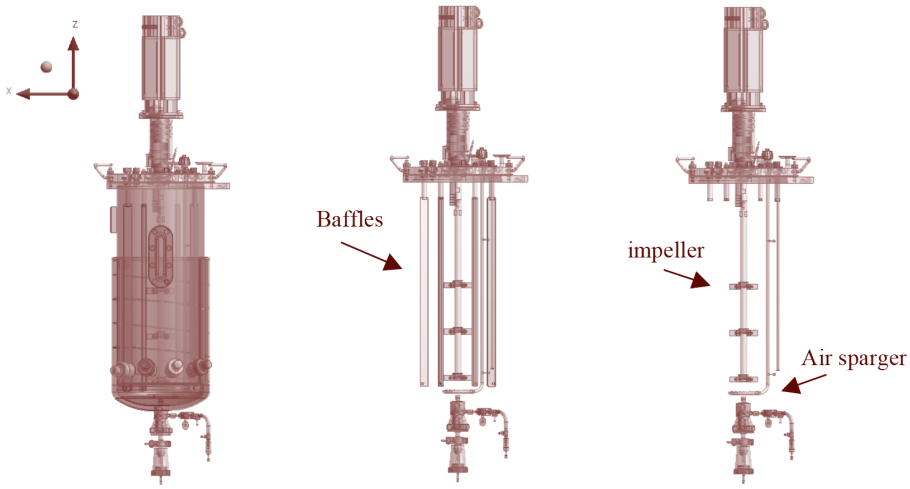

Fig.1 – Different views of the bioreactor.

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DEVELOPMENT AND EVALUATION OF A COMPOSITE MADE OF WOOD WASTE, POLYMERS AND THEIR INDUSTRIAL USE

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Wood is considered an essential element and a fundamental part as far as the civilization growth is concerned. Wood is used in applications such as paper, furniture and construction. Currently, among the most representative companies that produce wood in Antioquia region, there are more than 400 enterprises of different sizes and production levels which are dedicated to obtaining and transformation of wood. In such processes it has been identified that the waste of the lase species use is close to 40% of the standing tree [1]. Therefore, it is urgent to search for exploitation alternatives that mark an environmental awareness, and that also allow the protection and efficient use of natural resources. Wood is commonly used in several constructions that require higher demanding for the mechanical properties. Currently, wood waste material such as chips and powdered wood is used in co-firing production. There are new applications as a result of new processes in the reuse of the wood waste in combination with other materials, for example, advanced wood and plastic composites. This study is aimed at investigating the alternative use of wood waste (patula pine) in order to obtain wood–polymer matrix composites using a mechanical process. The wood particles used as a basis material (patule pine) are commercially produced as wood waste. This type of material was characterized and several parameters were measured such as aspect ratio, size, shape and density. The physical properties of final composites (density, and mechanical properties (modulus of elasticity, and modulus of rupture) were determined. The use and requirements of wood–polymer matrix composites in various applications were discussed. A Design of Experiment approach (DOE) [2] was used to conduct experiments and to analyze the effects of particle size on mechanical properties.

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DEVELOPMENT OF A FILM BASED ON MICROFIBERS OF THE POLYLACTIC ACID BIOPOLYMER WITH POTENTIAL USE AS PACKAGING FOR MEAT PRODUCTS

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This research presents the production of a film using the electrospininng technique, with a potential use as packaging for meat products. It is intended that the main function of this packaging is the preservation, inhibition or/and retardation of the microbial multiplication in food. As a matrix for the production of the film, two different biopolymer mixtures were used from polylactic acid. One mixture was the carrier of the active agents, through the incorporation of copper ions supported on zeolite nanoparticles. The other mixture provided mechanical support to the film by incorporating nanofibrillated cellulose. The mixture was subjected to an electrospinning process in dual configuration at a constant flow of 0.1 mL / h, an electrical voltage of 24 kV and with a distance of the injector to the collector of 20 cm. The fibers of the new generated film were characterized morphologically by scanning electron microscopy coupled with an elemental detector (SEM-EDX). The mechanical properties were determined by tensile test. The morphological analysis revealed that the diameter and continuity of the fibers were influenced to a large extent by the parameters of the process. The elemental analysis confirmed the presence of copper in the fibers of the tissue. The tensile test indicated that the incorporation of nanofibrillated cellulose increased the mechanical resistance to traction.

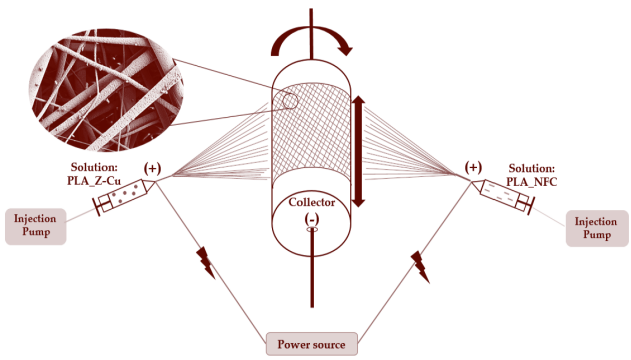

Fig.1 – Schematic representation of the manufacture of a biofilm, by simultaneous injection of two polymer mixtures using an ascending vertical electrospinning in dual configuration.

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ENERGETIC POTENTIAL OF DAIRY WHEY IN HIDALGO STATE, MEXICO

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Every year 208 million liters of dairy whey are produced in Hidalgo State, of which only 20% is used for animal feed, and the rest is poured into soil and water bodies, causing severe environmental issues. Currently, there are a diversity of alternatives to using the dairy whey; however, not all of them are feasible or accessible to be applied by small or medium cheese producers. Among the available alternatives, anaerobic fermentation is a good option for our case of study, because it is a relatively simple and economical way to transform the dairy whey into biogas and electrical energy. Therefore, in this work we evaluated the energetic potential of the dairy whey by computer simulation, using the commercial software Biodigestor-Pro v.3.5 (Grupo AquaLimpia Constructores, Argentina). The input variables were the characteristics of the substrate (COD, BOD, pH, T), operation variables (organic volumetric load, hydraulic retention time, conversion efficiency, total suspended solids), the volume of dairy whey, the hydrological characteristics of the site and the type and configuration of the treatment. The simulation was carried out for the three municipalities with the highest generation of dairy whey: Atitalaquia (11,932 m^3/year), Ixmiquilpan (11,548 m^3/year) and Tizayuca (51,184 m^3/year), considering to use of 100% of use of the dairy whey. According to results, if all whey produced in the Hidalgo State (208,107 m^3/year) were anaerobically digested, 2,071,912 m^3/year of methane or 6,126,890 kWh/year of electric power could be produced, and the contribution of the studied municipalities would be as follows: Tizayuca 25%, Atitalaquia 5.5%, and Ixmiquilpan 6%, of the state production. If we consider an average consumption of 2484 KWh/year per house [1], the energy produced from whey could satisfy the energy requirements of 2466 houses. Indeed, that energy could be used in the dairy plants, which would amortize the cost of the anaerobic digestion plant. On the other hand, the reduction of greenhouse gases by CO_2eq would be 31,206 tons of CO_2eq per year at the state level, and the municipalities would contribute with the same percentages that for the energy production. This amount of CO_2eq is same as 3,511,421 gallons of gasoline consumed or the carbon sequestered by 808,739 tree seedlings grown for ten years [2]. The results obtained from the simulation are promising, nevertheless, it is planned in near future propose alternative schemes of biorefinery for the use of dairy whey.

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ENHANCING AROMATICS PRODUCTION FROM WASTE TIRES PYROLYZED OVER HZSM-5 AND NI/HZSM-5: A PY/GCMS STUDY

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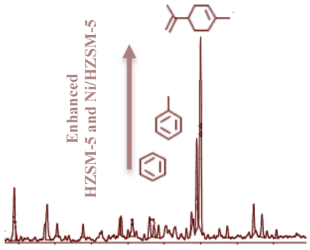
The increasing yearly generation of waste tires, due to the growth of the automotive park in Chile, pose technical and environmental burdens for their disposal and treatment. Particularly, the national mining industry generates tons of waste tires each year, which due to the lack of a conscious and efficient strategy for their treatment, has led to a critical accumulation of this polymeric residue. Disposal of waste tires is a challenging task because tires have a long life and are non-biodegradable. The traditional method of disposal of waste tires have been stockpiling or illegally dumping or landfilling, all of which are short-term solution. In the recent years, the use of thermocatalytic degradation processes has emerged as alternative for treating waste tires [1]. This strategy can led to the production of petroleum-like liquid fuels, carbon black and steel, favoring the establishment of an industrial metabolism for the tire production chain.

With the endeavor of contributing to solve this problem, the present study deals with the catalytic pyrolysis of rubber from waste tires over synthetic zeolite (HZSM-5) and zeolite-supported nickel (Ni-HZSM-5). The effects of catalysts and operation conditions on the composition of pyrolysis vapors were assessed by analytical gas chromatography-mass spectrometry (Py-GCMS). With that aim the Catalyst-to-Waste mass ratios (1:1–10:1) and temperature (450–550 °C) were varied according to a 2^k experimental design. Catalysts were characterized for textural and structural properties, through N_2 adsorption-desorption at 77 K, X-ray diffraction (XRD), scanning electron microscopy coupled to energy dispersive spectroscopy accessory (SEM-EDS) and Transmission Electron Microscopy (TEM). The use of catalysts, increased the composition in aromatic compound, regardless the reaction temperature. Furthermore, the Ni promoted the formation of aliphatic hydrocarbons, while hindered the formation of oxygenated compounds. Effect of intrinsic catalytic properties such as metal dispersion and support nature remains a question. The study will be scaled to BENCH scale seeking to demonstrate reproducibility of the results.



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EVALUACIÓN DE FIBRAS OBTENIDAS DE *Apium graveolens*, *Pisum sativum* Y *Cynara scolymus*, PARA POTENCIAL USO EN MATERIALES AISLANTES TÉRMICOS

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En la actualidad es indispensable que las edificaciones cuenten con una adecuada envolvente térmica para disminuir el consumo de energía destinada a climatización y de esta forma aumentar la eficiencia energética de los edificios.
Los materiales biobasados cada vez toman más relevancia en la industria ya que tienen un menor impacto ambiental tanto en su producción como al final de su vida útil.
Por otra parte, las industrias de alimentos generan una gran cantidad de desperdicios orgánicos, entre ellos fibras residuales derivadas de la elaboración de sus productos.
Este trabajo evalúa la posible utilización de este tipo de fibras como materia prima para la fabricación de un material aislante térmico de bajo impacto ambiental. Las fibras de origen vegetal estudiadas corresponden a las de *Apium graveolens*, *Pisum sativum* y *Cynara scolymus*. Junto con la extracción de las fibras, homogenización y posterior secado, se realizó una caracterización química, física las diferentes fibras vegetales.
Los resultados obtenidos de los estudios morfológicos muestran que las tres fibras evaluadas poseen una estructura interna porosa, con gran porosidad. Las fibras muestran una baja conductividad térmica, lo que da indicios de su posible factibilidad como material aislante.
La posibilidad de la utilización de fibras de origen vegetal para la elaboración de materiales aislantes térmicos aún se encuentra en estudio, pero los resultados preliminares de conductividad térmica obtenidos muestran valores que permiten pensar que sería factible el uso de estas en una eventual aplicación de este tipo.

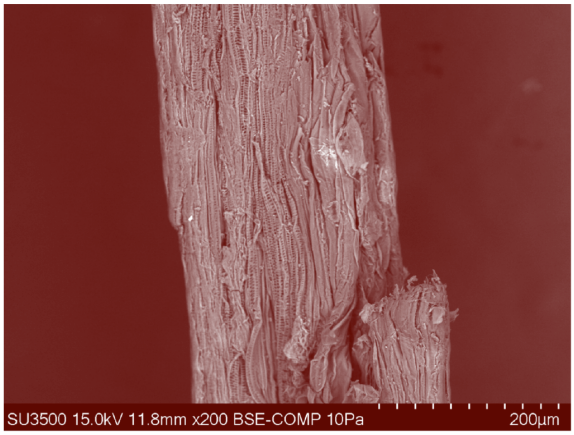

Fig.1 – SEM fibra de *Apium graveolens*.

EVALUATION OF THE POTENTIAL OF SOLAR TECHNOLOGY IN WASTEWATER TREATMENT

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Nowadays, the elimination of contaminants that can affect human health and ecosystems is one of the great challenges in science. In the case of water treatment, heterogeneous photocatalysis has been presented as a solar technology able to mitigate water pollution. In addition, it proceeds at room temperature and atmospheric pressure, saving costs and energy. At the same time, the activation of the photocatalyst is produced by solar radiation, minimizing energy consumption. The high efficiency of the process allows to degrade a large number of compounds, even those that can not be adsorbed or those that are not biodegradable [1].

The main objective of this work is to evaluate the potential use of solar energy for the treatment of polluted water. For this, bimetallic photocatalysts based on copper and molybdenum were prepared by solvothermal method, from copper acetylacetonate, ammonium heptamolybdate and furfural that it is a common waste from the agricultural industry (corn, wheat, sawdust, etc.). It is also widely used in the biorefinery industry for the production of fuels and chemicals [2]. The pollutant selected was tartrazine, an artificial colorant commonly used in several countries in the food industry.

This work propose the use of solar radiation for the treatment of wastewater, using C-based materials obtained from agricultural waste and metals relevant to Chile. In addition, to reuse water, improving its quality and avoiding its elimination with the presence of contaminants that can cause damage to health and ecosystems.

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Acknowledgement
Authors thank the financial support of the Franco-Chilean network BIOCval2E (REDES-170004 project), Funding from CONICYT PIA/APOYO CCTE AFB170007, the financial support of the Chilean FONDECYT project 1161068 and from Millennium Science Initiative of the Ministry of Economy, Development and Tourism, in Chile (grant Nuclei on Catalytic Processes towards Sustainable Chemistry).

EVALUATION OF THE PRODUCTION OF BIODIESEL BY MICROWAVE-ASSISTED FROM MICROALGAE LIPIDS OF *Nannochloropsis gaditana*

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The high demand for fossil fuels and their inevitable depletion has promoted the development of research involving renewable energy sources while providing economic and environmental sustainability. In this context, the objective of this research was to optimize the operating conditions for the production of biodiesel using lipids extracted from the microalgae *Nannochloropsis Gaditana* as raw material and a chemical pre-treatment to maximize the extraction efficiency.

Chemical disruption (acid hydrolysis) of microalgae cell wall was performed using sulfuric acid with a concentration in the range of 0.1 - 0.5 M, temperatures between 100 and 140 °C and reaction times (0 to 30 min.), in order to facilitate the process of solvent extraction of intracellular lipids. Once the lipids were obtained, the transesterification process was carried out using methanol as an acyl acceptor, three different catalysts (functionalized biochar 10% w/w, sulfuric acid at 10% w/w and the cationic resin DOWEX 10% w/w). At the same time, the transesterification process was carried out in situ using microalgae with 93% humidity, methanol (10:1 in relation to the dry weight of the microalgae), chloroform (co-solvent), and the same catalysts mentioned above. All transesterification trials were microwave assisted.

The highest proportion of extracted lipids (48%) after the chemical disruption was achieved by applying a hydrolysis time of 10 minutes, 0.5 M sulphuric acid and a temperature of 100 °C. The results of in situ transesterification were 7.9, 4.8 and 35.7 %, respectively at 5 minutes reaction time when functionalized biochar and DOWEX were used, while when using sulfuric acid the maximum FAME was 15 minutes.

The results obtained were analyzed using a factorial design, which gave a mathematical model deducing that in the extraction of microalgae lipids, the most significant variable is the sulfuric acid concentration. The extraction process of lipids is viable since, does not require a high energy imput, obtaining higher lipid extraction yields compared to conventional extraction methods.

Acknowledgements: This work was supported by CONICYT Project Nº ACT172128, RING GAMBIO.

FERMENTATIVE PROCESS WITH VERMICOMPOST LEACHATE FOR THE BIOETHANOL PRODUCTION FROM MANGO ATAULFO (*Mangifera Indica L.*)

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During a fermentative process, nutrients are required that contribute to the growth and metabolism of the yeast, at the laboratory and industrial level mineral salts derived from the chemical industry are used, which present a very high economic value when used at the industrial level, increasing the costs of ethanol production. The main objective of this investigation was to evaluate a means of fermentation added with leachates of vermicompost for alcoholic fermentation, using as a carbon source the Ataulfo mango pulp. (*Mangifera indica L.*).

A single-factor experimental design (analysis of variance ANOVA) was used to carry out the fermentation using sterilized serums of 124 mL with a work volume of 80 mL, 14 g of dehydrated mango and 10 mL of vermicompost leachate, were stirred at 150 rpm, at a controlled temperature of 30 °C for 48 h. Total soluble solids (SST) were determined, reducing sugars (DNS) were quantified, and the evolution of CO_2, the ethanol concentration was determined by HPLC. A higher ethanol concentration of 43.81 g/L was obtained for treatments that were supplemented with lombricomposta leachate, while in the case of mango it was only 37.52 g/L. This study shows that it is possible to obtain bioethanol in fermentation media added with vermicompost leachates.

Keywords: *Eisenia foetida, mineral salts, fermentation, Bioethanol*

GRAPE CANE BY-PRODUCTS AS FOOD ADDITIVES: CHANGES IN PHENOLIC PROFILE DURING PRODUCTION AND MICROENCAPSULATION

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Residues from wine industry have been the focus of many studies searching for such metabolites all around the world. Grape canes, obtained after annual pruning of vines, is a waste estimated in more than 120.000 tons per year only in Chile (Gorena et al., 2014). Grape canes have a wide diversity of polyphenolic compounds mainly oligostilbenoids and procyanidins with potential health benefits (Sáez et al., 2018). Consequently, polyphenols can be used for development of additives in functional foods.

In this work, an extract of grape canes (*Vitis vinifera* cv. Pinot noir) was produced at pilot-scale in a reactor of 750 L. The extract was encapsulated with *β*-cyclodextrins, and then dried by spray drying. Profiles and content of polyphenols were determined by liquid chromatography/electrospray ionisation-linear ion trap quadrupole-Orbitrap-mass spectrometry (HPLC/ESI-LTQ-Orbi-trap-MS). Change in the phenolics compositions was analysed and compared in the laboratory and pilot plant extraction as well as in microencapsulated extract.

Several changes in the phenolic profile between analytical and pilot extraction were observed such a decrease apparent of resveratrol, catechin, epicatechin and dimeric procyanidins, among others compounds. On the other hand, oligostilbenoids: **(i)** viniferin (*m/z* 453), **(ii)** hopeaphenol (*m/z* 905) and **(iii)** ampelopsin A (*m/z* 469) were successfully encapsulated.

The phenolic profile change during production and microencapsulation of the extract is relevant for evaluating in the future the efficiency and effectiveness of bioproducts as food additives.

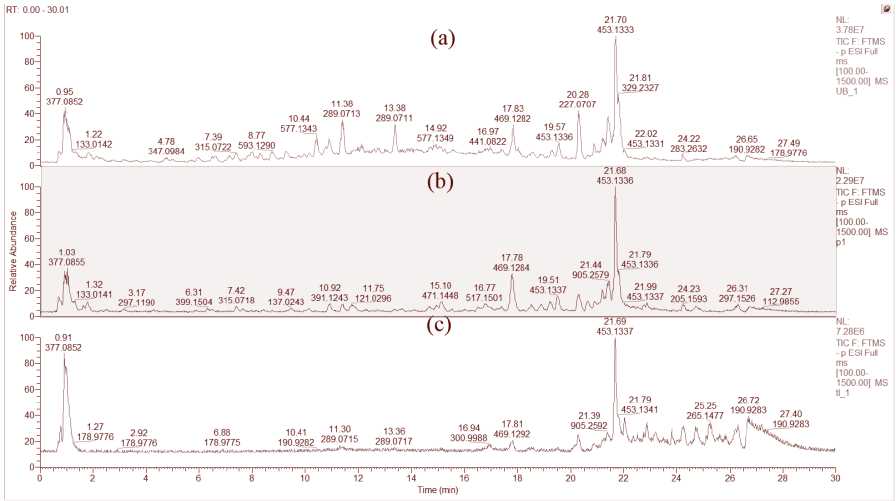

Fig.1 – Grape cane extract: FTMS chromatogram. (a) Analytical laboratory extraction; (b) pilot plant extraction; (c) Microencapsulated extract.

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MODELLING THE PRODUCTION OF DIMETHYL ETHER USING CATALYTIC DISTILLATION

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Dimethyl ether (DME) is an attractive substitute for liquefied petroleum gas (LPG), gasoline, and diesel fuel. DME is a cleaner alternative to conventional fuel because it burns without producing any particulates or sulphur dioxides, and only low amounts of nitrogen oxides, as well as being non-toxic, non-carcinogenic, and non-corrosive [1]. DME decomposes into CO_2 and water in the atmosphere, making it a very environmentally friendly fuel [1]. These properties give it significant potential not only as an automotive fuel, but also for electric power generation and domestic applications [2]. DME can be produced from a variety of plentiful and renewable resources such as coal, natural gas, forest products, waste from pulp and paper mills, agricultural by-products, fuel crops, and municipal waste [2]. This research focuses on the production of DME from the dehydration of methanol using catalytic distillation. Catalytic distillation, also known as reactive distillation, is the integration of a chemical reactor and a distillation column into a single unit operation [1]. The traditional method of producing DME requires three industrial units: A reactor, a distillation column for purification, and a second distillation column for purifying and recycling methanol [1]. With this new method, only one catalytic distillation unit is required, thus reducing the overall capital cost. The heat of reaction will reduce the energy consumption of the single column, allowing for lower operating costs. The catalyst will improve mass transfer inside the column, resulting in greater product separation. Internal recycling of methanol will take place within the reboiler at the bottom of the column. Lastly, catalytic distillation allows for constant separation of products from the reactants within the column, preventing the reaction from reaching equilibrium and creating better reactant consumption and a purer product. With the use of catalytic distillation, a higher purity product of DME can be produced with significantly less waste at a reduced capital cost and energy cost. By performing simulations using Aspen Plus at varying specifications such as feed location, feed rate, catalyst loading, reflux ratio, pressure, and reaction zone, we can determine their effect on the purity of DME and the optimal column specifications.

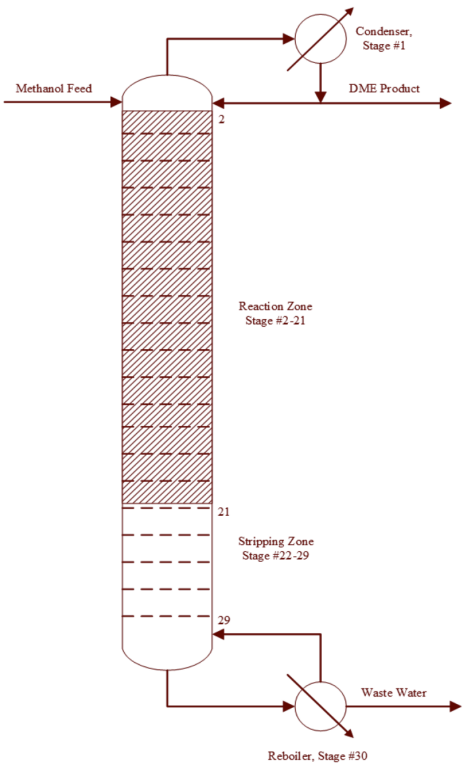

Figure 1: Schematic of catalytic distillation

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Opuntia BIOREFINERY PROPOSAL FOR ARID AND SEMI-ARID ZONES

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Few crops in arid and semi-arid zones have the potential to be used in a biorefinery scheme. *Opuntia* spp. have this potential due to a high biomass production (600-800 ton/ha•year), high water content (90%) and compounds with industrial applications as mucilage and pectin. *Opuntia* species are found distributed in North, Center, and South of Latin America, Center and South of Africa, Middle Orient, Australia, and India [1]. In Mexico, 3 million of hectares are occupied by wild species of nopal and around of 233 000 ha of cultivated, which represent an advantage for developing of *Opuntia* biorefinery.

In Mexico, the cladodes and prickly pear cactus are used by human consume. As well, cladodes of nopal are used as raw material for mucilage and pectin extraction. Every year, the scientific studies are increasing about the industry application of mucilage and pectin of *Opuntia*. The mucilage is a hydrocolloid with diverse applications: as a coagulant to wastewater treatment, as pills coating and as thickener and waterproofing in construction materials. On the other hand, pectin is a complex polysaccharide, used mainly like and food additive in products with high and low sugar contents, preserving sensory characteristics.

Another use of waste of nopal for produce biofuel (biogas rich in methane or hydrogen) represents a viable option for the water content that is more than 90%, and its easily degradable polysaccharides content (87% of the total solids) [3, 4]. For this reason, in this work, we present an experimental proposal of biorefinery scheme for obtaining bioproducts with high added value like mucilage and pectin, biogas rich in methane and biofertilizer from the cladodes of *Opuntia heliabravoana* Scheinvar.

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OXYGEN BARRIER AND FREE VOLUME PROPERTIES OF FULLY BIO-BASED POLYAMIDE 11/POLY(VINYL ALCOHOL) BLENDS

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The oxygen transmission rates, average volumes of free-volume-cavities (V_f) and fractional free volume (F_v) values of fully bio-based polyamide 11 (PA11)/poly (vinyl alcohol) (PVA) (i.e. $PA11_xPVA^{03}_y$, $PA11_xPVA^{05}_y$, $PA11_xPVA^{08}_y$ and $PA11_xPVA^{14}_y$) blend films reduced to a minimum value, when their PVA contents reached a corresponding optimal value. Oxygen transmission rate, V_f and F_v values obtained for optimal $PA11_xPVA^z_y$ blown films were reduced considerably with decreasing PVA degrees of polymerization. The oxygen transmission rate of the optimal $PA11_{72.5}PVA^{03}_{27.5}$ blown film was only 1.07 cm^3/m^2.day.atm, which is about the same as those of the most often used high barrier polymers, ethylene-vinyl alcohol copolymer. Experimental findings from dynamic mechanical analysis, differential scanning calorimetry, wide angle X-ray diffraction and Fourier transform infrared spectroscopy of the $PA11_xPVA^z_y$ blends indicate that PA11 and PVA in $PA11_xPVA^z_y$ are miscible to some extent at the molecular level when their PVA contents are $\leqslant$ the corresponding optimal values. The considerably enhanced oxygen barrier properties of the $PA11_xPVA^z_y$ blend films with optimized compositions are attributed to the significantly reduced local free-volume characteristics.

Keywords: Nylon 11; Poly(vinyl alcohol); Oxygen barrier; Free volume; Miscibility.

REACTIVIDAD DE POLIFLAVONOIDES MODIFICADOS DE CORTEZA DE PINO RADIATA EN LA CO- POLIMERIZACIÓN CON ÁCIDO ACRÍLICO

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La corteza de pino (*Pinus radiata*) generada en Chile tiene altas consecuencias ambientales debido a la gran contaminación que genera [1]. Como una estrategia para explorar nuevas rutas de valorización de extractivos polifenólicos de corteza, en el presente trabajo se modificaron los poliflavonoides de la corteza con anhídridos cíclicos insaturados (maleico, citracónico e itacónico) y luego se sometieron a reacciones de co-polimerización via radicales usando como co-monómero ácido acrílico e iniciador persulfato de potasio [2]. Se valuó el efecto de la temperatura y la relación molar en las características de gelación. Los tiempos de gelación transcurrieron entre varios segundos hasta horas, éstos variaron en function del tipo de derivado y las condiciones de polimerización. El derivado polifenólicos a base de anhídrido maleico mostró la reactividad más elevada, seguido del derivado en base a anhídrido citracónico. La gelación del derivado a base de anhídrido itacónico tuvo la polimerización más lenta. Por otra parte, tanto la temperature como la relación molar de monómeros influyeron también significativamente en la reactividad del sistema. La posición de la insaturación (*endo/exo*) parece ser el factor limitante de mayor asociación en la co-polimerizacion de derivados polifenólicos de corteza de pino con el ácido acrílico. Se concluye que las modificaciones químicas realizadas fueron altamente efectivas para aumentar la reactividad del tanino. Dicha ruta de polimerización conlleva a la preparación de nuevos materiales en base biológica para aplicaciones en las ciencias ambientales, la agricultura y la biomedicina.

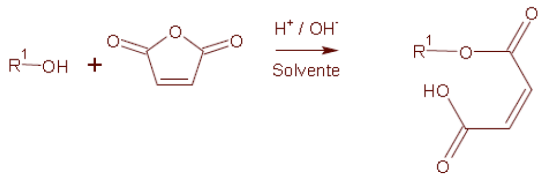

Fig. 1. Reacción de derivatización (funcionalización) de un grupo fenólico con anhídrido maleico.

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STUDY OF THE RELATIONSHIP BETWEEN INTRINSIC VISCOSITY AND ASPECT RATIO OF CELLULOSE NANOFIBERS SUSPENSIONS

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The relationship between the viscosity of CNFs suspensions and the intensity of mechanical treatment or degree of fibrillation has been widely reported. However, the available literature has not adequately addressed the relationship between rheological data of suspensions and the morphological characteristics of nanofibrils, therefore, it is not possible to establish a direct relationship between the viscosity of the suspension and the morphological characteristics of different CNFs. This work aims to approach the understanding of how the morphological characteristics of CNFs affect the viscosity of their suspensions and, thereby, to establish a relationship between both properties. Specifically, the goal is to determine the variation of the length and diameter (aspect ratio) of CNFs obtained by enzymatic-mechanical treatment, with the intensity of the applied treatment, as well as the intrinsic viscosity of the suspensions.

The CNFs suspensions used in this study were obtained from bleached eucalyptus kraft pulp with enzymatic treatment, followed by mechanical pre-refining in a PFI mill, to finally produce the actual disintegration of the wood fibers in a high-pressure homogenizer, varying the intensity of the mechanical treatment by the number of passes through the homogenizer.

The morphological analysis of suspensions clearly shows that by increasing the intensity of the applied mechanical treatment, CNFs are produced with increasingly homogeneous distributions of diameters and lengths and centered towards lower values. The mean diameter of the CNFs decreases significantly as the number of passes through the homogenizer increases; while for the average lengths of the CNFs, the decrease was significant only at the firsts numbers of passes (at the beginning of the process).

From the viscosity analysis of suspensions and their dependence on concentration, a strong relationship is observed between the intrinsic viscosity of the CNFs suspensions and their aspect ratio, which can be effectively correlated by the modified Mark-Houwink-Sakurada equation, obtaining the following expression: $\rho[\eta]_0 = 0.0012p^{1.85}$. By comparing the constants obtained in this work to those reported in the literature, it was possible to demonstrate that this equation is independent of the flexibility of CNFs. The obtained correlation was verified using commercial CNFs from two different suppliers, which correspond to CNFs with and without enzymatic pretreatment. These presented the same tendency with respect to the model, obtaining a variation of 5.0% for mechanical CNF and of 5.2% for CNF with enzymatic pretreatment.

Finally, it was possible to demonstrate that the morphological characteristics of CNFs, represented by their aspect ratio, can be described by the intrinsic viscosity, a rheological parameter.

Keywords: *Cellulose nanofibers, Rheology, Morphology, intrinsic viscosity, aspect ratio.*

SUGARCANE JUICE POTENTIAL IN A BIOREFINERY CONTEXT: HOW TO DEAL WITH THE INFLUENCE OF JUICE COMPOSITION DIFFERENCES IN THE JUICE QUALITY?

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Sugarcane (*Saccharum* spp.) is one of the main crops in the world, grown in more than 100 countries. World sugarcane production totalizes about 1.9 billion tones, and Brazil is the world leader in this crop production. This significant production may be justified by technological improvements in both the sugarcane agricultural production process and in the sugar and ethanol production processes. Besides its use as feedstock for sugar and ethanol production, sugarcane juice *in natura* is very appreciated in the whole world. It is an energetic drink, not alcoholic, whose taste is pleasant, due to its characteristics of refreshment and sweet flavor, allowing people from all ages to consume this drink. However, the juice characteristics are also one of the main factors that can affect the quality of the final products. It relates with the crop maturity, crop variety and type of soil but also to degrading processes occurring during storage and processing. In fact, sugarcane juice has to be treated and clarified, because minutes after its extraction, it gets a dark color which may negatively influence its composition. There are at least four mechanisms that contribute to color formation, namely: (a) melanoidins formed during reactions of the reducing sugars-amino acids by the Maillard reaction; (b) thermal degradation and condensation reaction of sugar by caramelization; (c) alkaline degradation and condensation reactions of reducing sugar; (d) oxidative reaction of phenolic compounds. The first three are non-enzymatic reactions, while the oxidative reaction of phenolic compounds to chemically reactive quinones is an enzymatic reaction and occurs prior to the milling process, when sugarcane is milled to extract juice. Compounds that most affect juice color are those naturally found in sugarcane, that is, phenolic compounds and flavonoids, responsible for 60–75% of juice color. But those compounds represent also an added value in a biorefinery context. Therefore, this work aims to present the actual knowledge on the composition of sugarcane juice obtained from different varieties and cultivated in different edaphoclimatic conditions and also, the variation in the juice composition introduced by storage and processing conditions. The knowledge acquired will help to identify options for valorization of the compounds that most affect juice color and that can improve the quality of the juice for carbon-based materials production.

THE EFFECT OF LARGE PELLET FEEDSTOCK PARTICLE SIZES AT DIFFERENT WATER CONTENTS ON PELLET QUALITY, TRANSPORT EFFICIENCY AND COMBUSTION EMISSION

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In 2015, more than 25 million tons of wood pellets have been consumed worldwide for domestic and commercial heating, industrial power generation and co-generation. The European Pellet Council stated that the pellet sector should address four key factors to be successful in the future. These factors are 1) production efficiency, 2) pellet quality, 3) logistics, and 4) conversion efficiency. Feedstock particle size distribution (F_{psd}) and water content (WC) affect wood pellet properties, transport parameters and combustion emissions in small heating appliances. Four feedstocks with different shares of fibers (> 3.15 mm) and fines (< 1 mm) were conditioned at 12 and 24 % WC. Pellets were produced and their bulk density, durability, length and sorption behavior was evaluated. Bulk density and sorption behavior was used to calculate the transport parameters. The pellets were combusted in a pellet stove and the combustion properties were correlated to the pellet properties. The 24 % WC feedstock pellets (P_{24}) showed a low durability ($\bar{x}$ = 79 %) and were short ($\bar{x}$ = 6.3mm). The P_{24} with the highest share of fibers showed the highest durability ($\bar{x}$ = 89 %). The 12% WC feedstock pellets (P_{12}) with a high share of fines (< 1 mm) and a low share of large particles (6.3 – 16 mm) had a low durability ($\bar{x}$ = 95 %), but the pellets produced with a high share of fines (< 1 mm) and fibers (3.15 – 6.3 mm) had a high durability ($\bar{x}$ = 98.5 %). The P_{12} had lower transport costs, energy consumption and greenhouse gas emissions than the P_{24} because of a higher bulk density (619 kg×m^{-3} and 362 kg×m^{-3}, respectively). The combustion parameters of the P_{12} were affected by the length and the density of the pellets. The flue gas oxygen content was inversely correlated to the flue gas temperature and affected by both pellet length and durability. The carbon monoxide (CO) emissions increased with decreasing durability and showed a weak correlation to the organic gaseous carbon emissions (R^2 0.467 – 0.621, depending on F_{psd}). The F_{psd} with the highest share of particles in the range of 3.15 – 6.30 mm showed the highest durability ($\bar{x}$ = 98.5%) and the lowest CO emissions ($\bar{x}$ = 280 mg×m^{-3}). Based on these results it was discussed whether moist large particles in combination with dry fine particles can have a positive effect on pellet durability, transport properties and combustion emissions. This is a new perspective on pellet production optimization.

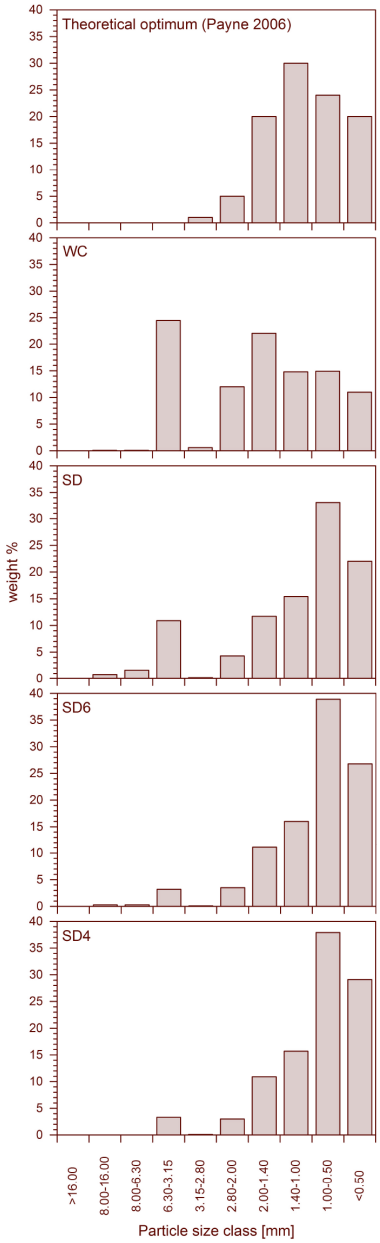

Figure 1. Feedstock particle size distribution used for pellet production in weight % of size classes. Theoretical optimum: recommended feed particle size distribution for high quality pellets (Payne 2006). WC: wood chips, 6mm screen; SD: untreated sawdust; SD6: sawdust, 6mm screen; SD4: sawdust, 4mm screen.

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Acknowledgement

The authors would like to thank Mr. Jodok Braun for his technical support. The contribution of Mr. Rodrigo Labbé was funded by the National Commission for Scientific and Technological Research (Conicyt) and the Ministry of Energy, Chile (Energy program, grant number ENER170062). The work of Mr. Michael Russ and Mrs. Victoria Knappe was funded by the Universtiy of Applied Science Rottenburg and the Ministry for Science and Research, Germany (Project BiCoLim, grant number 01DN16036), respectively.

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