

III Latin American Congress Biorefineries

Ideas for a sustainable world
November 19th to 21st 2012, Pucón, Chile

Conferences [Abstract]

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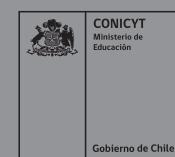
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Conferences [Abstract]

Biogas production potential and ammonium release in anaerobic digestion of spent microalgae.

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Biodiesel from microalgae seems as an important step for the development of biofuels that could replace actual fossil fuels. However, the low energetic yield of the process is an important issue that must be overcome. Anaerobic digestion (AD) of the spent biomass appears as an alternative to solve this, due to the production of biogas from spent microalgae, which allow valorization of this waste. Although anaerobic digestion is expected as a solution to energetic yield in biodiesel process, it presents also drawbacks that may affect anaerobic digestion performance, such as, drying step in microalgae, possibility of ammonium inhibition and co-digestion as solution, and effect of solvent in anaerobic consortia . All these drawbacks were studied in microalgae *Botryococcus braunii*, found a negative effect of drying step in spent microalgae, 68% nitrogen release, which will allow operating an hypothetical anaerobic reactor at microalgae concentrations lower 13% in order to reduce ammonium inhibition phenomena, an additive co-digestion when sludge and glycerol is used as co-substrate, which does an interesting and viable way to overcome problem associated with low C/N ratio in microalgae , and toxicity effect of petroleum ether at concentration over 2 g/L.

Acknowledgements: This work was funded by Consorcio DESERT BIOENERGY S.A, Innova-CORFO



Conferences [Abstract]

Value-added uses of co-products from biofuel industries: a path forward in sustainable biorefinery.

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The liquid biofuels (ethanol, butanol and diesel) from biological resources are gaining importance in recent years. First generation of biofuel is an important initiative in moving towards non-food based biofuels, well-known as second generation as well as third generation of biofuels. In the dry milling corn ethanol production, equal quantity of alcohol, distiller's dried grains with solubles (DDGS) and carbon dioxide (CO_2) are being generated. Both DDGS and CO_2 are considered as co-products. Although DDGS finds some uses in animal feeds, CO_2 in many corn ethanol industries are exposed to atmosphere. Value-added uses of these co-products can provide better economic return. Similarly in lingo-cellulosic ethanol industries, in general ethanol and lignin are being produced nearly at 1:1 ratio. Lignin is also a well-known co-product from pulp and paper industries. So far lignin has find very insignificant industrial value-added uses. In both food and non-food resource-based biodiesel production, "crude glycerol" has been considered as byproducts that has find very limited low-value applications. The disposal of "crude glycerol" from many biodiesel industries has become a critical problem. These co-products and byproducts from biofuel industries show immense potential in the design and engineering of new biobased materials. This provides two way benefits; (i) in providing value-addition to these co-products and byproducts thus can help these industries in getting additional economic benefits and (ii) in substituting certain petroleum-based plastics and materials with newly engineered biobased materials from these co-products. Biorefinery concept looks to find uses of each out-put component of biological conversion process. This helps both improving the economic with potential of environmental and societal benefit. Three important factors that govern sustainability are economy, environment and society that need to overlap for the realization of true sustainable development. The sustainable development and environmental communication should be substantiated by data, life cycle analysis (LCA) and appropriate standards for the market growth.

Acknowledgements: This research is financially supported by the Ontario Research Fund (ORF) Research Excellence (RE) Round-4 from the Ontario Ministry of Economic Development and Innovation (MED); Ontario Ministry of Agriculture, Food, and Rural Affairs (OMAFRA)-New Directions Research Programs; OMAFRA- University of Guelph Bioeconomy for Industrial Uses Program; Natural Sciences and Engineering Research Council of Canada (NSERC)-CRD grant; Grain Farmers of Ontario (GFO); and Manitoba Pulse Growers Association (MPGA).



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Conferences [Abstract]

New microalgae biorefinery concept.

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The future of microalgal biofuels could be most promising, if the biorefinery concept is included in the processing of microalgal biomass. Production of energy from spent microalgae biomass after to lipid extraction for biodiesel production seems a logical step in that direction. In addition, the microalgae is characterized for contain a high amount of protein that could be used as alternative for protein source to human consumption or animal feed.

The aim of this work was to propose a new microalgae biorefinery concept in which was include the follow steps: 1) protein extraction, 2) lipids extraction to biodiesel production and 3) biogas production from the final residue of the process.

A freshwater microalgae was used as feedstock. First, the protein extraction from microalgae culture previously centrifuged (132 g/L) was investigated. The response surface methodology (RSM) was used in order to optimize the interaction of three variable: temperature, time and pH. Subsequently, the biomass after to protein extraction was dried for 24 hours at 40 °C and milled. After, the lipids were extracted by using a soxhlet extraction system with petroleum ether as solvent. Finally, the spent microalga was used to determination of methane potential in 117 mL serum bottles at 35°C.

The results obtained showed that in the first step was possible to reach until 34 g/L of protein in the upper layer to optimized conditions at: pH 12, 50° and 40 minutes of reaction time. In the second step, the biomass after protein extraction was used in a lipid extraction to biodiesel production reaching 14% of lipid production yield. Finally, the spent microalgae (about 75 wt% of the total biomass), was used in the determination of methane potential reaching 350 mL CH₄/gSV in one month of production.

The lipid production yield reached was similar to the reported. In addition, considerable protein extraction and very high biogas production were reached. Therefore, was possible to conclude that the biorefinery concept should be considered in the investigations about biofuels from microalgae. In this sense, the process proposed could be an alternative to get a competitive microalgae industry.

Acknowledgements: This work was supported by Consorcio Desert Bioenergy S.A., Innova-CORFO, CONICYT Project 78110106, Chilean Fondecyt project 3120171and PIA project DI12-7001 from University of La Frontera.



Conferences [Abstract]

Bagazo de sorgo dulce, una alternativa para la producción de etanol de segunda generación.

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El bioetanol es el combustible más utilizado para el transporte en todo el mundo. La producción de etanol de segunda generación es una de las estrategias para reducir el consumo de combustibles fósiles y mitigar la contaminación del medio ambiente. En Colombia, las plantaciones de sorgo dulce se hacen generalmente para la alimentación del ganado, sin embargo, desde un punto de vista biotecnológico el sorgo dulce es una fuente abundante de carbohidratos y por lo tanto es una fuente potencial para la producción de etanol. El sorgo dulce tiene dos fuentes de carbohidratos: en primer lugar el jugo, que es similar al zumo de caña de azúcar y es posible su transformación a etanol. La otra fuente es el bagazo, un material lignocelulósico, rico en celulosa (alrededor de 24,1%) que se produce en grandes cantidades (42994 toneladas de producción anual) y es susceptible de ser transformada a etanol, después de la liberación de azúcares por medios químicos y enzimáticos.

El uso de bagazo de sorgo dulce implica el estudio de pretratamientos químicos con el fin de eliminar la lignina y facilitar el acceso de las enzimas celulósicas para liberar moléculas de glucosa. También es necesario el estudio de las condiciones para una hidrólisis enzimática adecuada a fin de reducir los costos de producción. Este artículo trata de los resultados de un estudio comparativo sobre la producción de etanol mediante sistemas SSF y SHF, en el que dos variables de optimización fueron consideradas, la concentración de la levadura y la adición de una fuente de nitrógeno externo para el proceso de fermentación. Una vez que las condiciones óptimas se obtuvieron los resultados fueron confirmados mediante fermentaciones adicionales. Un contenido de etanol de 40 g/L se obtuvo usando el sistema SSF, mientras que en el sistema SHF se alcanzó una concentración de 32 g/L.

Palabras clave: sorgo dulce, lignocelulósico, etanol, deslignificación alcalina.



IN SITU TRANSESTERIFICATION OF *Nannochloropsis gaditana* WET BIOMASS: INFLUENCE OF PROCESS CONDITIONS ON LIPID EXTRACTION AND FAAE YIELD.

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The conventional process for obtaining FAAE (Fatty Acid Alkyl ester) from microalgae comprises different stages, such as: drying, cell disruption and lipid extraction, which are highly demanding of energy. An alternative process to produce microalgal derived FAAE is in situ transesterification of microalgal biomass, where cell disruption, lipid extraction and transesterification are carried out in one step, with a direct reaction of oil-bearing biomass to FAAE. In the same way than the normal process, the presence of water affects negatively the FAAE yield. Therefore, is necessary more research regarding to the operational condition in order to apply this methodology directly on wet biomass, which could decreases the energy demand. Therefore, the aim of this work was to investigate the influence of operation conditions in both the yield of lipid extraction from biomass and the yield of FAAE conversion from the extracted lipids. Wet *N. gaditana* biomass (75% water content, w/w) and two acyl acceptors, a short chain alcohol (acyl acceptor 1) and a middle long chain alcohol (acyl acceptor 2) were used. Due the high free fatty acid content of the oils of *N. gaditana*, an acid was used as catalysts for the transesterification reaction. A 2² factorial design was employed with alcohol to biomass ratio (w/w) (6:1 and 12:1, wet basis) and acid to biomass ratio (w/w) (1:5 and 2:5, wet basis) as factors. Oil extraction yield (% w/w of initial biomass, dry basis), FAAE content (% w/w of oil extracted) and FAAE yield (% w/w of initial biomass, dry basis) were the responses used to analyze efficiency of the direct transesterification process. Using this methodology it was possible to establish operational conditions that maximized FAAE yield for both acyl acceptors in the range of conditions studied. For acyl acceptor 1, the best conditions were alcohol to biomass ratio of 6:1 and acid to biomass ratio of 1:5, giving a FAAE yield of 3.5% (g FAAE/g biomass, dry basis), an oil extraction of 10% (% w/w of initial biomass, dry basis) and FAAE content of 35% (% w/w of oil extracted). For acyl acceptor 2, best conditions were alcohol to biomass ratio of 6:1 and acid to biomass ratio of 2:5, giving a FAAE yield of 5% (g FAAE/g biomass, dry basis), an oil extraction of 10% (% w/w of initial biomass, dry basis) and a FAAE content of 55% (% w/w of oil extracted). The preliminary results of this work indicate that the direct transesterification can be performed at higher water content, decreasing the necessity of biomass drying.

Acknowledgements: This work was supported Consorcio Desert Bioenergy S.A., Innova-CORFO, FONDECYT project N°11110282, CONICYT Project 79090009, CONICYT Project 78110106 and Chilean Fondecyt project 3120171.



Conferences [Abstract]

Enhancing the Biochemical Methane Potential of Microalgae via Biomass Pretreatment.

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There is an increasing interest in microalgae as a feedstock for biogas production based on their large areal productivities compared to conventional crops, despite the economic feasibility of the process could be limited by the high cultivation costs of microalgae. Microalgae-based wastewater treatment can provide a low-cost biomass for anaerobic digestion. Preliminary studies on anaerobic digestion of microalgae have shown low methane productivities likely due to the strong cell walls of microalgae or the lack of optimum conditions during the biochemical methane potential tests (i.e substrate to inoculum ratio and biomass concentration). In this context, the anaerobic digestion of three microalgae mixtures at different substrate to inoculum (S/I) ratios (0.5, 1 and 3), concentrations (3, 10 and 20 gTS·kg⁻¹) and pretreatments (thermal hydrolysis, ultrasound and aerobic biological treatment) was here studied. Microalgae A was a mixture of microalgae cultivated in a synthetic mineral salt medium in a tubular photobioreactor. Microalgae B and C were cultivated in 180-L open photobioreactors operated in a continuous culture mode at 36 days of hydraulic residence time treating anaerobic digestion effluent and synthetic biogas.

An S/I ratio of 0.5 supported the highest final methane productivities regardless of the microalgae tested, while the highest S/I ratio induced a certain degree of inhibition in the anaerobic digestion. The lowest initial microalgae concentration supported the highest content of methane on the biogas (72-78% at 3 gTS·kg⁻¹, 63-68% at 20 gTS·kg⁻¹) and the lowest biodegradabilities. The application of thermal hydrolysis, ultrasound and biological pretreatments to microalgae resulted in an increase on the solubilization degree (SD). The highest SD values were reached at ultrasound energies of 57000 kJ·kgTS⁻¹ (SD of 32%, 60% and 62% for microalgae A, B and C) and during thermal hydrolysis at 170°C (SD of 32%, 63% and 40% for microalgae A, B and C). Despite an increase on the ultrasound energy (10000-57000 kJ·kgTS⁻¹) increased the SD in all microalgae tested, it did not result in enhanced methane productivities. The highest increase on CH₄ productivity was 62% for the thermal hydrolysis of microalgae C. The lowest SD values were recorded during the biological pretreatment, which even caused a reduction on the final CH₄ productivities (of up to 18 %). The results here obtained confirmed the lack of correlation between the solubilization degree and the methane enhancement potential and pointed out that anaerobic digestion of algae after thermal pretreatment is a promising technology for renewable energy production from microalgae.



Conferences [Abstract]

Walking the tightrope of bioavailability: Microbial dynamics on vapour-phase chemicals.

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Increasing attention has been devoted to the effective and environmentally-sound production of biomass-derived fuels based on whole-cell catalysts. Effective biotransformation of chemicals requires both adequate habitat conditions and a suitable contaminant bioavailability to transforming microbes. Compound bioavailability however, is ‘Janus-faced’; i.e. is essential and likely promoted by the organism for assimilative uptake, whereas, when too high, may lead to toxic effects and provoke avoidance strategies (e.g. tactic responses) of the target organisms. Although the bioaccessible compound pool for both effects may be identical, the exposure of individual organisms to environmental chemicals has opposite consequences and may particularly interfere, when a metabolisable substrate causes toxicity at high bioavailability. Such situation leads to a microbial tightrope walk that is often poorly considered in biotransformation approaches where one tends to assume that effective substrate-utilizing bacteria tolerate any exposure to these substrates. Using a semivolatile model compound (naphthalene, NAH) and NAH-degrading *Pseudomonas putida* (NAH7) we here studied the effect of vapour-phase concentrations gradients on microbial motility and growth dynamics. The highlights of this paper give evidence of down-gradient, i.e. negative (chemo-)tactic movement of *P. putida* (NAH7) away from a NAH point when exposed to vapour phase NAH (surprisingly at even at gaseous concentrations lower than aqueous concentrations that clearly induce chemo-attraction). They secondly elucidate the tightrope walk of substrate bioavailability for assimilative growth and growth inhibition of *P. putida* (NAH7) in vapour-phase NAPH gradients: Microcosm experiments revealed that high cell densities increased growth rates close (< 2 cm) to the NAH source, whereas intercellular competition for NAH decreased growth rates and biomass at larger distances despite the high NAH gas phase diffusivity. Finally, such varying growth kinetics is explained by a combination of bioavailability restrictions and NAH-based inhibition. To account for this balance, a novel, integrated ‘Best-equation’ describing microbial growth influenced by both substrate availability and inhibition is presented. Our work demonstrates the importance of microorganisms to transform vapour-phase compounds and to influence vapour-phase concentration gradients even at the centimeter-scale, respectively. It further underlines the importance of high active biomass and concomitant effective reduction of their exposure to inhibitory substrates in order to create environments favourable for survival (e.g. in biodiesel-producing three-phase solid–gas–liquid (SGLB) bioreactors using gaseous alcohol and liquid rapeseed oil).



Conferences [Abstract]

The Mutual Interdependency of Pretreatment and Enzymatic Hydrolysis to Ensure the Effective Production of a Competitive Sugar Stream from Biomass Substrates.

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The resistance of lignocellulosic materials to enzymatic attack is due to nature using physical, mechanical and chemical mechanisms to make it remarkably difficult to actually access the chemical bonds that we in the bioconversion community want to ultimately hydrolyze. It has been shown that, regardless of substantial differences in the source, structure and chemical composition of lignocellulosic feedstocks and the pretreatment technology used to open up the substrate, the susceptibility of the cellulose to enzymatic hydrolysis is strongly dependent on the specific surface area (SSA) of the cellulose to the enzymes. An effective pretreatment process should ideally provide good recovery of the lignin, hemicellulose and cellulose in a useable form, be inexpensive and applicable to a wide range on feedstocks, while significantly increasing the SSA. However, various compromises often have to be made to try and meet all of these goals. It is apparent that the optimum enzyme cocktail used to hydrolyze the cellulose is significantly influenced by both the nature of the substrate and the pretreatment technology used. By maximizing the synergies between pretreatment and enzymatic hydrolysis it is possible to both minimize the dehydration reactions that decrease carbohydrate recovery while enhancing the SSA of the cellulose so that effective hydrolysis can be achieved at low enzyme dosages. We will discuss how key components in the enzyme mixture and mechanisms such as amorphogenesis all play a role in increasing SSA and allowing the enzymes actually access the β -1,4 bond.



Furans as offspring for broad applications in chemical and polymer industry.

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In the near future an adequate alternative to chemical compounds for fine chemicals, solvents, monomers and finally fuels needs to be available. Therefore the Fraunhofer ICT developed batch and continuous processes for the production of the fine chemicals Furfural and 5-Hydroxymethylfurfural based on renewable resources. These processes can use raw materials coming from the biorefinery, where biogenic resources and residues of forestry and agriculture are disintegrated into their components.

This work in particular discusses the results of the experiments that were accomplished for the catalytic dehydration of C₆- and C₅- carbohydrate raw material to obtain the furan derivatives 5-(hydroxymethyl)-2-furaldehyde and furan-2-carbaldehyde, also known as 5-Hydroxymethylfurfural HMF and Furfural, via heterogeneous catalysis.

5-Hydroxymethylfurfural can be obtained through elimination of three moles of water per molecule of C₆-containing raw material coming from renewable resources such as cellulose and sugars. This compound possesses two functional groups, the hydroxyl and the aldehyde. Thus HMF can be fitted twice with functional groups, either symmetrical or asymmetrical.

Furfural is derivable from the hemicellulose fraction that comes from organic raw material such as straw, wood and grass as well as of five carbon sugars. Via threefold intermolecular water elimination the hydroxyl molecules can be neutralized with two double bondings and an aldehyde function being built. After this preliminary defunctionalization, the molecule can be refunctionalized again with nearly unlimited possibilities of functional groups.

These renewable substances are predestined to substitute fossil compounds on a large scale for polymers, solvents, fine chemicals and finally fuels. In favor of that highly charged industrial oxide catalysts were tested and own metal based catalysts were developed and prepared in cooperation with Heilbronn University. The main point that distinguishes this inquiry from other existing work on these compounds is the fact that we entirely disclaim supercritical fluids, organic solvents, phase modifiers, ion exchangers and ionic liquids that are commonly described in literature. Hence the process targets mild reaction conditions also to prevent a contamination of the reaction products with compounds that are hardly to be removed in cost-intensive purification steps. The experiments were executed in both batch mode and continuous sequencing in order to find preliminary reference points first with an optimization in a continuous stirred tank reactor on the laboratory plant afterwards.

The results show that molar yields of more than 46% for 5-Hydroxymethylfurfural as well as for Furfural are possible in batch mode starting with fructose respectively xylose, more than 35% yield for 5-Hydroxymethylfurfural in continuous mode can be reached with heterogeneous catalysts and water as the sole solvent. Additionally the Fraunhofer ICT ran oxidation reactions to the forward-looking Furan-2,5-dicarboxylic acid FDCA that can find a wide application in the polymer industry to substitute terephthalic acid as monomer for polyesters and polyamides. These experiments succeeded in kilogram scale with yields higher than 99% coming from 5-Hydroxymethylfurfural. This result opens a promising future for commodity plastics and further chemical modifications for specialty products.



Conferences [Abstract]

Pulping by-products: past, present and future.

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This presentation will give a comprehensive overview on current industrial isolation or manufacture of pulping by-products, covering kraft, sulphite, organosolv, and mechanical pulping processes. In addition, a number of interesting historical by-products and their isolation processes are presented, and finally, some future speculations will be outlined.

Today, 3.5 million tons of chemicals (or biofuels) are being produced as pulping by-products, of which tall oil (1.6 million tons), lignosulphonates (1.2 million tons), and turpentine (0.2 million tons) dominate. Numerous other, minor products include xylose and other sugars, ethanol, yeast, ribonucleic acids, vanillin, furfural, and acetic acid. Current production figures, main producers, and various production trends will be discussed.

Many other products have been isolated or manufactured in the past (c. 1900-2011), including arabinogalactan, pekilo protein, p-cymene, alcohols other than ethanol, bioactive substances, oxalic acid, formic acid, methanol, acetone, 2-butanone, oil fractions, dimethyl sulphide, dimethyl sulfoxide, and even ammonia. An overview of the corresponding innovative processes will be given. In addition, main reasons for the discontinuation of their production will be summarised. In this section, products from prehydrolysis-kraft pulping processes (for the utilisation of the prehydrolysates) will also be discussed.

Finally, some future trends and potential of novel types of pulping by-products will be addressed, including hydroxy acids and hemicelluloses from kraft pulping processes.



Conferences [Abstract]

Assessment of concepts for wheat grain and straw based biorefineries.

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The production of ethanol from wheat grain is a well-established process in Europe. Nevertheless increasing requirements for greenhouse-gas-saving potentials of fuel ethanol as well as the aim to generate high value by-products are the drivers to develop numerous possibilities for optimization. Therefor consortium of 16 partners of the project "Bioraffinerie2021" (<http://bioraffinerie2021.de>) was funded by the German Federal Ministry for Education and Research (BMBF) to develop sustainable of concepts of ethanol based biorefineries. The partners from industry and academia developed different technologies for the optimization of existing wheat based ethanol plants.

Based on the research of the project partners, different process configurations of an integrated production of ethanol and other products from grains and straw were elaborated. Aim of the process development was to integrate the main findings of the different research activities. The results of three years of work on process development and assessment will be presented. To analyse the mass and heat balances, plant concepts were simulated with flowsheeting software such as Aspen-Plus and SuperPro Designer. A thorough assessment of the different process options was made and technical, ecological and economic parameters were calculated. Parameters that were assessed for each of the concept include: production costs, greenhouse-gas emissions, cumulated energy demand, eutrophication and acidification.

The need to reach high concentrations of substrates and products within the process streams as well as a sound concept for heat re-utilization throughout the plant became clearly visible. Furthermore the assessments show that, given the possibility to use lignin fractions as an energy source for process steam production, the integration of straw into existing bioethanol plants can significantly improve the ghg-balance. The results were used to give a feedback to the technology developers within the consortium. A comparison of different process configurations will be presented and their weaknesses and strengths on behalf of their respective sustainability will be highlighted.



Conferences [Abstract]

One vision on Biorefinery in Chile.

Antes, Rudine¹ ; Mariani, Silvana²

Before the year 2000 if one would search for biorefinery or ethanol would find only few technical articles or web pages and most of them related to a Norwegian company called Borregaard which in year 2012 claimed to have more than 40 years of experience in biorefinery field. In 2005 this subject started to get attention from many industries like fuel, pulp, paper, enzymes among others.

According to National Renewable Energy Laboratory (NREL)'s a biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic bio based industry.

The main reasons for the increasing interest in this field are based few drivers like: The statement of the mankind responsibility for the global warming (2007), oscillation in oil prices and lacking of competitiveness of pulp and paper industry in North hemisphere, especially in North America.

Also in the beginning of this decade we witness the increase of numbers of production facilities of first generation ethanol from sugar-cane (Brazil) and corn (USA). This also motivated investments in new technologies of second generation biofuels from agricultural residuals and woody material due the potential cheaper raw materials.

It is clear that every country accounts with its own drivers in order to establish biorefinery Industries. Because oil price is a commodity the cost of biofuel production, efficiency of the process (yield), biomass yield per hectare will attract the Industry investments or not. Environmental pressure by the society on government could generate that the use biofuel in certain country would be mandatory or could be used as incentives in prices of vehicles, pay tolls, etc.. In case of Chile and ethanol it could be a problem regarding that the ethanol should be imported in the first instance what could affect final price of fuel, especially in the months of low production in Brazil or USA.

The main obstacle to create the Biorefinery industry in Chile would be the price of electricity (Chile detains the 5th most expensive price for energy). At the present technology still is more profitable to convert one metric ton of wood in energy than fuel. Meanwhile the energy production from biomass is an established industry usually jointed to the pulping industry the first commercial facilities to produce second generation biofuels are just beginning.

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Conferences [Abstract]

Producción semi industrial de biometanol de glicerina procedente de la oleoindustria del biodiesel.

PhD Gabriel Jaime Cano Ospina.

En el mundo, existe un gran interés por encontrar materias primas y fuentes de energía alternativas, que sirvan como sustituto parcial o total a los recursos no renovables, ya que las reservas de este tipo de fuentes, se encuentran disminuyendo de una manera acelerada. Muchos gobiernos están implementando políticas que van orientadas hacia la sustitución de estas energías por combustibles alternativos, enfocando principalmente su atención en el Gas Natural, el Hidrógeno y los Bio- Carburantes.

Entre los Bio-Carburantes más utilizados como sustituto parcial o total del combustible Diesel convencional se encuentra el Biodiesel, producido por medio de un mecanismo llamado Transesterificación, donde la molécula de triglicérido presente en el aceite vegetal o grasa animal reacciona con un alcohol, comúnmente metanol, produciendo Biodiesel y Glicerina; siendo esta equivalente a un 10% de la masa del triglicérido.

A nivel mundial, Europa es considerado como el mayor productor de Biodiesel, seguido por los Estados Unidos y por los países del Pacífico Asiático; en América del Sur, entre los principales productores se encuentra Brasil, Argentina, quien es el cuarto productor mundial y Colombia, donde se ha planeado la construcción de 9 plantas, con las cuales se tendrá una capacidad instalada de 696.000 toneladas – año cuyo proyectos productivos han dado comienzo en el año 2008. Como una consecuencia directa de esta producción mundial, de forma alterna se produce la glicerina en cantidades que su mercado internacional ha y será incapaz de absorber, existiendo excedentes importantes, dando como resultado, una disminución del precio, convirtiéndose en una materia prima importante para la obtención de productos de mayor valor agregado.

En Colombia no se produce metanol para el consumo interno, este debe ser importado, en orden de prelación, de países como Venezuela, Estados Unidos y Canadá, haciendo necesario que las plantas de Biodiesel se vean en la necesidad de importar 69,600 toneladas - año de este insumo a un mayor costo de producción.

En la actualidad, a nivel mundial, el metanol es producido del gas de síntesis (H_2+CO) obtenido principalmente del Gas Natural, utilizando equipos que operan a condiciones de presión y temperatura extremas, haciendo de esta una tecnología de difícil adquisición en el país. Por esta razón, durante los estudios doctorales se desarrolló un catalizador sólido bimetálico, que con un alto grado de selectividad, transforma la glicerina en BioMetanol utilizando un mecanismo denominado Hidrogenólisis, bajo estas condiciones, se ha construido una planta piloto con una capacidad de 10 tonelada – mes y en la actualidad se está construyendo una semi-planta industrial que producirá unas 100 toneladas – mes que servirá como planta demostrativa para la replicación de la tecnología en las propias plantas de Biodiesel para que realicen la transformación de la glicerina en la segunda materia prima más importante del proceso productivo. Por otra parte, Colombia será el único país en Latinoamérica que posea tres biocombustibles, el Biodiesel, el Bioetanol y el Biometanol, ayudando de esta forma a reducir de manera sustancial la dependencia del petróleo, ahorrando en divisas que son destinadas para la compra de biocombustibles que ayudan a completar la demanda interna y con la posibilidad de reducir el precio de los carburantes para el consumo interno.



Conferences [Abstract]

Torrefacción de biomasa forestal residual en Chile.

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Las condiciones agroclimáticas de las zonas centro y sur del país, la actividad forestal y la importante reserva de bosque nativo, sitúan a la biomasa forestal como una alternativa atractiva para diversificar la matriz energética chilena. Sin embargo, existen barreras tipo logístico, derivadas principalmente de la baja densidad estérica y heterogeneidad del recurso, lo que encarece los costos de manejo y transporte, haciendo indispensable la densificación energética. En este contexto, la torrefacción de biomasa surge como una solución tecnológica sencilla y eficiente, que consiste en un tratamiento termoquímico, desarrollado en condiciones de presión atmosférica, ausencia de oxígeno y a temperaturas entre 200 y 300 oC. Se caracteriza por bajas razones de calentamiento, menor a 50 oC/min y largos tiempos de residencia, usualmente 1 hora. En el proceso se pierde casi totalmente la humedad, además, se volatiliza entre el 10-30 % de la masa seca, producto de la descomposición térmica parcial de los componentes de la biomasa, conservándose alrededor del 90% del contenido energético inicial, lo que se traduce en una densificación energética. Como resultado del proceso, el sólido generado resulta homogéneo, prácticamente seco, con mayor poder calorífico, mayor carácter hidrofóbico y más quebradizo, disminuyendo la energía requerida en molienda hasta en un 90%, comparado con la biomasa de origen, además, los pellets producidos a partir de biomasa torrefactada pueden alcanzar densidades de hasta 850 kg/m3.

En el marco del proyecto Fondef B09I1015, se realizaron ensayos de laboratorio con Pino Radiata y Eucaliptus Glóbulus, utilizando un reactor de lecho fijo, en el que el calor es entregado a través del contacto directo con nitrógeno. Se ensayaron temperaturas de 220, 250 y 280 oC, con tiempos de residencia de 15 y 30 oC. Dependiendo de la severidad del tratamiento, las pérdidas de masas fluctuaron entre 9 y 33% para el Pino y entre 14 y 45% para el Eucaliptus. Con respecto al aumento del poder calorífico, éste fluctuó entre 7 y 17% para el Pino y entre el 8 y el 20% para el Eucaliptus, lo que implica una mayor reactividad con respecto al Pino. Se observó además, que el efecto de la temperatura es mayor al del tiempo de residencia. Se construyó el gráfico de Van Krevelen para el Eucaliptus, en el que se aprecia la disminución de las razones H/C y O/C con el aumento de la severidad de la torrefacción.

Del cálculo del rendimiento energético del proceso, se dedujo que los procesos leves (220oC) y medios (250oC) eran energéticamente favorables, debido a que a mayor temperatura, la pérdida de energía por masa volatilizada no es compensada con el aumento en el contenido energético del sólido remanente.

Por otro lado, se construyó una planta piloto, basada en un reactor vertical de tres etapas de contacto directo con vapor sobrecalentado a presión atmosférica. La planta semicontinua, diseñada para una capacidad de procesamiento máximo de 100 kg/h de chips de madera, está en puesta en marcha y contempla partir su operación en Agosto de 2012.



Conferences [Abstract]

The Integrated Biomass Research Initiative: Pretreatment and Conversion Systems for the Production of Advanced Biofuels and Bioproducts.

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In support of 2nd and 3rd generation biofuels production, the United States has the potential to produce over 1.3 billion dry tons of lignocellulosic biomass per year, of which 998 million dry tons are derived from agricultural residues and energy crops and 368 million dry tons from forest resources. The fermentable sugar from that biomass could produce enough biofuel (21 billion gallons) to replace one third of the current demand for transportation fuels in the US. Lignin usually comprises between 1-20% of the cell walls in herbaceous plants and 20 and 35% (by weight) of woody tissues in hardwoods and softwoods, respectively. If one chooses mid-range lignin compositions for the agricultural and forest resources, 10% and 27% respectively, then nearly 200 million dry tons of lignin waste will be available to be processed and utilized in the US each year.

Significant biochemical pathway barriers to ethanol production from lignocellulosic material include: (1) *biomass recalcitrance*, the restricted access of enzymes or chemicals to cellulose caused by the close association of lignin with cellulose, which limits the extent and rate of hydrolysis; and (2) *pretreatment chemistry*, the degree of crystallinity of natural and pretreated cellulose, which also limits the extent and rate of hydrolysis. The extent of cellulose conversion is directly related to the removal of the cell wall components hemicellulose and lignin. Lignin is the most recalcitrant in preventing maximum sugar release from lignocellulosic biomass. Given its concentration in the feedstock and the inhibition to fuel fermentations caused by degradation products generated during biomass pretreatment, lignin represents one of the most pressing problems related to cellulosic biofuel process design and operation. Conversely, lignin-derived aromatic compounds represent a potentially valuable opportunity to generate functionalized aromatic monomers with much higher unit value than transportation fuels or boiler fuel.

The Integrated Biomass Research Initiative has directly addressed a variety of novel biomass pretreatment methods for lignocellulosic materials, several in collaboration and consultation with researchers at Novozymes North America. There have also been productive efforts to understand and evaluate methods to effectively depolymerize or otherwise transform lignin into small molecules useful in chemical product synthesis.



Conferences [Abstract]

How to take an idea from a laboratory to market – Contract R&D organizations.

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A biorefinery is often defined as a facility for achieving large-scale integrated production of fuels, power and chemicals from biomass. The possibility of integrated processing of a number of products from biomass is a concept that is gaining increased attention in many parts of the world.

A biorefinery operation is based on a number of conversion processes and requires supply of biomass feedstock, preferably of a specific quality. Possible sources of feedstock include agricultural crops and residues, wood residues, woody and not-woody energy crops, algae and microbial fermentation products. If supplies are of heterogeneous type and quality, the feedstock has to be mechanically separated into fractions and, where necessary, pre-treated to give interim products of the required specification for the different applications. The final conversion to energy, fuels or other products is carried out using a range of thermochemical and biochemical processes – some of which are already at a stage of commercial development while others require further research and technological development.

The move from laboratory to full-scale production of a bioproduct is rarely possible in one step. A pilot or demonstration project is usually needed to confirm that biomaterials meet expected market specifications or that full scale-production will be economically feasible. Pilot studies may involve post-harvest processing, extracting and processing of raw materials from crops or biomass, development of necessary technologies, procedures for analysis, quality control and quality assurance, development of biosafety and environmental protocols.

The lack of intermediate-scale facilities available for testing is often a serious bottleneck derailing the biorefinery projects. There is a big leap from obtaining rather small quantities of novel bioproducts in the laboratory to large-scale commercial production. Biotechnology companies are forced to contract out their R & D, and often the preliminary stages of manufacturing, due to limited resources and their focus on technology rather than production. Bioprocessing services is a growing business which has recently come of age.

In the past, companies were pursuing their own end products and had operational R&D facilities that were often vastly underutilized. Most of these facilities had a high level of specialization geared to particular product or process. Today, biorefinery approach, require combining multi-faceted R&D expertise with suitable and diversified processing equipment. In many research projects, the science is outpacing engineering and the production gap is a major obstacle for fast transfer of the discovery from the laboratory to the marketplace. Some of the major bioprocessing challenges include the design of large scale continuous systems and the gentle but efficient product separation, purification and recovery. A well-known principle in engineering is that costs increase exponentially from concept, to system study, and next to the laboratory model, to pilot plant and finally to the production facility. The need to develop new types of flexible processing facilities serving the biorefineries is evident.

The key ingredients that the contract R&D partner must bring to the equation are confidentiality, a recognized staff's expertise and multifunctional facilities, respected track record for delivery of programs, an international presence and strong adherence to quality principles.



Conferences [Abstract]

Comparison of several olive oil mill wastewaters as electron donor in a bioelectrical system.

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Olive oil extraction is one of the most traditional agriculture industries in Spain where 30% of the world's oil production is produced. Two main wastewater streams are produced in the olive oil industry. The wash water generated during the initial washing of olives and the wash water generated during the purification of virgin olive oil. The wash water generated during the initial washing of olives complies with regulation for irrigation; therefore no further treatment is necessary. The wash waters generated during the purification of olive oil is characterized by high content in organic compounds such as phenolic compounds, substances characterized by its antioxidant and recalcitrant character to its microbial degradation. The treatment of such wastewater is essential for a sustainable olive oil production. Depending in the olive and olive oil production process used, two different wash waters generated during the purification of olive oil can be obtained. When the purification process is done by centrifugation (WWC), where a water input is used or when is done by decantation (WWD), where there is not water input to the system. Bioelectrochemical Systems (BESs) use micro-organisms to catalyze an oxidation and reduction reaction at an anodic and cathodic electrode respectively. Oxidation of organic and inorganic electron donors occurs in the anode. Examples of such electron donors are waste organics. At the cathode, an electron acceptor is reduced. The anode and the cathode are connected through an electrical circuit. If electrical power is harvested from this circuit, the system is called a Microbial Fuel Cell (MFC). In the present study both wash waters (i.e. WWC and WWD) were used as electron donor in the anode of a MFC. $\text{Fe(III)[CN]}_6^{3-}$ was used as electron acceptor in the cathode. The experiments performed showed that electricity generation using olive oil mill wastewaters is feasible with both WWC and WWD, although recalcitrant organic matter degradation and improvement of electricity production has to be further investigated in order to make it more suitable for real application.



Conferences [Abstract]

Evaluation of lignins recovered from different pretreatment processes for use as replacement of phenol in adhesives for plywood production.

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Increasing petroleum prices, concerns over security of supply and about climate change are major drivers in the search for alternative renewable energy sources, and the biorefinery from lignocellulosic biomass could be an alternative to obtain biofuels and biomaterials. Currently, the lignin from biomass is mainly used as a fuel in power generation in the pulp industry, however, it can also be considered as a raw material with high potential for transformation, and could be used for the production of different material such as; carbon fiber, adhesives, activated carbon, and various other phenolic and aromatic compounds with high added-value. Different characteristics of the lignin have been considered relevant for the replacement of phenol in the synthesis of phenol-formaldehyde adhesives, such as a high amount of free phenolic hydroxyl groups and low molar mass. The Biomaterials subproject of the BioEnercel Consortium aims to use the lignin of different pretreatment process of wood (such as organosolv, steam explosion and autohydrolysis) for total or partial replacement of phenol in formulations of lignin-phenol-formaldehyde (LPF) adhesives for panelboards production. Results indicate that the organosolv lignin from *E. globulus* and *P. radiata* have low weight-average molecular weight and lower polydispersivity than others lignins. Also organosolv lignin from *E. globulus* shows a slightly higher reactivity towards formaldehyde than lignins from the other processes. Organosolv lignin from *E. globulus* were directly used as replacement for phenol in the synthesis of LPF resins in the proportions of 10, 30 and 50% w lignin/w phenol, with a solid content of 46% and molar radio between 2.4 - 3.1. Formulations were used as adhesive in the preparation of tri-plywood samples. All resins formulated with different poly-condensation time showed a broaded range of viscosity between 50-600 cps. It was observed that an increasing in the amount of lignin in replacement of phenol caused a reduction in the poly-condensation time and increase in viscosity. Different tests for shear strength measurement such as boiling test and vacuum-pressure were carried out according to the Norm PS1-09. Results obtained suggested that the procedures for adhesives and plywood manufacture could be optimized to better strength properties with the LPF resins. Furthermore, some modifications in lignin should be evaluated to increase the reactivity with formaldehyde and to decrease the amount phenol used in the formulations.

Acknowledgments: This work was supported by BioEnercel S.A. and CORFO (grant 08CTE03).



Conferences [Abstract]

CMCase production by the newly isolated *Myceliophthora* sp.I-1D3b in packed bed solid state bioreactor.

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Bio-ethanol can be produced from lignocellulosic biomass through either chemical or enzymatic routes. The chemical breakdown of the fibers produces large amounts of wastes, which require further treatment, while enzymatic processes are environmentally friendly. However, the cost of the enzymes is prohibitive and researches for production of biocatalysts at low cost are mandatory. Solid state fermentation (SSF) is a promising process, since solid industrial by-products can be used as sources of nutrients for the microorganisms, reducing the prices of the bio-products. SSF has been successful in producing enzymes at larger quantities than the submerged fermentation (SbF), but scaling-up the process into industrial conditions requires the development of bioreactors. Usually, bioreactors for SbF are available in a variety of commercial options, while equipments for SSF need to be developed for each specific microorganism-substrate condition. This work aimed to produce cellulase (endoglucanase) from sugar cane bagasse and wheat bran using the thermophilic strain *Myceliophthora* sp. I-1D3b by SSF in a packed bed bioreactor. This fungus was isolated from sugar cane piles in Olímpia – SP, Brazil, and produced cellulases with high activities in glass flasks experiments. The packed bed bioreactor was made of stainless steel, 7.62cm diameter and 50cm long, and was wall-refrigerated through a jacket. Temperatures were measured at several axial positions during the process. Air, at 95% relative humidity, percolated the bed at 80, 100 and 120L/h. Two fermentation temperatures were used, 45 and 50°C. The proportion bagasse/bran was fixed at 7.3 (weight), and the initial moisture content at 75% (wet basis). The results showed high CMCase activities (up to 700IU/gram of dried solid) in relatively short fermentation time, 96h. The air flow rate did not influence the production of enzymes, although it influenced the increase of temperature during the experiments. The highest temperature increase, 6°C above the imposed temperature, was observed for the lowest flow rate. It was noticed some segregation on the moisture content and enzyme activity in the longitudinal axis. The experiments carried out at 50°C produced enzymes as active as the ones produced at 45°C, however in shorter fermentation time.

Acknowledgments: to the Brazilian research council FAPESP (procs. 2010/12624-0; 2008/52811-4) and to the INCT-Bioetanol.



Conferences [Abstract]

Market orientation in wood biorefinery research.

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The approach of the FP 7 project AFORE is to develop novel, industrially adaptable and technoeconomically viable solutions for the separation, fractionation, and primary upgrading of valuable chemical components from forest residues, wood chips, and chemical pulping liquors to be used as starting materials for current and novel value-added applications. Wood components can find a variety of different applications which makes the economic assessment a challenging task. In order to widen economic assessment beyond core value or system analysis [1], AFORE takes market information into account by carrying out business-to-business-surveys as this kind of information is frequently lacking [2] in contrast of its proven importance for successful product development [3]. AFORE project has envisaged both high value-low volume as well as high volume-lower value applications to be investigated from the fractionated and further functionalized components. In this paper we present two dynamic approaches of providing market information for technical development.

First example is a tool for assessing the market value of technical fibers in composite applications. Beside high end cellulosic fibers wood biorefineries are able to produce carbon fibers from lignin. In this work the relationship between value of reinforcement fibers and the fiber properties was studied. Data from 32 fibers was collected by nine producers and used in a regression model. The results show that an optimized model including four parameters (MOE, density, fineness and strength) significant at a level of 5% reaches an R-square of 0.621. MOE was found to be the most relevant factor for the fiber value.

The second example is a low value-high volume commodity, precisely packaging films which could also be based on hemicelluloses. However, the market potential is mainly dependent on the properties of the produced films. Based on information from a B2B-survey in the food packaging industry a demand model based on film properties was developed. A total market potential for a hemicellulose-based film of 927t/a has been calculated based on 26 packaging companies. The high oxygen barrier of the films is a key issue for the food sector, while the high water vapor permeability and the lack of sealing capabilities are considered major limitations. Once the films could be heat sealed the market potential would increase significantly from 927t/a to 30.328t/a for the same 26 companies. Heat sealing indicates how further developments could trigger higher market potential than the one currently identified.

This kind of economic assessments used in the AFORE project ensures the base for successful product development and therefore secures the economic impact of the project results.

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III Latin American Congress
Biorefineries
Ideas for a sustainable world
November 19th to 21st, 2012, Pucón, Chile

Conferences [Abstract]

Sustainability Assessment, Classification and International Perspectives of Bioenergy-driven Biorefineries and Biomaterials - Activities of IEA Bioenergy Task 42 "Biorefinery".

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The International Energy Agency (IEA) was established more than 30 years ago. The IEA Bioenergy is one of a number of Implementing Agreements (IAs) of the IEA. IAs operate within an institutional structure and contribute to both the IEA technology collaboration programme and national programmes of the contracting parties. The IEA Bioenergy's mission is to facilitate the commercialisation and market deployment of environmentally sound, socially acceptable, and cost competitive bioenergy systems and technologies and to advise policy and industrial decision makers accordingly. This is being done by providing platforms for international co-operation and information exchange in bioenergy research, development, demonstration, and deployment. The activities of IEA Bioenergy are organised in 12 Tasks. The IEA Bioenergy Task 42 "Biorefinery" is active since 2007 and has 11 participating countries (A, AUS, CA, DK, FR, G, I, IR, NL, T, US). The aims of Task 42 are:

1. Assess the worldwide position and potential for biorefineries.
2. Gather new insights for the simultaneous production of human food, animal feed, chemicals, materials, fuels, power and/or heat from biomass in a socially and environmentally acceptable and economically profitable way.

The Task 42 made the following definition on biorefinery: "Biorefining is the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, materials) and bioenergy (biofuels, power and/or heat)". "Energy-driven" biorefineries and "product-driven" biorefineries are distinguished. A classification system for biorefinery was developed to describe each biorefinery by the following four features: 1) platform, 2) Feedstock, 3) products and 4) processes, e.g. "A 3-platform (lignin, C6&C5 sugar, electr.&heat,) biorefinery using wood chips for bioethanol, electricity and phenol".

Based on the activities of the participating countries the task identifies and assesses the current status and development potential of "energy-driven" biorefineries and "product-driven" biorefineries based on different biomass feedstocks. So far the most interesting "energy-driven" biorefinery concepts until 2025 and the most interesting biochemicals were identified. For these biorefinery concepts and biochemicals the framework for the sustainability assessment is set and their future integration and deployment options in industrial infrastructure are analysed; e.g. biorefinery concepts based on wood (e.g. wood chips, saw mill residues, sulphite liquor) to produce the following transportation biofuels: bioethanol, FT-biofuels, biomethane and hydrogen. The sustainability assessments are based on a "Full Value Chain Approach", covering raw material issues, conversion processes and final product use in an integrated approach and assessing economic, socio-economic, environmental and social aspects in comparison to conventional processes and products.

The key issues of the sustainability assessment based on examples and the classification system of biorefineries will be presented. Based on existing international success stories for biorefineries and the experiences in the 11 countries of IEA Bioenergy Task 42 the international perspectives of bioenergy-driven biorefineries and biomaterials will be presented.



Conferences [Abstract]

Comparativa energética entre biodiesel de higuerilla (*Ricinus communis*) vs diesel.

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En últimas fechas el empleo de fuentes energéticas alternas a los hidrocarburos ha cobrado gran auge. Esto gracias a la preocupación actual que existe sobre los contaminantes emitidos y a las reservas cada vez menores de los hidrocarburos.

Existen diferentes fuentes alternas como son la eólica, la solar, la geotérmica y la biomasa, dentro de este último grupo se pueden encontrar combustibles como el etanol, gases obtenidos a partir de la descomposición de materia orgánica y el biodiesel. Cada una de estas alternativas presentan una fuente energética viable si se consideran adecuadamente las condiciones donde se desean aplicar, ya que por ejemplo existen zonas en las que las condiciones geográficas y climáticas hacen que la instalación de aerogeneradores y celdas fotovoltaicas resulte muy rentable.

Tocando el tema de los biocombustibles (obtenidos a partir de la biomasa), la producción de éstos ha aumentado en últimas fechas, siendo el biodiesel y etanol los representantes mayores observados de esta categoría.

En cuanto al biodiesel, éste se puede obtener de distintos tipos de oleaginosas, en el presente trabajo el biodiesel evaluado fue obtenido del aceite de higuerilla (*ricinus communis*), planta que puede adaptarse a distintas condiciones climáticas y geográficas.

Éste combustible se presenta como una alternativa interesante al empleo en motores diesel de combustión interna, ya que las propiedades del mismo permiten su empleo en dichos motores sin realizar modificaciones importantes en ellos.



Conferences [Abstract]

Reconversión de depósitos de tanques de biodiesel en una nueva materia prima industrial.

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El biodiesel ha pasado en la última década de ser un producto de laboratorio a un combustible usado de manera general. La producción de biodiesel (BD) en Argentina ha crecido a tasas interanuales superiores al 80 por ciento en los últimos años, con una capacidad instalada que a fines del 2011 que llegaba a 3 millones de Tn y ventas estimadas en 3.600 millones de dólares.

Una de las consecuencias de la producción masiva de BD a partir de aceite soja y palma entre otros cultivos, ha sido la aparición en varios puntos de la cadena de producción, transporte y utilización del mismo; de depósitos de material insoluble. Estos componentes insolubles han aparecido en las fábricas de BD, en los tanques de almacenamiento, contenedores usado para su transporte y en los filtros de los motores que lo usan como combustible. Este hecho ha causado la falla de estos últimos por la presencia de material sólido en los filtros de combustible que se formó en el BD posteriormente a la salida de la planta de producción. Si bien, estos reportes provenían principalmente de los productores de BD de Europa y EE.UU. las fábricas de Argentina de este combustible se han encontrado con la presencia de este mismo tipo de componentes insolubles.

En los últimos años ha sido sugerido primero, y demostrado posteriormente que estos depósitos formados en el BD están constituidos por estéril-glucósidos (SG de su siglas en inglés). Los esteril-glicósidos esterificados con ácidos grasos (6-O-acil-esteril glicósidos, de su sigla en inglés ASG) son constituyentes glicolipídicos comunes en las plantas superiores. Teniendo en cuenta las últimas estimaciones de producción de BD en Argentina para el año 2012 y que los SG en el biodiesel de soja tienen una concentración promedio de 100 ppm, es de esperar que este año se generen más de 300 Tn de este "desecho". Estos depósitos generan inconvenientes para las compañías productoras de biocombustibles y en general una vez recogido de los tanques de almacenamiento sólo se los aprovecha quemándolos en calderas teniendo un valor equivalente al fueloil. Debido a la producción masiva de BD que conlleva la generación de una cantidad sin precedentes de SG, nos propusimos explorar distintas alternativas que permitan reinserir este desecho industrial en la cadena productiva y utilizarlo en la generación de productos de alto valor agregado. Para ello, como primera etapa caracterizamos químicamente los desechos de tanques de plantas de biodiesel de nuestro país, determinando inequívocamente que se trataba de SG. Seguidamente, se logró optimizar un método de purificación de los mismos para disponer de este nuevo material adecuadamente refinado para utilizarlo en el desarrollo de nuevos productos. Actualmente nos encontramos desarrollando nuevos producto de interés industrial a partir de SG, cuyos primeros avances se discutirán en este congreso.

Valorización de la paja de trigo para la obtención de componentes químicos de uso industrial.

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La biomasa lignocelulósica, tanto de origen forestal como de residuos agrícolas, es una fuente rica en carbohidratos (celulosa y hemicelulosas) y de compuestos fenólicos como la lignina. Estos componentes químicos son y han sido considerados desde siempre, como materias primas intermedias o precursores, de los cuales se pueden obtener y desarrollar una amplia gama de productos finales de alto valor agregado.

En Chile, como en muchos otros países, año a año los residuos agrícolas, como la paja de trigo, son quemados in situ en los campos, debido a que no existen alternativas de uso aplicables, industrialmente, que consideren los volúmenes generados de este recurso. En nuestro país, se estima una generación promedio de aproximadamente 2,5 millones de toneladas al año.

Hoy en día, existe una preocupación en buscar soluciones para este recurso. Se puede mencionar los intentos en utilizarla para fines energéticos, la cual ha resultado muy difícil de implementar, debido a problemas logísticos y de operación.

El siguiente trabajo presenta una alternativa de uso de la paja de trigo, en la cual se utiliza un proceso de fraccionamiento químico o deslignificación, amigable con el medio ambiente, que permite obtener integralmente los tres componentes químicos, pulpa celulósica, carbohidratos disueltos (hemicelulosas) y lignina. Para ello, se utilizó una mezcla de ácidos carboxílicos, ácido acético y ácido fórmico, los cuales en condiciones tenues de operación, temperatura de ebullición y a presión atmosférica, permiten la separación de estos tres componentes. Se muestra, además, un posterior proceso de ozonación a la pulpa para mejorar la blancura y su potencial de aplicabilidad.

Se observó que el contenido de agua en la mezcla de deslignificación es un factor relevante y no debe superar el 20% (base a la solución). Esto se debe a que la reacción deja de ser selectiva y se privilegian reacciones de hidrólisis que generan rompimiento en la cadena de celulosa y condensación de la lignina, no permitiendo separarla de su matriz. Por otro lado, las mayores concentraciones de ácido fórmico, mayor al 80% (base a la solución), resultan en pulpas de buena calidad (viscosidad intrínseca de 1100 ml/g). Al incorporar ácido acético en la mezcla, se permite disminuir costos y disminuir la corrosividad y explosividad. Sin embargo, no debe superar el 20% de la composición de la mezcla, ya que la calidad de la fibra disminuye drásticamente. El proceso posterior de ozonación mejoró levemente el grado de blancura manteniendo la calidad de la fibra. A partir del proceso seleccionado, se fabricó papel obteniéndose características levemente superiores a la pulpa mecánica de fibra corta. La lignina y carbohidratos fueron caracterizados químicamente, previendo la aplicación de lignina para resinas adhesivas y material de encapsulamiento y las hemicelulosas para uso directo en alimento animal o fabricación de biomateriales.



Conferences [Abstract]

Producción de etanol en biorreactor continuo con retención celular.

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Frente al carácter finito de los combustibles fósiles que se utilizan hoy en día, el etanol, producido a partir de materiales lignocelulósicos surge como una alternativa interesante de reemplazo. Los materiales lignocelulósicos a diferencia de las materias primas que se utilizan hoy en día para la producción de etanol, requieren de un pretratamiento previo a la hidrólisis enzimática para lograr una liberación adecuada de azúcares que serán finalmente fermentados a etanol. En numerosos países se están realizando estudios tendientes a desarrollar tecnologías para llevar a cabo las distintas etapas del proceso de tal forma lograr un reemplazo favorable y económicamente viable. El objetivo de este trabajo se centra en la etapa de fermentación y comprende el diseño, puesta en marcha, análisis y evaluación de un sistema continuo de alta densidad celular para la fermentación alcohólica de hexosas.

El sistema consiste en un biorreactor que opera con 1 litro de volumen de medio y que dispone de agitación y aireación variable y control automático de pH y temperatura. El biorreactor tiene adosado un microfiltro con tamaño de poro de 0,8 µm, el que retiene totalmente las células. Para la operación del sistema se dispone de bombas peristálticas para la alimentación, el reciclo a través del microfiltro y purga del biorreactor.

Se realizaron experiencias con *Saccharomyces cerevisiae* ATCC 4026 en medio mineral definido con una concentración de glucosa a 120 g l^{-1} . Los cultivos se llevaron a cabo a 30°C , pH 4,2, 200 rpm de agitación, $0,06 \text{ l min}^{-1}$ de aireación y a una tasa de dilución de $0,5 \text{ h}^{-1}$. En estado estacionario de conversión de glucosa a etanol, se lograron en la corriente de salida del sistema concentraciones de etanol de 52 g l^{-1} y concentraciones de glucosa cercanas a 0 g l^{-1} . La concentración de etanol obtenida representa un 85% de la concentración máxima teórica, mientras que la productividad volumétrica que alcanzó a $26 \text{ g l}^{-1} \text{ h}^{-1}$ es 15 veces mayor a la lograda mediante un proceso de fermentación por lote convencional.

Finalmente, se desarrolló y validó un modelo teórico descriptivo del sistema. El modelo matemático considera aspectos cinéticos específicos del sistema en cuestión y de cultivo tales como: inhibición del crecimiento celular por etanol, inhibición por acumulación de células, muerte celular y efecto del volumen ocupado por las células. La aproximación teórica entrega predicciones confiables del proceso fermentativo, considerándose adecuada para propósitos de simulación y optimización.

Agradecimientos: Consorcio Bioenercel S.A., proyecto INNOVA-CORFO 208-7320, Chile.



Conferences [Abstract]

Procedimiento SATIB-HPPB y Conversión Energética de la Basura.

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El procedimiento SATIB-HPPB fue desarrollado en Chile a partir de un nuevo concepto de “Pyrogasificación” autosustentable de alto rendimiento energético produciendo combustibles gaseosos y/o líquidos, sin emisiones, patentado y en proceso de extensión al nivel internacional.

La conversión energética de los residuos : WTE (Waste To Energy) constituye al nivel mundial una problemática Medio Ambiental, de reducción de las emisiones y de la “Huella de Carbono” así como una necesidad de valorizar nuevas fuentes de Energías Renovables No Convencionales (ERNC).

El procedimiento SATIB-HPPB constituye una de las tecnologías claves para el futuro “Observatorio Latino Americano para el Tratamiento de los Residuos”.

Se presentara los resultados y avances conseguidos con la primera unidad PG 250, Piloto Industrial:

- El proceso de “Pyrogasificación” SATIB-HPPB
- Tipos, contenido energético y problemática de composición “CHONAS” de los residuos
- Balanceo en el procesos de residuos problemáticos tipo RSD o de alto contenido en humedad (Lodos)
- Búsqueda del “Carbón Boundary Limit” y optimización de los parámetros de “Pyrogasificación” en la producción de Syngas, Bio-Oil y Char/Biochar
- Descontaminación y procesamiento de los subproductos combustibles: Syngas y Bio-Oil
- Auto-Procesamiento de los desechos de la actividad y estabilización de las cenizas: “Pyroslags”
- Capacidades de tratamiento del procedimiento SATIB-HPPB
- Creación del Centro de Investigación sobre el Tratamiento Ecológico de los Residuos : CITER
- Aplicaciones y Perspectivas de Desarrollo

Análisis de ciclo de vida de procesos de co-combustión de carbón y biomasa.

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El reemplazo parcial de combustibles fósiles por recursos biomásicos en generación eléctrica (co-combustión) permite reducir de forma costo-efectiva las emisiones de gases de efecto invernadero (GEI). Sin embargo, el aumento del uso de biomasa en la producción de energía puede tener efectos adversos, no evidentes a simple vista, sobre los sistemas ecológicos, sociales y económicos.

En consecuencia, el análisis de sustentabilidad ambiental de esta alternativa debe considerar no sólo el beneficio asociado a la disminución del uso de combustibles fósiles, sino además utilizar herramientas que permitan evaluar los distintos aspectos ambientales asociados al ciclo de vida de la biomasa, esto es desde su producción, cosecha, transporte y uso final. Utilizando herramientas metodológicas objetivas, como es el Análisis de Ciclo de Vida (ACV), es posible no sólo cuantificar impactos sobre distintos componentes ambientales (humano, ecosistemas y recursos naturales), sino que además identificar en qué etapas del ciclo de vida del recurso se verifican los principales impactos potenciales.

En este trabajo se presentan los principales resultados relativos al Análisis de Ciclo de Vida y cálculo de Huella de Carbono para una unidad funcional de 1MWh en un complejo termogenerador del SING. Se comparan dos escenarios de generación eléctrica: i) generación exclusiva en base a carbón ii) sustitución máxima de 20% (máximo) de carbón por biomasa de origen forestal. Se utilizó un enfoque de la cuna a la puerta, esto es, desde la extracción de las materias primas hasta la generación . La metodología de evaluación de impactos correspondió al Eco-Indicator 99, enfoque igualitario. Para el procesamiento del inventario y la ejecución del modelo de impacto se utilizó el Software SimaPro 7.2.

La mayor reducción (18.8%) de los impactos ambientales por efecto de la co-combustión se verifica en la categoría de impactos a la salud humana, específicamente asociados a la emisión de inorgánicos respirables.

En segundo lugar, destaca la disminución (cerca de 8.5%) del impacto sobre cambio climático. No se observa una relación lineal directa entre porcentaje de sustitución (20%) y reducción del impacto sobre cambio climático (8.5%), por cuanto la relación causa- efecto en este caso no es directa. En efecto, si bien se está sustituyendo un porcentaje importante de fósiles por biomasa (20%), durante el ciclo de vida de ésta también se verifican consumos de combustibles fósiles (cosecha y transporte). La misma razón explica también la ligera disminución de los impactos asociados a la presión sobre recursos no renovables o fósiles (10.4%).

Los resultados relativos a la Huella de Carbono muestran en primer lugar que, en el escenario de generación exclusivamente en base a carbón, el complejo presenta una Huella de Carbono promedio de 2.8 ton CO₂e/MWh. Este valor disminuye en un 17.5% al incorporar un 20% de sustitución máxima de biomasa por carbón.

Finalmente, se observa que el mayor aporte a la huella de carbono corresponde al proceso de generación eléctrica (sobre el 77%), seguido de los procesos de extracción (20%), siendo el transporte de las materias primas el de menor efecto en este parámetro.



III Latin American Congress
Biorefineries
Ideas for a sustainable world
November 19th to 21st, 2012, Pucón, Chile

Conferences [Abstract]

Lignocellulose deconstruction as shown by 2D-NMR.

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The LIGNODECO (from LIGNOcellulose DECOConstruction) European project focuses on the detailed chemical characterization of changes in the lignin-carbohydrate matrix during the pretreatments of fast-growing Brazilian woody and nonwoody crops for the production of fuels (bioethanol and biogas) and improved cellulose products in lignocellulose biorefineries. The project is coordinated by Prof. Jorge Colodette (Viçosa University, Brazil) and, together with the Spanish CSIC (CIB-Madrid and IRNAS-Sevilla) also includes Novozymes (Bagsvaerd, Denmark), Suzano (Brazil), VTT (Espoo, Finland) and Centre Technique du Papier (CTP, Grenoble, France). The present lecture describes the potential of two-dimensional nuclear magnetic resonance (2D-NMR) as a powerful analytical tool to characterize the modification/removal of lignin (a key step for the industrial utilization of plant feedstocks) during biomass pretreatment in lignocellulose biorefineries. Lignin analysis by 2D-NMR includes determination of its aromatic-unit composition, and abundance of inter-unit linkages and terminal groups. We also describe the possibility to analyze the changes in the lignin polymer (and plant polysaccharides) without its prior isolation, by 2D-NMR of the whole lignocellulosic material at the gel stage (after swelling in deuterated dimethylsulfoxide). The 2D-NMR analyses include the characterization of changes in *Eucalyptus globulus* and *Pennisetum purpureum* feedstocks during their biological pretreatment using an oxidative enzyme (fungal laccase) in the presence of a redox mediator, in a sequence that included several successive enzymatic and alkaline extraction stages (resulting in up to 48% and 32% removal of initial *E. globulus* and *P. purpureum* lignin, respectively). 2D-NMR of the treated materials revealed the differential removal of lignin units, and a moderate removal of *p*-coumaric acid (present in *P. purpureum*) without a substantial change in polysaccharide cross-signals. However, the most noticeable change observed is the strong increase of C_α-oxidized syringyl units (representing up to 60% of all the lignin units in the treated eucalypt wood) in agreement with the mechanism of lignin attack by laccase-mediator proposed after model dimer studies. 2D-NMR was also used to characterize the changes in the above woody and nonwoody feedstocks after their physical and chemical pretreatment, based on solvent fractionation and modified alkaline cooking to high-lignin pulps, respectively.



Conferences [Abstract]

La fibra de corteza de *Eucalyptus nitens* y su aplicación como refuerzo en materiales termoplásticos.

Freddy Muñoz A.^{1-2*}, Paulina Valenzuela C.³, Aldo Ballerini A.⁴, William Gacitúa E.⁴

Se estudió la variabilidad en las propiedades morfológicas, físicas y térmicas de la fibra de corteza de *Eucalyptus nitens* (Deane & Maiden) en 24 árboles procedentes de 2 sitios y 6 familias; mediante técnicas de microscopía óptica convencional, microscopía electrónica (SEM) y análisis termogravimétrico (TGA). A nivel ultra-estructural, se realizó una nano-caracterización para determinar la variabilidad entre fibras de corteza y de madera de *E. nitens*; evaluando módulo de elasticidad (E), dureza (H) y razón de ductilidad (E/H) en lamela media (ML) y capa $S2$. Dichas propiedades son determinantes para que una fibra lignocelulósica alcance una posible aplicación industrial como material de refuerzo en una matriz termoplástica. Se detectaron diferencias estadísticas significativas en las propiedades de la fibra al analizar el sitio de procedencia, la familia y la altura de fuste. Existe diferencia significativa para E_{S2} y H_{S2} al comparar tipo de fibra; para fibra madera $E_{S2} \approx 12.52 \text{ GPa}$ y $H_{S2} \approx 0.31 \text{ GPa}$, para fibra de corteza $E_{S2} \approx 10.81 \text{ GPa}$ y $H_{S2} \approx 0.26 \text{ GPa}$. No se observó diferencia estadística significativa en la razón de ductilidad (E/H) en capa $S2$ y ML al comparar ambos tipos de fibras (madera, corteza). Destacan en los resultados de propiedades físicas de la corteza su espesor promedio (4.4 mm), su peso específico (0.757), sus propiedades morfológicas tales como razón longitud/diámetro de fibra ($l/d_f = 69.14$) y presencia de fibra (45%). La estabilidad térmica de la fibra de corteza de *E. nitens* hasta los 200 °C y la baja temperatura de fusión de termoplásticos como el polietileno de alta densidad (HDPE), indican que esta fibra natural es una buena opción de utilización en combinación con fibras de madera o por separado como material de refuerzo en matrices termoplásticas; esto particularmente orientado a la manufactura mediante procesos de extrusión de nuevos biomateriales termoplásticos y productos de ingeniería, con aplicaciones en el área de la construcción.

Palabras clave: Fibras de corteza, *Eucalyptus nitens*, SEM, TGA, nano-indentación, biomateriales

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Process Intensification for Advanced Biodiesel Production from Residual Oils.

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Biodiesel production is conventionally carried out a batch process employing a homogeneous alkaline catalyst such as NaOH or CH₃ONa. This extant route, however, is not competitive with petrodiesel due to the need for high quality, expensive oil feedstocks, handling of caustic materials, considerable downstream processing to separate excess alcohol, catalyst, and soap from the biodiesel product, and generation of a substantial volume of wastewater. The use of immobilised lipase as catalyst overcomes many of the problems associated with homogeneous alkali catalysts, and allows the use of cheaper waste and inedible oils high in free fatty acids. Unfortunately, lipase catalysts albeit with superior selectivity, have higher costs and lower reaction rates than inorganic catalysts. Even so, the judicious combination of the non-ideal phase equilibrium characteristics and the nonlinear reaction kinetics of the complex reaction environment provide a strategic window for the application of process intensification principles via separating reactor operation to improve production economics. This is the objective of the present paper. Work in our laboratory focuses on the ethanolysis of residual (or spent) cooking and non-edible oils to biodiesel over commercial supported lipase as catalyst.

Influencia de inhibidores provenientes del pretratamiento de astillas de eucalipto sobre el comportamiento de la cepa *Zymomonas mobilis* nrrl b-806.

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El etanol producido a partir de materiales lignocelulósicos es una alternativa a los combustibles de origen fósil y su proceso de producción está siendo desarrollado fuertemente a nivel mundial. Dada la naturaleza de la materia prima, el proceso requiere de etapas dedicadas a liberar los azúcares contenidos en la celulosa y hemicelulosa para ser convertidos a etanol mediante fermentación. Para llevar a cabo la hidrólisis enzimática de estos polímeros es necesario pretratar el material lignocelulósico para alcanzar un grado razonable de depolimerización. Sin embargo esta operación en función de su severidad conlleva la generación de inhibidores de la fermentación, fundamentalmente derivados de furanos y fenoles, que afectan el comportamiento de los microorganismos productores y la productividad de la fermentación. En este trabajo se tuvo como objetivo evaluar la tolerancia de la cepa bacteriana *Zymomonas mobilis* NRRL B-806, productora de etanol, a los inhibidores generados en los pretratamientos de astillas de eucalipto mediante explosión con vapor y autohidrólisis.

Las experiencias se realizaron en matraces con un volumen de 100 mL de medio de cultivo a 30°C y pH inicial de 5,5. El medio de cultivo se preparó en base al licor proveniente de los pretratamientos en concentraciones de 100%, 50% y 15% a lo que se le agregó en cada condición 100g/L de glucosa, extracto de levadura y sales minerales. La autohidrólisis se llevó a cabo a 176°C por 51 minutos y la explosión por vapor a 196°C por 9,5 minutos. Las concentraciones de etanol, glucosa y algunos inhibidores se determinaron mediante HPLC. Masa celular fue determinada por turbidimetría utilizando curva de calibrado.

Los resultados demostraron que las condiciones de pretratamiento de autohidrólisis fueron más severas que las de explosión con vapor. En el primero de los casos se alcanzó 18 g/L de ácido acético contra 6,8 g/L en el segundo. Las concentraciones de furfural e hidroximetilfurfural también fueron mayores para el caso de autohidrólisis alcanzando 2,6 g/L y 1,2 g/L respectivamente. En ambos casos syringaldehido alcanzó valores inferiores a 0,2 g/L e hidroximelbenzoico y vainillina no fueron detectados. En las experiencias con licor de explosión con vapor la glucosa fue consumida totalmente en todos los casos, tomando más tiempo mientras más concentrado se encontraba el licor. Sin embargo las productividades volumétricas no se vieron tan afectadas comparando con la condición control sin inhibidores ubicándose en el rango de 1,7 a 1,8 g/L·h. Utilizando licor proveniente de autohidrólisis, la glucosa se consumió totalmente solo cuando se usó a una concentración de 15%. Para las otras condiciones (50% y 100%) prácticamente no hubo crecimiento celular.

A las condiciones de severidad con que se realizó la autohidrólisis, se vio negativamente afectado el crecimiento celular y la producción de etanol, incluso al utilizar el licor diluido a la mitad.

Agradecimientos: Consorcio Bioenercel S.A., proyecto INNOVA-CORFO 208-7320, Chile.



Conferences [Abstract]

Implementación de una estrategia de optimización en tiempo real para mejorar la producción de biológica hidrógeno.

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El hidrógeno se presenta como una alternativa muy prometedora para remplazar el actual modelo energético, ya que presenta ventajas en eficiencia exergética, podría cubrir las demandas energéticas y tiene poco impacto sobre el medio ambiente. Una metodología que puede aportar a su producción, es la etapa fermentativa de la digestión anaerobia de la materia orgánica, donde se pueden usar sustratos de desecho. En este proceso, es necesario mantener condiciones adecuadas para lograr una alta productividad y un sistema productor de hidrógeno estable en el tiempo. El objetivo de este trabajo fue implementar una estrategia de optimización en tiempo real que permitiera mantener condiciones de estabilidad y máxima productividad del proceso de producción biológica de hidrógeno por vía fermentativa, variando el caudal de alimentación. El proceso se llevó a cabo usando glucosa como sustrato en concentraciones entre 5 a 20g L⁻¹. Se partió de lodo digerido pretratado térmicamente y se utilizó un CSTR de 0.9L de volumen de trabajo. En el montaje del sistema de adquisición de datos se usó un sensor de hidrógeno y un medidor del flujo volumétrico de biogás en línea. Inicialmente se evaluó el efecto de la velocidad de carga orgánica (VCO), variando principalmente el caudal de alimentación, con el fin de determinar su efecto sobre la producción de hidrógeno, y determinar si era posible emplear esta variable para la implementación de la estrategia. Con la variación de la VCO en el rango entre 20 a 78 g DQO L⁻¹d⁻¹, se pudo determinar que la variación del caudal de alimentación tenía un efecto directo sobre la producción volumétrica de hidrógeno, lográndose encontrar una máxima productividad de 19.58 LH₂ L⁻¹d⁻¹ para una VCO de 78 g DQO L⁻¹d⁻¹. A partir de esta experiencia fue posible implementar la optimización en tiempo real manipulado automáticamente el caudal de alimentación de sustrato.



Conferences [Abstract]

Efecto del uso de mezclas de lignocelulosas en la producción de bioetanol de segunda generación.

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La actual industria del etanol está basada en la transformación de caña de azúcar y maíz. Ambos cultivos son plantas de metabolismo C4 y por ello tienen un valor $\delta^{13}\text{C}$ característico. La industria de etanol de primera generación es posible en países como EEUU o Brasil en donde existe una amplia disponibilidad de suelos agrícolas y favorables condiciones climáticas. En Chile, este tipo de producción no es posible debido a la crítica escasez de suelos agrícolas y la competencia por alimentación. Sin embargo la diversidad de condiciones climáticas y tipos de suelos, generan un mosaico de escenarios agrícola-forestales que pueden combinar la existencia de plantas de metabolismo C3 y C4.

Por esta razón, el uso de mezclas de residuos para producir bioetanol de segunda generación es una posibilidad que se investiga en este trabajo, utilizando como herramienta la abundancia natural de carbono 13. La aplicación de esta técnica en estudios con bioetanol es escasa y sólo existe discreta información sobre el efecto de sustratos marcados natural o artificialmente durante la fermentación. El presente trabajo consideró los siguientes objetivos: a) determinar las contribuciones parciales de distintas materias primas en el rendimiento global de etanol después de su fermentación conjunta y b) describir la existencia de efectos sinérgicos o antagonistas en el rendimiento global de etanol a partir de mezclas.

Residuos de eucalipto (C3), paja de trigo (C3) y rastrojos de maíz (C4) con valores contrastantes de $\delta^{13}\text{C}$ en su fracción de holocelulosa, fueron pretratados y sacarificados, usando hongos de pudrición blanca e hidrólisis enzimática convencional, respectivamente. El material fue fermentado con levaduras convencionales usando dos tipos de medios de cultivo, usando glucosa proveniente de materiales solos o mezclados, respectivamente. Los rendimientos de etanol se determinaron mediante cromatografía de gases. Alícuotas de licores fueron inyectados en un sistema Purge Trap - Gas Chromatography - Isotope Ratio Mass Spectrometer para determinar el valor de $\delta^{13}\text{C}$ del etanol proveniente de los licores. El efecto del uso de materiales solos o mezclados sobre el rendimiento de etanol se determinó mediante comparaciones simples entre tratamientos. Los aportes individuales de un material en particular (%) se determinaron usando un modelo de componentes finales, basado en la determinación del valor de $\delta^{13}\text{C}$ en: a) etanol producido a partir de glucosa de un material particular y b) etanol generado durante la fermentación de mezclas de materiales.

Los resultados indicaron que los rendimientos de etanol dependen del tipo de material usado en la fermentación. Los valores de $\delta^{13}\text{C}$ en el etanol generado reflejan claramente el origen del material, indicando una fermentación efectiva de distintos materiales cuando son mezclados. La contribución de residuos de plantas C3 en el rendimiento final de etanol en medios mezclados son mayores a los aportes de materiales de origen C4, lo anterior evidencia fraccionamiento isotópico durante la fermentación. Experimentos adicionales contribuirán a clarificar efectos antagonistas durante la fermentación de mezclas.

Agradecimientos: Esta investigación ha sido financiada por Proyecto FONDECYT de Iniciación 11110368.



Conferences [Abstract]

Efecto del contenido de lignina sobre la acetilación de aserrín de madera de pino radiata.

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Existe un interés creciente en todo el mundo por contar con biomateriales que puedan remplazar a plásticos de origen fósil. La tendencia general apunta a que estos nuevos materiales deben estar originados a partir de materias primas renovables y además poseer la cualidad de ser biodegradables. Entre los biomateriales de estas características más producidos en la actualidad se encuentra el acetato de celulosa, en donde su materia prima principal es celulosa con un alto grado de pureza. Este alto grado de pureza requerido para su producción se presenta como una desventaja en términos de costos, lo que ha restringido su producción y su masificación. Por otra parte, la lignina es un polímero con propiedades termoplásticas, propiedades que se manifiestan sólo en su forma nativa, cuando forma parte de materiales lignocelulósicos; al ser extraída por métodos convencionales deja de manifestar esta propiedad.

El presente trabajo apunta a la comprensión fenomenológica del efecto de la lignina en la acetilación de celulosa con el fin de realizar acetilación sobre aserrín para obtener un producto termoplástico compuesto lignina-acetato de celulosa de un valor económico competitivo.

Se realizaron ensayos de acetilación variando el contenido de lignina de dos formas, 1) mediante la incorporación de lignina organosolv y 2) mediante la deslignificación de pulpa de madera de pino mediante cocción organosolv y posterior blanqueo con ozono. Las mezclas lignina-celulosa así obtenidas fueron sometida a un proceso de esterificación con anhídrido acético usando ácido acético como solvente y ácido sulfúrico como catalizador.

Al incorporar distintos porcentajes de ligninas al algodón para realizar la acetilación, se observa que la lignina interfiere negativamente en la reacción de acetilación. El grado de sustitución aparente se mantuvo entre 2,39 y 2,03 para un porcentaje de lignina que va desde 5% a 25%, es decir, la presencia de lignina dificulta el proceso de acetilación disminuyendo el número de grupos sustituidos en la molécula de glucosa. Un efecto similar se observó en las muestras deslignificadas mediante el proceso organosolv. En este caso es necesario destacar que el contenido de hemicelulosas presentes también afecta al material acetilado, en general, a mayor contenido de hemicelulosas, fue menor la estabilidad térmica. El análisis térmico (TGA), evidencia que los valores de la temperatura de descomposición disminuyen producto de la incorporación de lignina en las muestras. En general las mezclas lignocelulósicas con un contenido de lignina bajo 15% presentaron DS aparente similares a los obtenidos sin lignina.

En base a los resultados, se concluyó que es factible la obtención de un material acetilado compuesto a partir de aserrín de pino radiata utilizando ácido acético como agente deslignificante y medio solvente en la acetilación. Materiales con un contenido de lignina inferior al 15% alcanzaron un DS similar a celulosa pura, sin embargo la presencia de lignina residual acetilada tiende a disminuir la solubilidad y la temperatura de descomposición térmica del material.



Conferences [Abstract]

Efecto de la explosión con vapor en *Eucalyptus globulus* sobre las características estructurales y la producción de bioetanol.

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El pretratamiento de explosión con vapor para biomasa lignocelulósica, aplica vapor a alta temperatura y presión en tiempos cortos de reacción favoreciendo la autohidrólisis de las hemicelulosas y luego una descompresión súbita provocando la ruptura y disgregación de las fibras por evaporación del agua interna. A medida que aumenta la severidad ocurren reacciones de deshidratación en los azúcares, formando compuestos inhibidores (furfural e hidroximetilfurfural) de la sacarificación y fermentación simultánea (SFS). Así también, la lignina es ampliamente modificada por recondensación, aumentando la recalcitrancia y el contenido. Comprender los cambios físicos y químicos que sufre la madera al ser sometida a explosión con vapor permitirá seleccionar las variables de temperatura y tiempo para obtener materiales pretratados con alto grado de digestibilidad enzimática, baja degradación de azúcares y disminución de la recalcitrancia. En este trabajo se estudiaron 3 condiciones de pretratamiento a severidades baja (Log Ro= 3.53), intermedia (Log Ro= 3.80) y alta (Log Ro= 4.51), evaluando las modificaciones en la madera mediante microscopía electrónica de barrido (SEM) y espectroscopía de infrarrojo medio (FT-IR). Además, se determinó el efecto del pretratamiento sobre la composición química, grado de polimerización de la celulosa (DP), hidrólisis enzimática (H.E.) y producción de bioetanol mediante SFS. La microscopia (SEM) mostró que el grado de desfibramiento incrementó con la severidad del proceso, el grado de polimerización disminuyó significativamente desde 3493 a 317 y la remoción de xilanos alcanzó 95% en la condición de mayor severidad. En el análisis de bandas IR características de algunos componentes de la madera se observa un aumento en la intensidad de las bandas de 1605 y 1511 cm⁻¹ correspondientes a lignina, atribuibles a recondensación, lo que reafirma el aumento en el contenido de lignina en los materiales pretratados, además de un alto grado de desacetilación (1736 cm⁻¹). Respecto a la cristalinidad de las muestras, la banda de 1427 cm⁻¹ indica una mezcla entre celulosa cristalina I y celulosa amorfa, sin observar corrimiento de la banda entre madera tratada y sin pretratar, sin embargo al aumentar la severidad la intensidad de esta banda aumentó, indicando un incremento de la relación entre celulosa cristalina y amorfa, lo que corresponde a una mayor perdida de celulosa amorfa. La banda entre 1235 y 1230 cm⁻¹ corresponde a la tensión del enlace C-O en xilano, esta disminuyó la intensidad a medida que aumenta la severidad, relacionada con la remoción de hemicelulosa. El rendimiento en la H.E. fue de 70% base material seco pretratado a severidad 3.80 con desfibramiento parcial. Igual valor fue alcanzado a severidad 4.51 pero en menor tiempo, esto debido a que este ultimo presenta un menor grado de polimerización. El mayor rendimiento de etanol obtenido por SFS en base madera seca fue a severidad de 3.80 (69.6%), debido que se removió menos glucosa que a severidad de 4.51. Los resultados muestran que la explosión con vapor es un pretratamiento eficiente para *E. globulus* y no requiere condiciones de elevada severidad para obtener materiales adecuados para SFS.

Agradecimientos: A Consorcio Bioenercel S.A. y proyecto Innova Chile Corfo 208-7302.



Conferences [Abstract]

Determinación de un Método de Dosificación de Agentes Oxidantes y su Efecto en la Selectividad de un Proceso de Pretratamiento de Lignina en Medio Alcalino.

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En este proyecto, además de explorar nuevos métodos analíticos para la determinación del contenido de lignina de una muestra dada, se busca determinar si la selectividad del pretratamiento aumenta significativamente cuando el pretratamiento se realiza por etapas. Se usan dos etapas de deslignificación: Etapa *P* correspondiente al uso de peróxido de hidrógeno (5% v/v) como agente oxidante en donde se tienen en cuenta 2 temperaturas (50 y 70°C) y dos tiempos de operación (30 min y 1 h); Etapa *E* correspondiente al uso de hidróxido de calcio (0.1 g Ca(OH)₂/ g biomasa) como agente alcalino. Al igual que la etapa *P*, la etapa *E* se lleva a cabo a 2 temperaturas (80 y 100°C) y dos tiempos de operación (2 y 4 h). Por medio del modelo predictivo de concentraciones de constituyentes de la biomasa obtenido a través del software VISION propio de la espectrofotometría NIR se calcularon las concentraciones de lignina y carbohidratos de forma más ágil que por los procedimientos convencionales. Se estimaron los parámetros del modelo cinético del proceso, los cuales estadísticamente son satisfactorios de acuerdo a los intervalos de confianza en los cuales fueron obtenidos y a partir de ellos se evalúa la selectividad de carbohidratos en el proceso.



Conferences [Abstract]

Detección de genes involucrados en el metabolismo de ácidos grasos de la microalga *Botryococcus braunii*.

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El biodiesel es un biocombustible elaborado a partir de lípidos naturales provenientes de plantas y microalgas, capaces de sintetizar una gran cantidad de aceites. Éste se obtiene a través de un proceso de transesterificación o pirolisis en el cual los triacilglicéridos son separados en glicerol y cadenas largas de ácidos grasos que corresponde a la materia prima para la producción de biocombustible. *Botryococcus braunii* (Chlorophyta) sintetiza grandes cantidades de ácidos grasos, siendo esta acción de gran interés en la industria biotecnológica, como una fuente renovable en la producción de biodiesel. Descifrar las rutas biosintéticas en que estos compuestos son metabolizados es de gran importancia biológica y productiva, ya que conociendo el mecanismo de síntesis de estos compuestos, existirá la posibilidad de optimizar este proceso mediante técnicas genómicas y obtener así biodiesel en mayor cantidad, en forma constante y estable, y en menor tiempo. Esta investigación se centra en la predicción de genes y rutas metabólicas involucradas en la síntesis de ácidos grasos a través de herramientas bioinformáticas y moleculares.

La elaboración de una librería genética a partir del transcriptoma de la microalga *Botryococcus braunii*, permite obtener una idea de aquellos genes que se están expresando en un momento específico en la vida de este organismo. En esta investigación se analizaron tres librerías genéticas obtenidas por pirosecuenciación. Los dos primeros corresponden al transcriptoma de *B. braunii* raza A, el primero obtenido desde la cepa proveniente de cultivos masivos (Bazaes et al., 2012), el segundo corresponde al transcriptoma de *B. braunii* cepa A de la colección UTEX572 que se encuentra disponible en la base de datos de GenBank y el tercero corresponde al genoma de la microalga *Botryococcus braunii* raza A y que fue secuenciado usando la tecnología de Illumina. Para realizar el análisis in silico se usaron softwares bioinformáticos tales como KAAS, Blast y programas de predicción de genes, entre otros. Los resultados obtenidos permitieron la detección de secuencias genómicas asignadas a rutas metabólicas variadas involucradas en el metabolismo de ácidos grasos en la célula. A través del ensamblaje con cap3, asignación con KAAS y comparación a través de Blastx con bases de datos no redundantes y Swissprot se obtuvo un número considerable de secuencias relacionadas a enzimas del complejo sintasa de ácidos grasos, síntesis de triacilglicéridos y síntesis de ácidos grasos insaturados. Los fragmentos asociados fueron comprobados a través de comparación contra el genoma de la microalga y posterior predicción de fragmentos de mayor tamaño a través de Genscan y Fgenesh. Los resultados obtenidos se presentan con un grado de identidad, valor de e-value y score considerables para afirmar que la predicción de genes es correcta. La importancia de la reconstrucción de las rutas metabólicas que participan en la síntesis de ácidos grasos es un paso clave para la optimización del proceso de la producción de biodiesel ya que proporciona información para estudios posteriores en el ámbito molecular y la manipulación genética de este microorganismo enfocados a sobreexpresar el proceso de producción de biodiesel y otros compuestos de interés.

Agradecimientos

Este trabajo fue financiado por CICITEM, DESERT BIOENERGY S.A. e INNOVA CORFO.

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Conferences [Abstract]

Conversión de biomasa Lignocelulósica a Biocombustibles. Análisis de Alternativas Tecnológicas para Chile.

Passeron, G; Urzúa, A; Valenzuela, P.

Desde el año 2007 ENAP Refinerías Sociedad Anónima se encuentra desarrollando proyectos en el ámbito de los biocombustibles leñosos o de segunda generación, particularmente en tecnologías de gasificación de biomasa y síntesis de FT y de pirolisis y upgrading. Estos desarrollos los ha realizado a través de dos empresas coligadas ForEnergy creada en el año 2007 y Biocomsa creada en el año 2009. Se han realizado levantamientos de biomasa, se ha caracterizado esta, nos hemos concentrado en cultivos energéticos y se ha realizado un levantamiento de tecnologías a nivel mundial para determinar aquellas que podrían aplicarse en Chile para producir combustibles a base de biomasa leñosa. A partir del levantamiento tecnológico se han analizado diversas más de 16 configuraciones de plantas para producir Biodiesel y gasolina de segunda generación, mediante procesos termoquímicos. La metodología empleada corresponde a visitas tecnológicas, revisión de literatura especializada y la contratación de Ingenierías conceptuales. Estos estudios se refieren tanto a la concepción de unidades de preparación de biomasa como a plantas productoras de biocombustibles. A base de la cantidad y calidad de biomasa en Chile, el mercado de combustibles doméstico y las tecnologías disponibles a nivel mundial y considerando los cinco años de investigación; ForEnergy – Biocomsa pueden dar algunas indicaciones de los caminos que Chile podría seguir en este ámbito. Se deduce que los biocombustibles que se pueden obtener con algunos de estos procesos son de gran calidad; que los niveles de inversión constituyen una importante barrera de entrada para éstas tecnologías; que en las condiciones actuales de mercado muchos de los productos requerirían en Chile un nivel de subsidio; que aun cuando no hay plantas en el mundo operando a nivel industrial todo indica que a corto mediano plazo se instalarán industrias en este ámbito, se deduce además que el tema de la preparación de la biomasa es crucial para el buen funcionamiento de estas industrias.



Conferences [Abstract]

Waste Tire Rubber Gasification Using Air-Steam for partial oxidation and N₂ as Carrier Gas.

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The high calorific value of waste tires (WT) and their composition similar to that of coal make it a promising resource for thermal treatment. This paper assesses the potential of WT for the production of gaseous fuels through thermal gasification using air and steam as oxidizing agents. The results of ultimate and proximate analyses were used to estimate empirical formulae, high heating value (HHV) and formation enthalpy. ASPEN Plus® using the RGibbs and the Redlich-Kwong-Aspen models for property estimation as well as the Chemical Equilibrium with Application (CEA) program (developed by the National Aeronautics and Space Administration, NASA) were used to simulate the process in order to calculate the composition of effluent gases in an adiabatic reactor. The effect of the equivalence ratio and steam to fuel ratio on adiabatic temperature, gas composition and energy recovery was determined performing sensitivity analysis on ASPEN Plus®. Syngas produced by the gasifier was cleaned and processed to produce 1536.13 kg h⁻¹ of ammonia and 17.63 kg h⁻¹ of pure sulfur, which constitutes over 93% of the sulfur pollutants generated.



Conferences [Abstract]

The VFA-platform for the production of chemicals and bioenergy from waste.

Robbert Kleerebezem.

The production of waste is a sign of inefficiency. Agro-industrial production and consumption in our western society is associated with the production of enormous amounts of waste. The VFA-platform aims to develop industry integrated processes for the production of chemicals and bioenergy from waste. Integration of industrial production processes with the effective valorization of the generated organic residues will minimize the ecological footprint, and contribute to more sustainable agroindustrial production. The VFA-platform is constructed around the concept of Microbial Community Engineering (MCE) and aims for using mixed (non-defined) microbial communities for conversion of organic residues to valuable products. In the first step of the VFA platform, water soluble volatile fatty acids (VFAs) are produced from complex organic material by microbial conversion of the organic substrates. In a second step, the VFA is converted to end-products like biopolymers, medium chain length fatty acids, or methane containing biogas. Herewith the VFA-platform is a direct alternative for biorefinery and gasification based biomass processing techniques. In this presentation several new concepts for VFA production from waste and subsequent end-product recovery after VFA conversion will be presented.

Within the VFA-platform concept we are working on the production of the bioplastic polyhydroxyalkanoate (PHA) from VFA-rich streams. PHA is a biodegradable and renewable polymer which has the potential to replace fossil fuel based polymers in a future biobased economy. Enrichment of a PHA producing microbial community is based on aerobic cultivation in the alternating presence and absence of carbon substrate resulting in a feast-famine regime. In recent years we have demonstrated that PHA production in microbial enrichments is as efficient and even faster than in current biotechnological production process based on (genetically modified) pure cultures of bacteria. The maximum cellular PHA content that can be established is 85-90% (g/g). The TU-Delft process opens up the possibility to use low value substrates, like those obtained from waste, for industrial PHA-production.

Further development and industrial introduction of the PHA production process requires involvement of different research disciplines. Knowledge is required on the downstream processing (DSP) of the waste based PHA-biomass mixtures, and on the application potential of PHA which may not be restricted to the use as polymer. The development of a waste based production process requires a collaboration between the traditionally different industrial fields of waste treatment and the biotechnological production of bulk chemicals. We have recently started a multidisciplinary research and development project that involves researchers on upstream processing and PHA production, DSP, utilization of the polymer produced, and Life Cycle Assessment (LCA) of the entire production chain. The project includes the construction and operation of pilot plant for PHA production that in October 2012 will be placed at the Mars Netherlands Chocolate factory, at Veghel, The Netherlands. The project involves the support of industries that are active in the life sciences and industrial polymer production (DSM, Purac) and companies involved in the treatment of waste (Paques). We think a very strong team has been established that allows for full coverage of the entire PHA production chain from waste substrate to end product. Herewith we are convinced that PHA-production from waste will be brought major steps closer to industrial production.



III Latin American Congress
Biorefineries
Ideas for a sustainable world
November 19th to 21st, 2012, Pucón, Chile

Conferences [Abstract]

Structural analysis by ATR-FTIR of pretreated sugarcane bagasse using ozone and ultrasound for cellulosic ethanol production.

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The cellulosic ethanol production from sugarcane bagasse via enzymatic hydrolysis requires pretreatment of bagasse in order to disrupt the lignocellulosic material, so that the access of the enzyme to the fiber is facilitated. In this context the structural analysis of sugarcane bagasse pretreated by Attenuated Total Reflection Fourier Transform - Infrared Spectroscopy (ATR-FTIR) is an important tool to understand the changes occurring in the fiber bagasse after pretreatment. The pretreatment of the bagasse was performed as follows. The bagasse was subjected to ozone for 1 hour, then was kept in suspension with NaOH 0.1 M for 2 hours, and finally subjected to treatment with ultrasonic waves for 5 minutes. A portion of the treated samples and controls *in natura*, were subjected to structural analysis by ATR-FTIR, and another part, as well as the control, were subjected to enzymatic hydrolysis with commercial cellulase for 24 hours in bath at 60 °C. The supernatant was used for quantification of total reducing sugars (TRS) by the method of Miller. The experiments were performed in duplicate. The peaks located in the region of 1600, 1510 and 1440 cm⁻¹ in infrared spectrum are related to the absorption due to the presence of lignin [1], while the peak observed at 833 cm⁻¹ is related to absorption by p-hydroxyphenyl one of the precursors of lignin [2]. The values obtained in the quantification of TRS after enzymatic hydrolysis of pretreated and *in natura* bagasse were 638±10 and 128±7, respectively. The peak observed at 897 cm⁻¹ is related to β (1-4) linkages between glucose units [3], and peak 1158 cm⁻¹ is due to the stretch of group C-O-C of β (1-4) glycosidic bound [4]. Comparison of the spectra acquired by the sugarcane bagasse and the pretreated bagasse were accomplished. It could be observed that the peaks related to the presence of lignin (1600, 1510, 1440 and 833 cm⁻¹) were almost totally eliminated from pretreated bagasse, compared to untreated. In the same way, the peaks related to the glycosidic β (1-4) suffered some modifications, indicating reduction of these bonds. Structural analysis of bagasse by ATR-FTIR shown that the pre-treatment significantly reduced the amount of lignin of biomass and also the connections between the glucose units. This facilitated the access of the enzyme to the cellulose/hemicellulose, increasing the saccharification of bagasse which reflected on the value of 638 ± 10 mg TRS/g bagasse, versus 128 ± 7 mg TRS/g of sugarcane bagasse.

Acknowledgments: FAPESP, CNPq and FUNDUNESP

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Conferences [Abstract]

Animal Fat from Knackeries for Liquid Fuel and Chemicals Production.

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The degradation of animal fat is reported in a moving bed of sodium carbonate and 5% wt of water at 430 ± 20 °C at a pilot scale plant with a capacity up to 40 kg/h. The main product with a yield of $65 \pm 5\%$ was bio-crude showing an acidity index of 0.5 - 1.8 mg KOH/g. The mean value for kinematic viscosity at 40 °C was 1.78 mm²/s. The net calorific value of bio-crude was 41.6 MJ/kg. Spectroscopic techniques such as FTIR, ¹H- and ¹³C-NMR reveal absorption bands characteristic for terminal double bonds with only traces of aromatic compounds. In ¹H-NMR integrals for aromatic protons in comparison to aliphatic protons showed relative concentrations of less than 2%. Neither CH nor quaternary C were to be seen in the ¹³C-NMR spectra. GC-FID and GC-MS of bio-crude showed main peaks with a distinct double structure at each carbon number. Mass spectra gave molecular mass numbers of alkanes and alkenes, respectively. In the values between different carbon numbers minor amounts of double bond isomers or alkenes with several double bonds were found. More than 50 non polar components could be identified in the range of 0.12% to 11.6% wt. The concentration of FFAs and ketones in bio-crude are 1mg/g and 18 mg/g, respectively. These results demonstrate that bio-crude from thermal degradation of fatty acids and animal fat mainly consists of long chain unbranched alkanes and alkenes. Terminal double bonds prevail in alkenes. The distillation curve of bio-crude is characteristic for hydrocarbon based bio-fuels in the boiling ranges of gasoline and diesel. Upon rectification 65.8% of bio-diesel and 13.3% of bio-gasoline were obtained. Methylheptadecylketone was isolated from the high boiling fraction of bio-diesel (320 – 340°C) and characterized by ¹H- and ¹³C-NMR. The bio-diesel has favorable low-temperature properties (cold filter plugging point = -18 °C) with oxidation stability between that of mineral oil based diesel and fatty acid methyl ester fuels. The gasoline fraction lacks low-boiling hydrocarbons as indicated by a vapor pressure of 26 kPa instead of 60-90 kPa (DIN EN 228). Thus, water-cooled condensers need to be improved for a full-scale plant. The gaseous products ranged from 25% to 30% wt. The presence of CO₂, H₂, CH₄, C₂H₆, C₂H₄ and C₃ to C₅ hydrocarbons as major components was established by gas chromatography. The results are discussed in terms of German specifications for standard fuels and alternative feedstock in chemical industry reducing the carbon footprint of fuels and petrochemicals.

Analytical pyrolysis as tool in biorefinery-related research.

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One of the challenges in research aiming at the production of biobased materials from biomass components is the characterisation of the starting materials and products. The starting materials, wood or other biomass, or biomass fractions such as lignin and hemicelluloses, are typically complex mixtures of biopolymers with random structures. Therefore, also the structural changes induced by chemical or enzymatic conversions are difficult to follow by analytical techniques typically applied in polymer research.

Pyrolysis combined with GC/MS detection (Py-GC/MS) has shown wide potential for the characterisation of biomaterials. A small amount of biomass (100 micrograms) is enough to provide semiquantitative information on its overall composition: lignin, various hemicelluloses and cellulose. Proteins *e.g.* in agricultural side streams can also be detected based on certain marker compounds. Application of in-situ alkylation reagents in Py-GC/MS provides a sensitive tool for the analysis of extractive components. In addition to composition analysis, structural information is obtained especially for lignin from the same analysis run, *e.g.* the ratio between syringyl and guaiacyl type structures (S/G) can be detected. The method has been compared with the conventional nitrobenzene oxidation (1).

Py-GC/MS has also been applied for the analysis of chemically and enzymatically modified biomaterials. In-situ methylation combined with Py-GC/MS can be applied for the detection of the degree of esterification, as shown by model compound studies (2). Esterification of lignin is a potential modification reaction aiming at increased thermoplasticity (3). A modified technique, based on thermal desorption-GC/MS, has been developed as a tool to simulate the formation of volatile organic compounds (VOCs) as degradation products during thermal processing of lignin. The effects of the tested chemical and enzymatic pre-treatment methods could thus be followed (4). A different type of application example is the detection of fatty acids in brewer's spent grain (BSG) fractions obtained by mechanical and enzymatic treatments. In this case, the strength of the in-situ methylation Py-GC/MS technique comes from the fact that no sample extraction is needed, and even the components trapped to the sample matrix will be detected (5).

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Conferences [Abstract]

The Integrated Biomass Supply Systems (IBSS) Partnership: Technology and Supply Systems for Integrated Production of Advanced Biofuels in the Southeastern US.

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USDA predicts that the southeastern United States will produce almost half of the 21 billion gallons of annual supply of advanced biofuels mandated by the RFS2 in 2022. Production of 21 billion gallons of advanced biofuels will require significant advances in biomass production and supply, and in conversion technology. These advances will be required for the economic, environmental and social sustainability of wide scale biofuels production.

The Southeastern Partnership for Integrated Biomass Supply Systems (IBSS) is working to reduce the risks surrounding the sustainable, reliable, and predictable supply of lignocellulosic feedstock needed to meet this goal. The IBSS Partnership is working with Rentech, Commerce City, CO, to evaluate woody and perennial feedstocks in their 20-ton/day biomass gasification and gas-to-liquids pilot plant.

Extensive data on the chemical and physical characteristics of pine, Eucalyptus, Poplar and switchgrass have been generated by the IBSS partnership. Financial and life cycle modeling tools have been developed to allow for the integrated economic and environmental evaluation of biofuels production strategies optimized for the southeastern US.

New pathway to fuels or fuel additives starting from short-chain alcohols.

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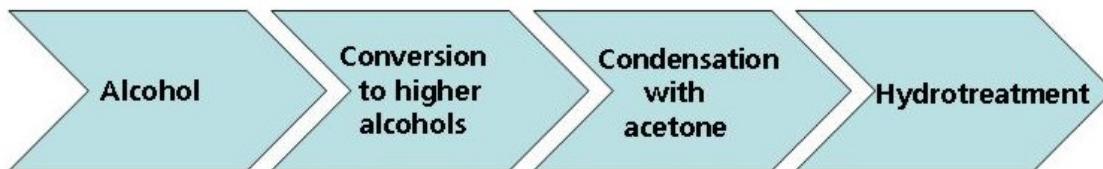
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A new catalytic gas-phase process developed by Fraunhofer UMSICHT allows coupling of short-chain alcohols and ketones to larger hydrocarbon molecules containing only one atom of oxygen. The main by-product is water. After an oxygen-removing step, for example hydrotreatment, fuels identical to fossil fuels are yielded. The overall conversion of feedstock to fuel additives or fuels is depicted below.



Schematic process flow for the production of fuel-identical hydrocarbons

The first step comprises the self-condensation of short-chain alcohols yielding a mixture of linear and branched longer-chain alcohols. Typical process conditions range from 300 to 400 °C at a pressure of up to 50 bars.

In a second step the obtained mixture of alcohols is blended with acetone and converted in a similar gas phase reaction to a mixture of branched and linear secondary alcohols and ketones. This condensation step also works with a typical aqueous ABE fermentation broth.

Separation of reaction water and additional removal of oxygen, e.g. by hydrotreatment, will not be discussed in the presentation, since it is considered state-of-the-art. Depending on raw materials and process conditions a tailor-made product distribution of hydrocarbons can thus be realized. The resulting mixture of products can be employed as fuel additive, as a neat fuel or as a blending component for either diesel or kerosene.

The presented overall process scheme offers an attractive alternative to other competing processes producing long-chain hydrocarbons like Fischer-Tropsch or hydrotreatment of fats and oils. Starting off from fermentation based alcohols and acetone made by fermentation of carbon-monoxide rich off-gas seems to be particularly attractive.



Formate-Assisted Pyrolysis (FAsP) of Woody Biomass.

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The technological need for producing fuels and chemicals from renewable feedstock has never been greater, due to increasing worldwide demands on fossil fuels, diminishing supply, and climate change. In recent years, several biomass conversion technologies have either been revived or emerged to meet this need. Because biomass is both diverse and less concentrated in nature, technologies that are flexible regarding process scale and biomass specificity, while remaining relatively inexpensive, will ultimately emerge. One method for concentrating biomass into liquid form that is relatively simple in concept is fast pyrolysis, where the biomass is fragmented through intermediate heating in inert atmosphere and quenched. The outstanding challenge with this technology, particularly in relationship to fuel production, is the removal of the large amount of oxygen in the biomass. This is currently being met by using either zeolite cracking catalysts and/or precious metal catalysts with added hydrogen, typically at elevated pressures. These catalytic processes are no longer robust, due to catalyst attrition, coking and lifetime issues.

In our research team, we have recently discovered a breakthrough in concentrating biomass into liquid form while removing significant quantities of oxygen using a fast pyrolysis method. In our method, we add an alkaline-earth salt of formic acid to the feedstock. The formate thermally decomposes *in situ* with the biomass during processing, releasing reactive hydrogen that removes oxygen from the biomass. In addition, and perhaps even more important, is the increase in carbon yield we observe relative to competing processes. We believe this is due to the *in situ* deoxyhydrogenation that stabilizes intermediate molecules that otherwise undergo polymerization reactions during either reaction or condensation resulting in char formation. We have shown this conclusively for lignin, a byproduct of the pulping industry that is currently used as a heat source due to its recalcitrance, and wood sawdust. In short, this new method avoids expensive/short-lifetime catalysts and processing at excessive pressures while increasing process yields and we believe it has the ability to transform renewable fuel and chemical production from whole biomass and wood waste products.

In this presentation, recent results from FAsP of pine sawdust/calcium formate will be reported. An oil of 8% oxygen and HHV of 40 MJ/kg has been produced at the bench scale in a one-step pyrolysis at atmospheric pressure. An accelerated ageing test indicated excellent stability of the oil. Deoxygenation occurred primarily through conversion of methoxy/hydroxy functionalities in the oil. FAsP will be compared to competing technologies.



Conferences [Abstract]

Lignins to Aromatic Compounds. The Base Catalysed Degradation in Continuous Reactors - A Tentative Review.

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Declining petroleum resources, the economical-independence minded activities of the chemical industry regarding fossil resources, environmental changes & last but not least new economical & ecological challenges of the pulp & paper industry force into the utilization of lignocellulose biomass for the production of fuel additives, bio based fuels & so called building-block chemicals. Only by economical pulping, separation & conversion techniques for biomass the production of sustainable bio-based materials, fine chemicals, & semi-finished chemical goods will be reasonable. Lignin (renewable resource) contains aromatic structures, & has sustainable & economical potential in bio based chemicals, materials and in the energy sector. The objective of the presented studies is the generation of aromatic compounds (monomer, oligomer) from different lignins (Organosolv lignin & Sulphur-containing technical lignin) via multi-stage processes. These multi stage processes (1st separation of lignin, 2nd base catalysed decomposition (continuous process), & 3rd separation of the organic phase from reactor water) have to be feasible in bio refineries & in new Pulp-mill bio refineries as a new technology module. Both, the Organosolv lignin & the technical lignin (sulphur: ~2%) were used for catalyzed conversion into oxy aromatics (monomer, oligomer). Subsequently (at p: - 250bars), the effect of parameters (catalyst, NaOH/ HCOONa mixture) & NaOH conc., minerals, dwell time ($\tau=5-15\text{min}$), Temperature (T: 250-350°C) was investigated. Liquid-liquid extraction of reactor water (pH=3) was also performed with different solvents (Snyder polarity). The extracts (oils) & filter-cakes (tars) were characterized regarding the yield & their composition. A characterization of the monomer composition was done using GC-MSD/FID & elemental analysis (EA: CHONS-carbon balance). Types of monomers were summarized into groups (e.g. guaiacol (G), syringol (S), catechol (C), oligomeric). Oligomers in the oils were identified by Infusion & LC MSD Ion Trap & the composition of the tar by Py-GC-MSD analysis as well as the formed tar by SEC & EA. On the one hand, depending on the botanical source & the lignin recovery process the used lignins differ in their structure (G-lignin, G/S-lignin, molecular weight, condensation degree), mineral & sulphur content. These substrate factors effecting the degradation process during the base catalysed cleavage of aryl-aryl-ether & aryl-methyl-ether bonds. On the other hand, process factors (p, T, τ , catalyst conc. (NaOH) & type of alkaline & earth alkaline cat ion have a main effect on the cleavage processes, on yield & composition of the oil, on the molecular characteristic (Mw, Mn) of tar & on the carbon balance. To get an overview about the main & side effects in such a complex situation, the studies on technical lignin were done using the DoE (Box-Behnken). A detailed evaluation regarding the main & side effects of process factors & substrate factors on the yield of oil & tar, on the concentration of guaiacol, syringol & catechol type monomers in the oil phase, on the carbon balance/conversion degree & on the Mw & Mn of tar will be given in that tentative review.



III Latin American Congress
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Conferences [Abstract]

Do microalgae biorefineries really exist? Concept, applications and future directions.

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Microalgae, a potentially suitable alternative feedstock for the next generation of biodiesel production which has not been fully exploited, have been suggested as very good candidates for fuel production, as they appear to be the only renewable biofuel that is capable of meeting the global demand for transport fuels.

Any high added value use of a part of the microalgal biomass besides oil for biodiesel, such as carotenoids and polyunsaturated fatty acids for the feed, food, cosmetic and pharmaceutical markets, is strongly desirable as a way to decrease production cost and increase economic competitiveness of the whole process. The production of a wide range of fine chemicals from microalgae has been extensively studied and reported during the last decades. However, these publications only cover the production of one product *per se*, identifying and optimizing the key parameters yielding to the highest productivity of each metabolite alone. This approach ignoring the global process is rather simplistic but unrealistic in the way that cannot support a cost-effective and sustainable commercial microalgal production. The number of studies and publications including patents supporting the global implementation of a real microalgal biorefinery has been rather scarce and will be presented and critically discussed.

The increasingly important adoption of life-cycle assessment studies will offer attracting possibilities to develop and expand microalgae biorefineries considering not only technical/economic aspects but also sustainability and societal issues. The personal experience of the authors in the co-extraction, fractionation and purification of different products (biofuels and fine chemicals) from microalgae following the principles of a real biorefinery, optimizing global mass and energy balances, will be shown. The authors are also extensively devoted to the study of the innovative combination of microalgae bioreactors undergo complementary nutritional modes. In such way the association of two bioreactors, photoautotrophic (photobioreactor) and heterotrophic (fermentor), connected by the gas phase, allowing an exchange of O₂/CO₂ gases between them, benefiting from a symbiotic effect, will be also described.

One pilot plant microalgae facility operating successfully in Central Chile (Clean Energy ESB) will be also presented as a case study of a microalgae biorefinery.

Acknowledgements

Portuguese Foundation for Science and Technology supported studies presented here through the SIMBIOALGA project (PTDC/AAC-AMB/112954/2009) FCOMP-01-0124-FEDER-013935 (also supported by FEDER funding through COMPETE- Programa Operacional Factores de Competitividade). The financial support of CYTED (Thematic Network SI3A P711RT0095) is also acknowledged.



Conferences [Abstract]

Biocombustible vehicular a partir de un subproducto de la industria de celulosa Kraft.

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La demanda creciente por combustibles para el sector transporte, junto con el constante aumento del precio de petróleo crudo, han llevado a crear un ambiente propicio para desarrollar fuentes alternativas al petróleo en la forma de biocombustibles. Uno de los grandes desafíos de la industria de los biocombustibles es desarrollar fuentes renovables que aseguren el suministro a costos competitivos y con bajo impacto ambiental.

Una fuente renovable atractiva para producción de biocombustibles a nivel nacional es el tall oil. El tall oil crudo (TOC) es un subproducto de la industria de celulosa Kraft de pino, compuesto de una mezcla de variados componentes, los cuales pueden clasificarse esencialmente en tres grandes grupos: ácidos resínicos (30-55%), ácidos grasos (35-60%) y una fracción de insaponificables o compuestos neutros (5-35%) [1]. Los ácidos grasos y ácidos resínicos de tall oil han sido estudiados como materias primas potenciales para la producción de hidrocarburos tipo diesel y gasolina utilizando diferentes catalizadores comerciales de craqueo catalítico y de hidrotratamiento [2-6].

En Chile, las empresas de celulosas producen anualmente cerca de 45.000 toneladas de tall oil, el que se utiliza como combustible industrial de bajo valor comercial. El presente trabajo propone la transformación de los componentes de tall oil en un biocrudo susceptible de ser convertido en combustible diesel y gasolina mediante un proceso catalítico basado en la tecnología Greasoline®.

La tecnología Greasoline®, desarrollada por el Instituto Fraunhofer Umsicht, consiste en la conversión de aceites vegetales y grasas de baja calidad en hidrocarburos tipo diesel y gasolina, utilizando carbón activado como catalizador [7]. A diferencia de los aceites vegetales, que están constituidos principalmente por triglicéridos, el tall oil contiene una fracción importante de ácidos resínicos (ácidos carboxílicos C20 del tipo diterpénicos), los que son más recalcitrantes al hidrotratamiento y craqueo catalítico [8-10]. Por lo tanto, se requiere una investigación acuciosa sobre los catalizadores, etapas de reacción y de separación necesarias para convertir los componentes de tall oil en hidrocarburos tipo diesel.

Los resultados de aplicación del proceso Greasoline® aplicado a tall oil crudo nacional, muestran que el rendimiento de hidrocarburos líquidos depende principalmente de la temperatura de reacción y del carbón activado utilizado. Bajo las condiciones estudiadas se han obtenido rendimientos de biocrudo de hasta 60%. La fracción líquida es una mezcla compleja de hidrocarburos compuesta por alcanos, olefinas, parafinas, bencenos ramificados, aromáticos policíclicos (PAHs), principalmente antracenos y fenantrenos, y ceras. Este biocrudo fue transformado en biocomponentes de diesel y gasolina mediante hidrotratamiento utilizando un catalizador comercial.

Agradecimientos

Proyecto FONDEF D08I1156. CONICYT.



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Conferences [Abstract]

Analysis and evaluation of extracts from microalgae *Nannochloropsis* sp. as renewable source for valuable chemicals.

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Microalgae are a versatile polyphyletic group of unicellular, eukaryotic, photosynthetic organisms. According to literature, they are more efficient in photosynthesis than many land plants and are able to double their biomass within 24 h. Therefore, microalgae are a booming research topic concerning their use as energy resource. However, the use of microalgae as renewable resource needs to be addressed in a biorefinery perspective, as "biofuel-only" options will not become economically viable due to high biomass production costs.

Fortunately, microalgae produce valuable substances, which are of economic interest for an application in the food and fine chemicals industry, e.g. highly valuable lipids (sterols, vitamins, etc.) and fatty acids (polyunsaturated omega-3 and omega-6 fatty acids, especially eicosapentaenoic (EPA) and docosahexaenoic acid (DHA)) as well as pigments and hydrocarbons (fatty alcohols and diols).

Omega-3 and omega-6 fatty acids are (conditionally) essential for most animals. They play crucial roles in biochemical processes and are often used as pharmaceuticals and in food supplements. Currently, they are mainly derived from fish oil, which has several disadvantages: the "fishy" odor is unpleasant, concerns about the contamination with heavy metals exist, and fish oil concentrates do not meet the needs of a vegetarian or vegan diet. This favors production of EPA and DHA from microalgae. According to Belarbi et al. 2000 the biomass production can cost around \$ 4 kg⁻¹_{dry} at an EPA content of 2.5%_m for economic viability of the process (*Enzyme and Microbial Technology* 26, pp516). Norsker et al. 2011 predict production costs at large scale (100 ha plant as raceway ponds, tubular photobioreactors or flat panel photobioreactors) to be around € 5-6 in a base case and below € 1 in an optimized case (per kg_{dry}) (*Biotechnology Advances* 29, pp24).

Basic knowledge on the efficient production of fatty acids from *Nannochloropsis* sp. shall be gained in our research project "PHOTOCHEM" (Koller et al. 2011, *Current Topics in Biotechnology* 6, pp72). The production of valuable substances shall lead to an economical viable production of energy from microalgae in the long run. Here we present the study of the effect of extraction techniques and solvents on the lipid composition of microalgae extracts. Biological microalgae samples (*Nannochloropsis* sp.) were purchased from Necton, Portugal. Several extraction solvents (n-hexane, n-hexane/2-PrOH (2:1_v), and EtOH (96.4%_v)) were tested with an Accelerated Solvent Extractor. The extraction was applied on freeze-dried and ground (1 mm) material at 60°C with varied extraction time. The gravimetric extraction yield, total fatty acid and EPA content were evaluated. The largest absolute extraction yield was achieved with EtOH (36 ± 4%_{m, input}). Additionally, an absolute amount of fatty acids of 16.7 ± 0.6%_{m, input} was achieved. The EPA content yielded 3.7 ± 0.1%_{m, input}. This indicates that the production of EPA from *Nannochloropsis* sp. can be done economically viable.

ACKNOWLEDGEMENTS: "PHOTOCHEM" is done in collaboration with Martin Koller, Philipp Tuffner and Gerhard Braunegg from the Technical University of Graz, and Herbert Böchzelt and Angela Pfleger from Joanneum Research, Graz. Financial support is provided by the Austrian Province of Styria.



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Conferences [Abstract]

Fractionation of flash pyrolysis liquids for chemical applications: an exploratory study.

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Bio-oil, the liquid product of flash pyrolysis of lignocellulosic biomass, is a complex and reactive mixture of hundreds of highly oxygenated compounds displaying a wide range of molecular weights. Crude bio-oil has high oxygen content and poor fuel properties and needs further processing. The production of added-value chemicals from bio-oil can provide additional revenues for bio-oil producers and contribute to the attractiveness of the flash pyrolysis platform. However, applications and markets must be found which do not demand expensive purification of bio-oil fractions.

An exploratory study was undertaken to evaluate simple alternatives of bio-oil separation. About 15 l fresh bio-oil was produced from *Pinus radiata* sawdust in a fluidized bed reactor at 500–550 °C. Bio-oil was characterized and analyzed by GC-MS and GPC. Distillation and liquid-liquid extraction of bio-oil were studied. Total carbonyl group and acid content were used mainly to assess separation.

Atmospheric distillation of bio-oil showed low recovery of total carbonyl groups in the distillate and residue, even in presence of alcohols that has been reported to lessen the extent of condensation reactions in bio-oil upon heating. Vacuum and steam distillation remove light-ends, including strong smelling compounds, and produces some “aging” of bio-oil which can ease posterior separation of lignin derived compounds.

Liquid-liquid extraction experiments of bio-oil exhibited notable differences for fresh and “aged” bio-oil. Selective extraction of acids from crude bio-oil with MTBE succeeded only for “aged” bio-oil with high water content. Separation of lignin derived compounds by addition of water proved to be the most effective separation in terms of carbonyl groups and acids, which were extracted by 80% into the aqueous phase. However, the organic phase, containing mostly the lignin derived compounds, forms a viscous precipitate that is not easily washed and handled without adding a solvent. Extraction of bio-oil with butyl acetate and water displayed similar separation of acids and carbonyl compounds as extraction with water alone, but better separation of phenolic monomers into the organic phase as revealed by GC-MS. The aqueous bio-oil fractions thus obtained contains acids and sugar like compounds and appears well suited after concentration for use as silage additive, whereas the organic fraction of phenolic compounds and oligomers can be used as active component in fenol-formaldehyde resins after azeotropic solvent removal.

Acknowledgments.

Dietrich Meier, Institute for Wood Technology and Wood Biology (vTI), Hamburg for support in bio-oil analysis. Conicyt Proyecto Basal PFB-27, Proyectos Semilla PCS2 and PCS3, FONDEF D07-I-1137, and Dirección de Postgrado, Universidad de Concepción for financial assistance.



Conferences [Abstract]

Agro biomaterials based on chitosan and starch functionalized with polyphenols from murta (*Urgni molinae turcz*) leaf extract.

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Biomaterials based on chitosan functionalized with polyphenols are being broadly developed for pharmaceutical, cosmetic and food applications [1, 2]. Antioxidant power of these biomaterials can be increased with the addition of polyphenol-rich aqueous extracts from leaves [1, 3]. However, the component of polyphenol-rich aqueous extract also can modify the physical properties and chemical structure of films, hence their functionality. Murta (*Urgni molinae Turcz*) is an endemic shrub in central-southern Chile from *Myrtaceae* family. Aqueous murta leaf extracts have high antioxidant activity *in vitro* and show phenolic acids like gallic acid, flavonoid glycosides from quercetin, myricetin and kaempferol are among the main compounds found [4, 5]. The objective was to investigate the effect of the polyphenol-rich aqueous extract from murta leaves (PEML) on rheology of solutions and the physical properties and microstructure of chitosan and chitosan-starch blend biomaterials.

PEML was obtained by extraction (25 °C, 90 min and 170 rpm) of leaf powder, ecotype 27-1, with distilled water (ratio 1:10). The PEML showed: 1.4% solids; antioxidant capacity of IC50_{ABTS⁺}: 0.038 mg GAE/mL; total phenol content of 40.67 (mg GAE/g d.m. murta leaves). Biopolymers: Corn starch (CS), containing 27 % amylose, and chitosan (CH), 190–310 kDa, with a deacetylation degree (DD) of 75%. CH (2% w/w) and CH-CS (1.5:0.5 %w/w) soluctions were prepared with 0.25 (g glycerol/g polymer), without or with 40% v/v of PEML (20 mL/g polymer, equivalent to 81.33 mg GAE/g polymer). Solutions were cast (40 g) onto plexiglass plates (125×125 mm), dried (40 °C for 24 h) and conditioned to 48% RH at 22°C.

The CH and CH-CS blend biomaterials show a slightly yellow color. In contrast, slightly orange color was observed when PEML was added on CH-PEML and CH-CS-PEML films. The incorporation of starch in the chitosan film did not change significantly the thickness (CH film: 71 µm and CH-CS film: 72 µm). PEML strongly increases thickness of CH-CS-PEML film (126 µm) and slightly increases thickness of CH-PEML film (78 µm). Tensile strength (TS) and elongation at break (EB) of CH films with 75% DD (TS = 29.69 ± 1.89 MPa and EB = 45.1 ± 1.4%) was close to TS and EB of chitosan films with 90 % DD (6) and (7), which show similar chitosan and glycerol concentration, conditions of film conditioning and tensile tests. CH films show higher TS and EB than CH-CS films (TS = 20.56 ± 1.78 MPa and EB = 13.52 ± 2.85 %). PEML decreased TS and EB of CH-CS film (17.13 ± 1.22 MPa and 6.57 ± 2.43 %, respectively). In CH film cross section, PEML formed elongate horizontal pores around 1-4 µm, whereas in CH-CS-PEML film the formation of horizontal layers and some discontinuous zones and pores was observed. The FTIR-ATR spectra of PEML-loaded CH and CH-CS films show differences in the range of 1800-1400 cm⁻¹, where the characteristic bands of substituted amino groups and carbonyl groups are located. Small new peaks around 1715 cm⁻¹ and peaks at 1627-1614 cm⁻¹ were observed when PEML was added to CH and CH-CS films.

The CH film was more ductile and elastic than CH-CS film. PEML in CH-CS film decreases mechanical properties, increases the thickness and became colored films, from yellow to orange. Supported by the film characterization the interaction mechanism of PEML with chitosan chains was due to electrostatic interactions, ester linkage and hydrogen bonds, while PEML linked with starch chains through hydrogel bonds and ester linkages.

ACKNOWLEDGEMENTS

We thank Mrs I. Seguel (M.Sc.) from Unidad de Recursos Genéticos, INIA Carillanca, Temuco, Chile, for the murta leaf ecotype. This work was supported by CONICYT CHILE grants N° 21070302, 24090134 and 29090088; CYTED project 309 AC0382; and the Spanish Ministerio de Ciencia e Innovación project AGL2008-00231/ALI.

Influence of different operational conditions on the pyrolysis of lignocellulosic biomass to produce biochar with adsorbent characteristics.

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Pyrolysis of lignocellulosic biomass leads to a variety of useful liquid, gaseous and solid products. The last one is known as biochar, which is a carbon-rich product with potential use as solid biofuel. In addition, biochar constitutes a promising adsorbent material due to its structural properties. In this sense, the operational conditions of the pyrolysis process play a very important role on the structural characteristics of biochar, such as specific surface area, pore volume, pore size distribution, texture and density. The factor that mostly affects the process is pyrolysis temperature, followed by heating rate, N₂ flow, while the residence time causes less effect on the increase in BET area (Lua, 2004). The aim of this work was to produce biochar using oat hull as raw material evaluating the effect of different operational conditions on the BET surface area, pore sizes and pore volume of the resulting biochar. Biochar was produced by pyrolysis on a semi-bench scale unit which can produce approximately 2 kg of biochar per batch. The experiments were performed at different temperatures: 300, 400 and 500°C; two increasing rates of temperature: 2.1 and 3.7 °C/min; and two nitrogen flows: an initial pulse of nitrogen of 1 l by 30 min and a constant flow 0.5 l N₂/min.

The yields in the products of pyrolysis showed different results for biochar, bio-oil and syngas. The amount of biochar varies depending on the final temperature of pyrolysis. Low pyrolysis temperature led to the highest yields, which decreased with increments in the temperature. For pyrolysis at 300°C, biochar yield may vary between 43 to 50% of the starting biomass by weight; bio-oil yield varies from 35 to 45%; and the synthesis gas yield ranges from 10% to 25%. For a temperature of 400°C, these values are 32 to 41% for biochar, 36 to 44% for bio-oil, and 21 to 28% for syngas. In the pyrolysis at 500°C the percentages obtained were 30 to 35% for biochar, 38 to 50% for bio-oil and 16% to 30% for syngas. The increase in BET surface area is mainly affected by the residence times in the pyrolysis process. The pore diameter remains constant with small variations; this because the size is highly dependent on the nature of the biomass (Lehmann, 2009).

Acknowledgements: This work was supported by Fondecyt N°11110388 project and FONDEF D07I1096 project.

Improvement of lignocellulose degradability using anaerobic rumen fungi.

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Biogas production from energy crops struggle with the problem of incomplete degradation of fermented material caused by high content of lignocelluloses in plant substrates. Anaerobic fungi are able to degrade lignocellulosic materials and thus contribute significantly to the utilization efficiency of plant substrates. These fungi can also be used in biotechnological applications aimed at obtaining further usable organic compounds such as VFA.

The present work focuses on the improvement of grass stillage hydrolyses by addition of anaerobic fungi in lab-scale and pilot-scale anaerobic reactors. Optimization of reactors performance were done by monitoring and modifying parameters such as hydraulic retention time, organic loading rate, pH value, production of soluble COD, production of volatile fatty acids, the quality and quantity of gas produced and the production of hydrolytic enzymes. As an inoculum, we used a mixture of anaerobic fungi *Anaeromyces* sp. (KF8) and *Piromyce* sp. (KF9), isolated from cow droppings and cow rumen fluid.

The experiments performed showed that the use of anaerobic fungi can increase the production of soluble COD five times and production of volatile fatty acids three times compared to the control with no fungi addition. A 5-15% increase of biogas production compared to the control was achieved in a semi-continuously operated 3L reactor by the introduction of a hydrolysis step, where the substrate (grass stillage) was pre-treated with by a mixed culture of anaerobic fungi. The degradability of grass stillage in this reactor increased from 55% (control without fungi) to 60-70% (reactor with fungi).

Keywords: Anaerobic reactors, rumen microorganisms, biodegradability, hydrolytic fungi, lignocellulosic substrates, biogas.



Conferences [Abstract]

Hydrogen production and partial characterization of a bacterial consortium obtained from Lagoon sediment.

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The global energy requirements are mostly dependent on fossil fuels. Hydrogen is a clean energy alternative to these fuels. Phototrophic bacteria are known by their capability to produce H₂ from organic compounds by an anaerobic light-dependent process. Therefore, in this study it was aimed to evaluate hydrogen production from organic acids by a previously selected photoherotrophic bacterial consortium obtained from lagoon sediment (Lagoa da Conceição Florianópolis/SC – Brasil), as well as to partially characterize this consortium. RCV modified medium containing sodium glutamate (2 mmol.L⁻¹), and acetic acid (30 mmol.L⁻¹), butyric acid 15 mmol.L⁻¹) or malic acid (15 mmol.L⁻¹) were used to hydrogen production. The initial pH was 7.0 and temperature 30°C. The bottles were illuminated with fluorescent lamp (4000 lux) for 72 h. The cultivations were carried out at 30°C and 7000 lux, during 6 days. The quantification of produced hydrogen was performed by gas chromatography. Hydrogen production was observed from all tested substrates. From substrates malic acid and butyric acid it were produced similar amount of H₂ reaching concentrations of 5.7 mmol.L⁻¹, while from acetic acid the production was 4.71 mmol.L⁻¹. However, acetic acid fermentation presented the highest hydrogen production rate (1.6 mL.L^{-1.h}⁻¹), followed by butyric acid (1.4 mL.L^{-1.h}⁻¹) and malic acid (0.9 mL.L^{-1.h}⁻¹). An attempt to identify bacteria comprising the selected consortium using PCR/DGGE methodologies was carried out. Gradient denaturating gel electrophoresis (DGGE) analysis resulted presence of only four bacterial ribotypes. The DNA sequencing of the DGGE bands harvested from gel showed similarities with different bacterial genera: band 1 - *Shewanella* sp (96 %), band 2 - *Pseudomonas* sp (93 %), band 3 - *Wolinella* sp (96 %) and band 4 - unidentified alpha proteobacterium (91 %). These bacterial genera are characterized by facultative anaerobic heterotrophic metabolism, being able to use various substrates. Particularly bacteria of the genus *Shewanella* are hydrogen producing fermenters from organic acids. Surprisingly, through the used methodology no phototrophic bacterium was identified. It is supposed that *Shewanella* would be responsible by hydrogen production.



Conferences [Abstract]

DIBANET: Collaboration in biorefinery research between Europe and Latin America.

Dr Daniel John Hayes

DIBANET (www.dibanet.org) is a €3.7m research project, funded under the EU's Seventh Framework Programme and coordinated by the Carbolea Research Group (www.carbolea.ul.ie) at the University of Limerick. It is a response to the Energy 2008 Call - "Significant enhancement of the cooperation between key researchers & industries from the EU & Latin America in the field of biofuels". There are 13 partners in the group, 5 from the EU & 8 from Latin America. One of these partners, Fundacion Chile, is from Chile. The central concept of DIBANET is that the maximal use is made of biomass. The most appropriate feedstocks are selected and then put through an acid hydrolysis process with the target being the production of levulinic acid and formic acid in high yields from the 6-carbon sugars contained in cellulose and hemicellulose and the production of furfural in high yields from the 5-carbon sugars contained in hemicellulose. Some of the sugars and most of the lignin will be incorporated into the solid residue of the process which can be used in gasification or for the production of biochar. The planned presentation will cover the areas being investigated at the University of Limerick:

1. The development of rapid analytical tools for biomass (using near infrared spectroscopy).
2. The development of a (patented) pretreatment process for obtaining a cellulose rich pulp and a hemicellulose/lignin rich liquor from biomass.
3. The production of levulinic acid and co-products in high yields from biomass (both virgin and pretreated). Ethanolysis experiments will also be discussed.

Second-generation ethanol in Chile: optimized autohydrolysis process of *Eucalyptus globulus*.

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Among chemical hydrolysis method, acid hydrolysis pretreatment is probably the most commonly applied. Particularly, autohydrolysis is a traditional and very efficient pretreatment process to breakdown some biomass like hardwood. On this study, we used Central Composite Circumscribed design (CCC) composed of a full factorial design and star points to maximize the potential to assess these trials. Condition selection of parameters was based on the results of preliminary experiments. Parameters such as temperature and cooking time were varied. Xylose recovery in liquid fraction and ease of enzymatic hydrolysis of pretreated solid at 10% w/v solid concentration were used as response variables to assess the efficient of pretreatment. A total of 11 points was generated, and data was analyzed using MODDE 7.0.0.1 (Umetrics). Response surface methodology was used to evaluate xylose recovery and glucose yield by enzymatic hydrolysis. Optimization of these two response variables individually and together resulted in two distinct pretreated materials with different physical and chemical response.

Without adding catalysts, our pretreatment was tested at 160 to 200°C for 15 to 60 minutes. The two optimized conditions showed that: a) over 50% of the xylose in the raw material was recovered in the liquid phase as well as a glucose yield of 80% (based on pretreated material) was obtained by enzymatic hydrolysis; and b) glucose yield of over 95% (based on pretreated material) was reached by enzymatic hydrolysis of the pretreated material but degrading almost all the xylose in the liquid phase. Under the first optimized condition, maximum ethanol production reached at these pretreated conditions was 247 L/ton of dry-raw material (3.5% v/v).

Pretreated material obtained under the second optimized condition was washed with sufficient water to remove fermentation inhibitors previous SSF. SSF tests were performed at 40 °C, 150 rpm, and high substrate loadings (15 and 20 % (w/v)). Different enzyme dosages of the Novozyme NS-series cellulase complex supplemented with β-glucosidase and a low dosage of the last generation Novozyme Cellic Ctec 2 enzyme complex were tested. All trials have a concentration of 6 g/L of the initial inoculum of the thermotolerant strain of *Saccharomyces cerevisiae* IR2-9a. Final ethanol concentrations over 5.5 % (v/v) with ethanol yields of 80 % (based on pretreated material) were achieved at enzyme dosages tested and increasing substrate loadings. Main differences between SSF's were observed on residence times since higher enzyme dosages shorted reaction times.

Physical characterization of pretreated materials showed significant morphology changes and fiber length reduction as pretreatment severity increased. These micro and macro structural changes are directly reflected on glucose yield by enzymatic hydrolysis. In consequence, high severity factor showed high glucose yield by enzymatic hydrolysis.

Acknowledgement: The financial support of this work was provided by Consorcio Bioenercel S.A. and by project Innova Chile Corfo 208-7302