

Introduction

Project CC05 Optimal treatment processes for second generation bioethanol

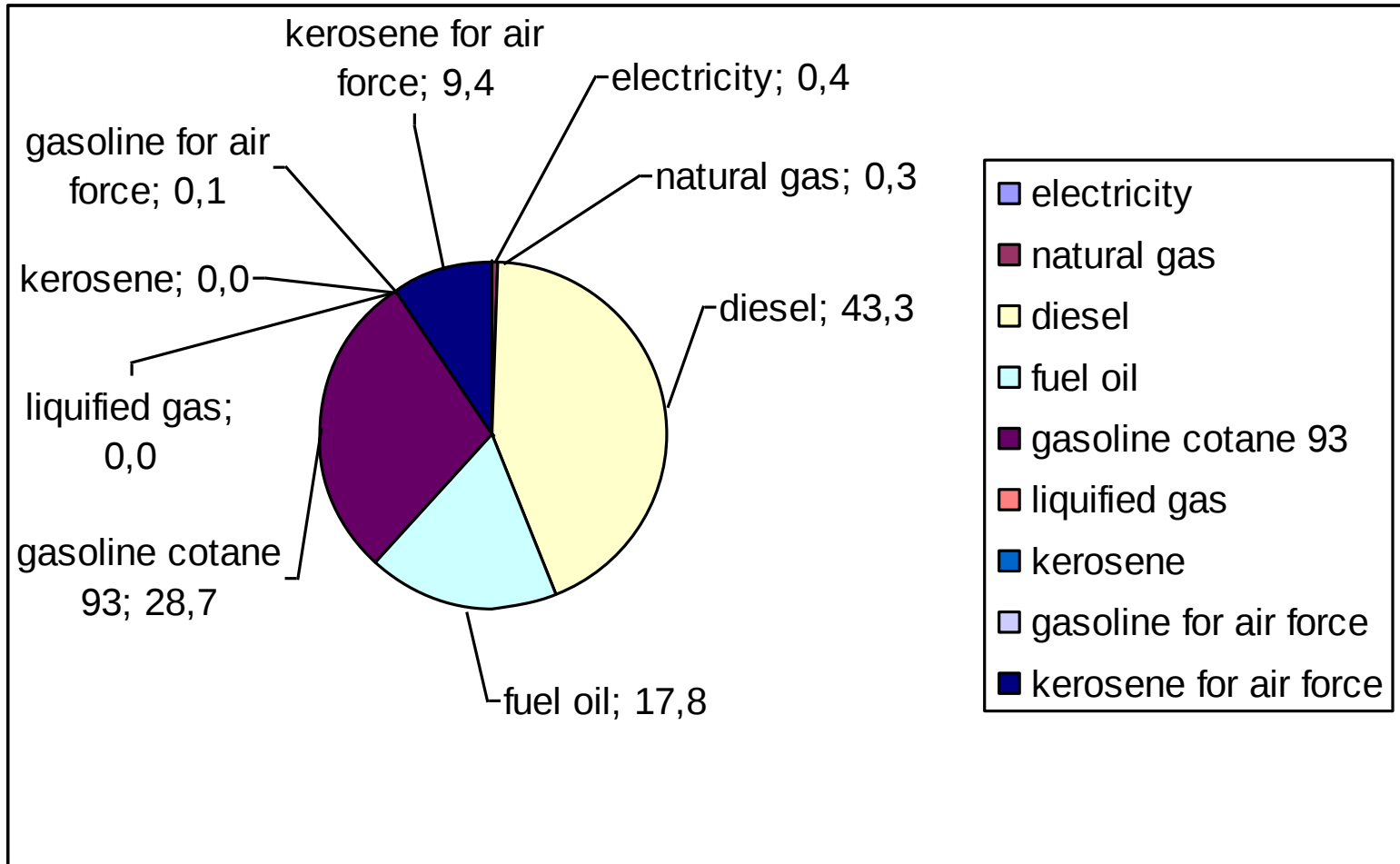
Chairman: Alejandro García
Faculty of Forest Sciences and Nature Conservation
Santiago, November 15th 2010



Chilean balance of energy

Energy source	Production (GJ)	Import (GJ)	Dependence
Crude oil	6,434,992	480,457,088	98,7
Natural gas	85,939,360	237,031,968	73,4
Coal	11,589,048	132,532,384	92,0
Hydroelectricity	111,758,824	0	0,0
Wood and other sources	197,907,384	0	0,0
Biogas	0	0	
TOTAL	413,629,608	850,021,440	

Power matrix for chilean transportation sector



Suppossing first generation biofuels

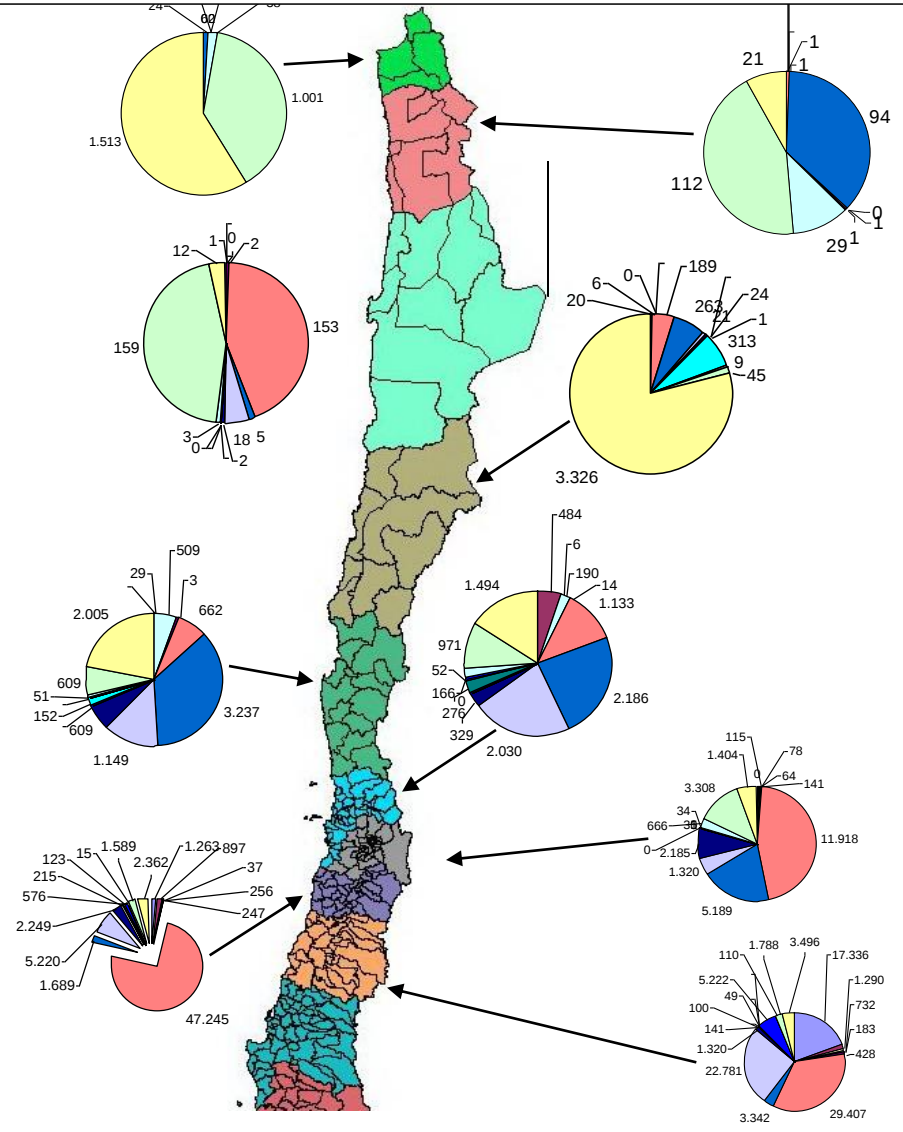
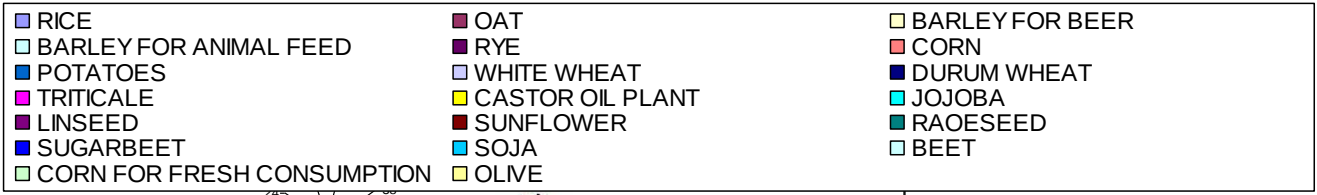
- Agriculture in Chile exhibits very high yields for many crops: sugarbeet (highest yield of the world and highest sugar content); rapeseed (up to the world average yield); wheat (up to the world major producers); corn (highest yields in the world).
- However there is a strong scarcity of agricultural soils in the country.

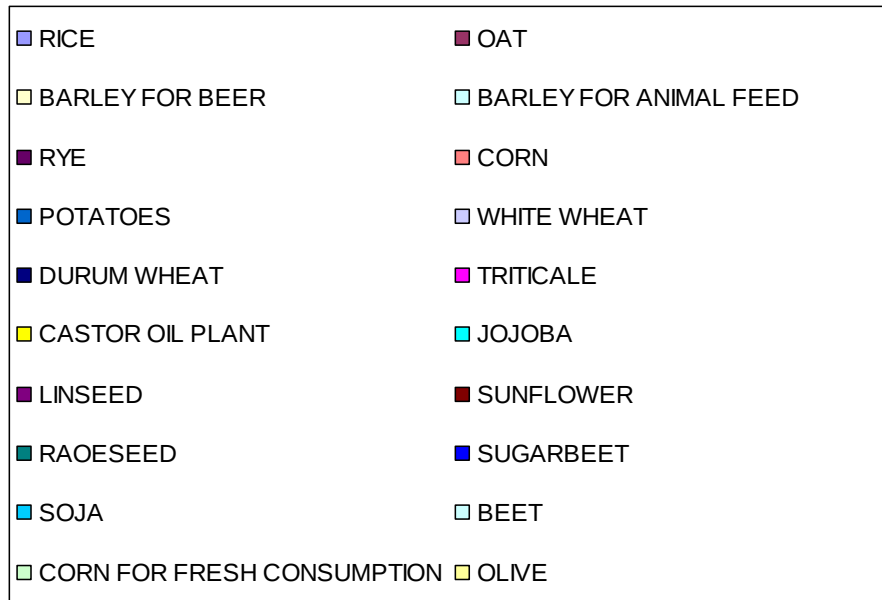
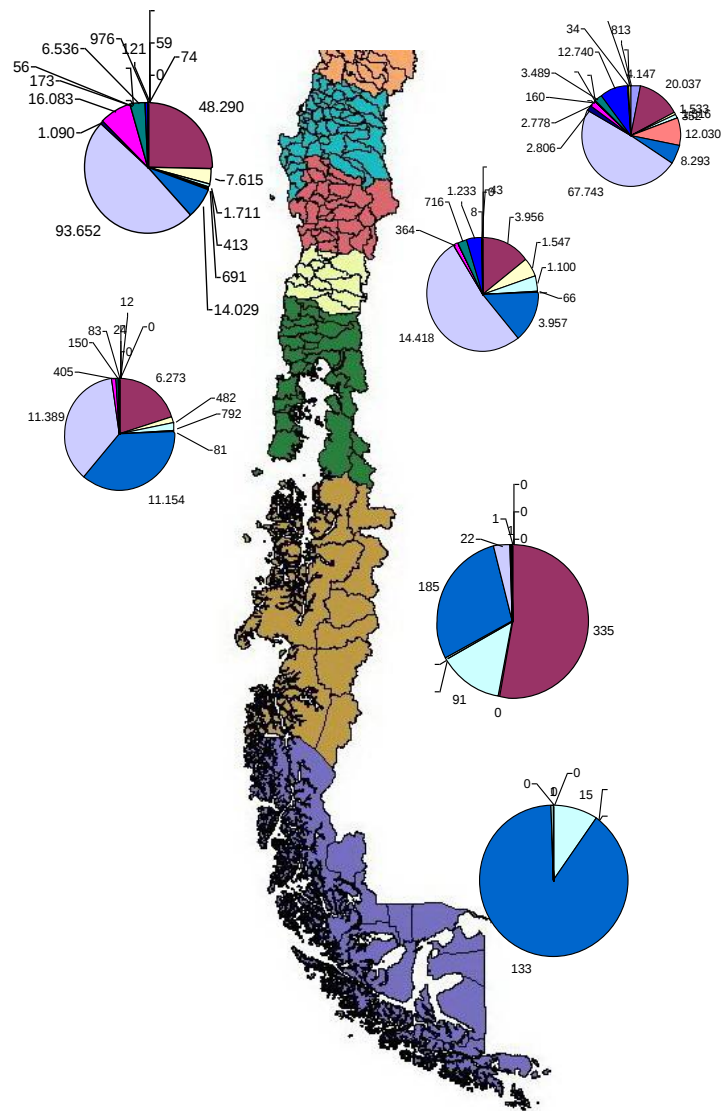
Use of soils in Chile

Use type	Use	Land capability	Surface (ha)	Percentage
Arable soils	Non restrictions	I	90,846	0.1
		II	711,625	0.9
	With restrictions	III	2,195,439	2.9
		IV	2,273,670	3.0
Non arable soils	Cattle	V	2,271,144	3.0
	Cattle-forestry	VI	6,510,613	8.6
	Forests	VII	12,339,882	16.3
	Conservation	VIII	14,200,000	18.8
Non agricultural lands	Unproductive lands		35,144,147	46.4
	TOTAL		75,707,366	100

Potential sown surface for most promising crops intended for biofuels production

Crop specie	Cropped surface (ha) for 2006-2007	Maximun available surface	Potential available surface
Sugarbeet	22,750	50,002	27,250
Wheat	282,400	315,000	32,600
Corn	134,930	150,000	15,070
Rice	26,530	29,500	2,970
Potatoe	63,910	65,000	1,090
Sunflower	2,680	90,000	87,350
Rapeseed	16,650	235,000	218,350





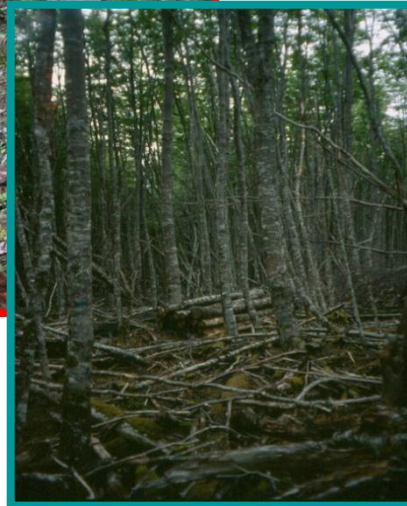
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Potential of forest resources

- 13.4 millions of hectares are native forests
- About 5 millions of hectares of native forests are productive and have possibilities to be managed
- Additionally, there are about 2.2 millions of hectares of industrial forestry plantations able to generate biomass for energy purposes.
- There are about 3 millions of hectares that have forest aptitude, but they are not covered by forests, this surface could be planted with species able to produce lignocelluloses.
- However, nowadays the forestry sector is an important supplier of wood, sawmills, and other residues derived from cellulose plants, contributing with 14% of the domestic consumption of energy. There is a clear idea about volumes of residues and location of residual biomass.
- Sawing industry associated only to Radiata pine plantations would generate a volume about 1.4 millions of m³.
- it does not include the volume of residues produced during the management of native forests. These last ones could reach a volumen close to 7 millions of m³ per year.
- The use of forest residues is something that could be expected and stimulated.

Residues and dead wood in Lenga forests



Lenga potentialities

- Nothofagus pumilio forests cover a surface that is equivalent to 25.3% of the Chilean native forest. In general terms, these forests are over mature and have low yields of sound wood for the industry. So, they can be interesting if considered as raw material able to provide lignocelluloses.
 - Productive surface of 600, 000 ha
 - Currently surface subjected to management strategies should be: 40,000 ha (2.000 ha per year)
 - Existent volumes:
 - 600 m³/ha + 120 m³/ha Volume of dead wood.
 - 150 m³ could be destined to industry
 - 50 m³ are eliminated
 - 10 m³ are used as wood
 - Current volume per year of residues generated under this management system would be 1.2 millions of m³ (1,2 MM m³)
 - If 5,000 ha of Nothofagus pumilio forests are subjected to this management, the estimated production should be 3 MM m³

It would avoid the loss of 3 millions of m³ of dead wood, it would be equivalent to 402.725 m³ of ethanol (considering a cellulose content of 40% and wood bulk density of 400 kg per m³ and a conversion rate of 134,25 L per m³ of wood) this should be equivalent to 14% of the total consumption of gasoline (octane 93), according to the last available energy balance.



**Residues derived
from harvest and
their actual “use”**

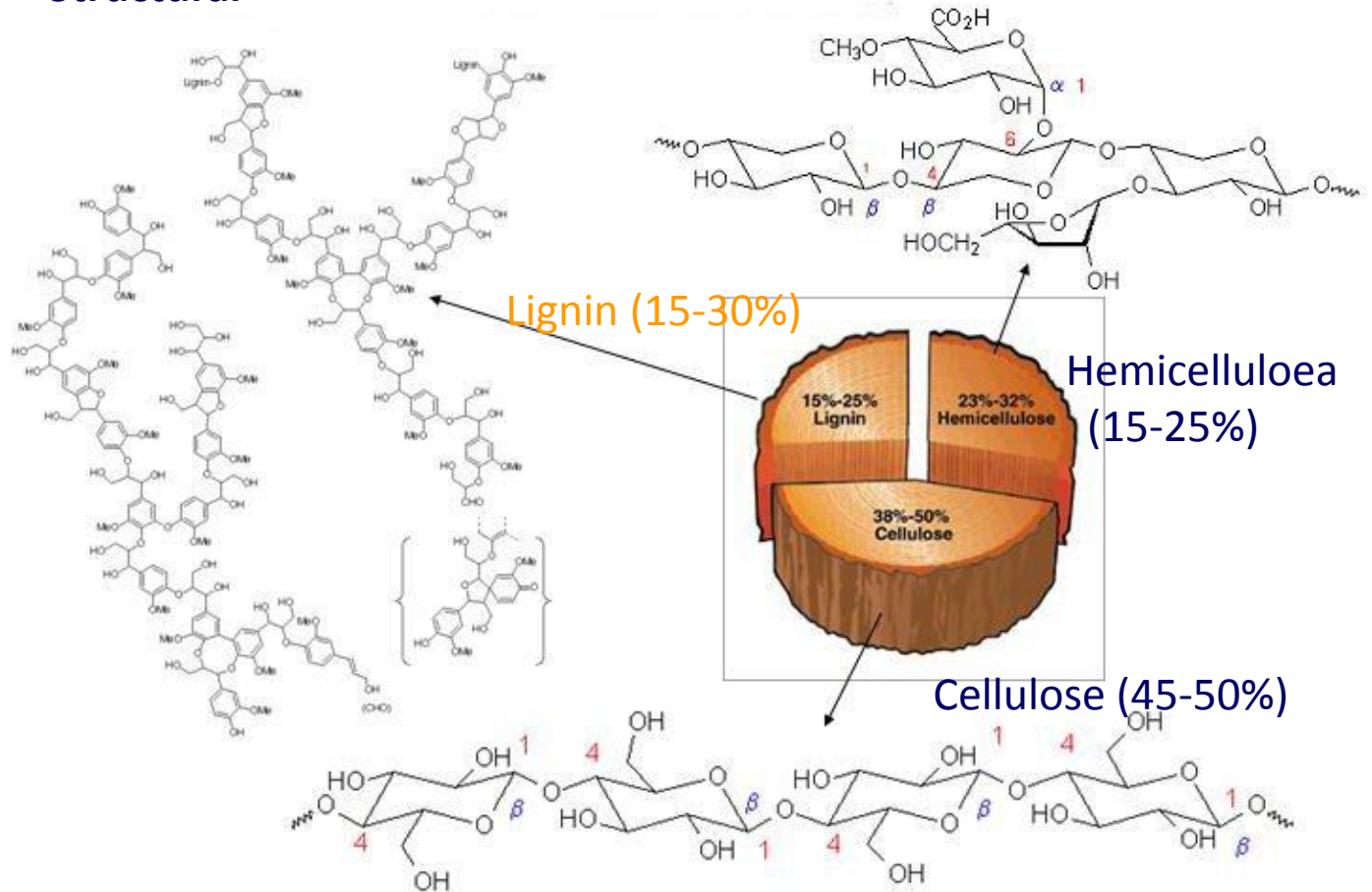


The potential use of wheat straw

- Cropped surface per year: 300.000 ha
- Average national yield: 4.8 tons of dry matter per hectare
- Volume of existant wheat straw:
 - Harvest index: 45%
 - Volume of wheat straw per hectare = 5.87 ton of dry matter per hectare
 - Estimation = 1,760,000 tons for all the country
- If we could use only 50% of available volume, it should be 880,000 tons of dry matter
- They would be equivalent to 295,353 m³ of ethanol, which represents 10.4% of the consumption of gasoline (octane 93).

Lignocelluloses

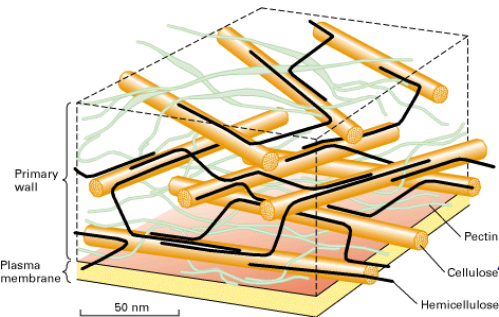
Structural



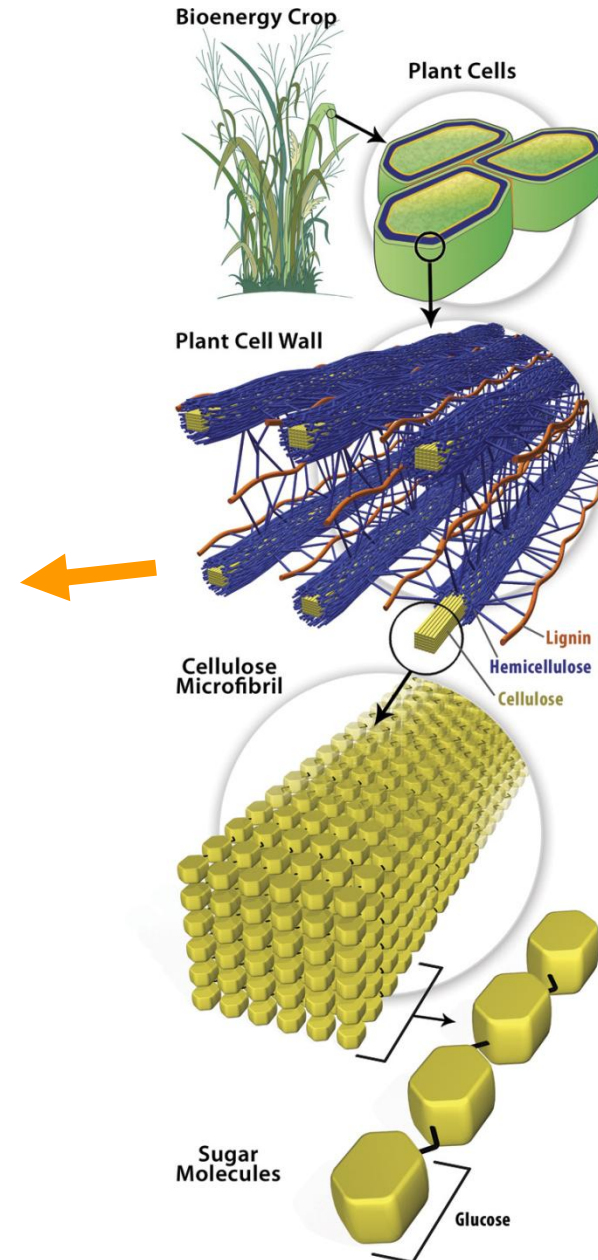
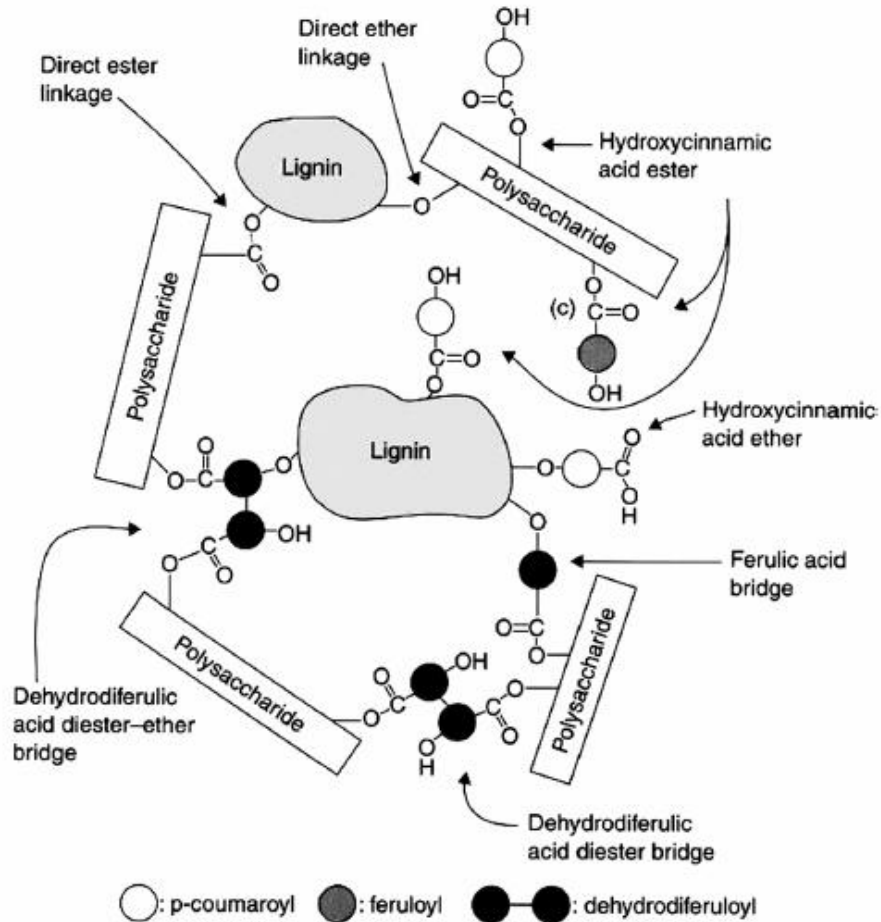
Non structural:

Extractable substances (Phenols, sugars and others)

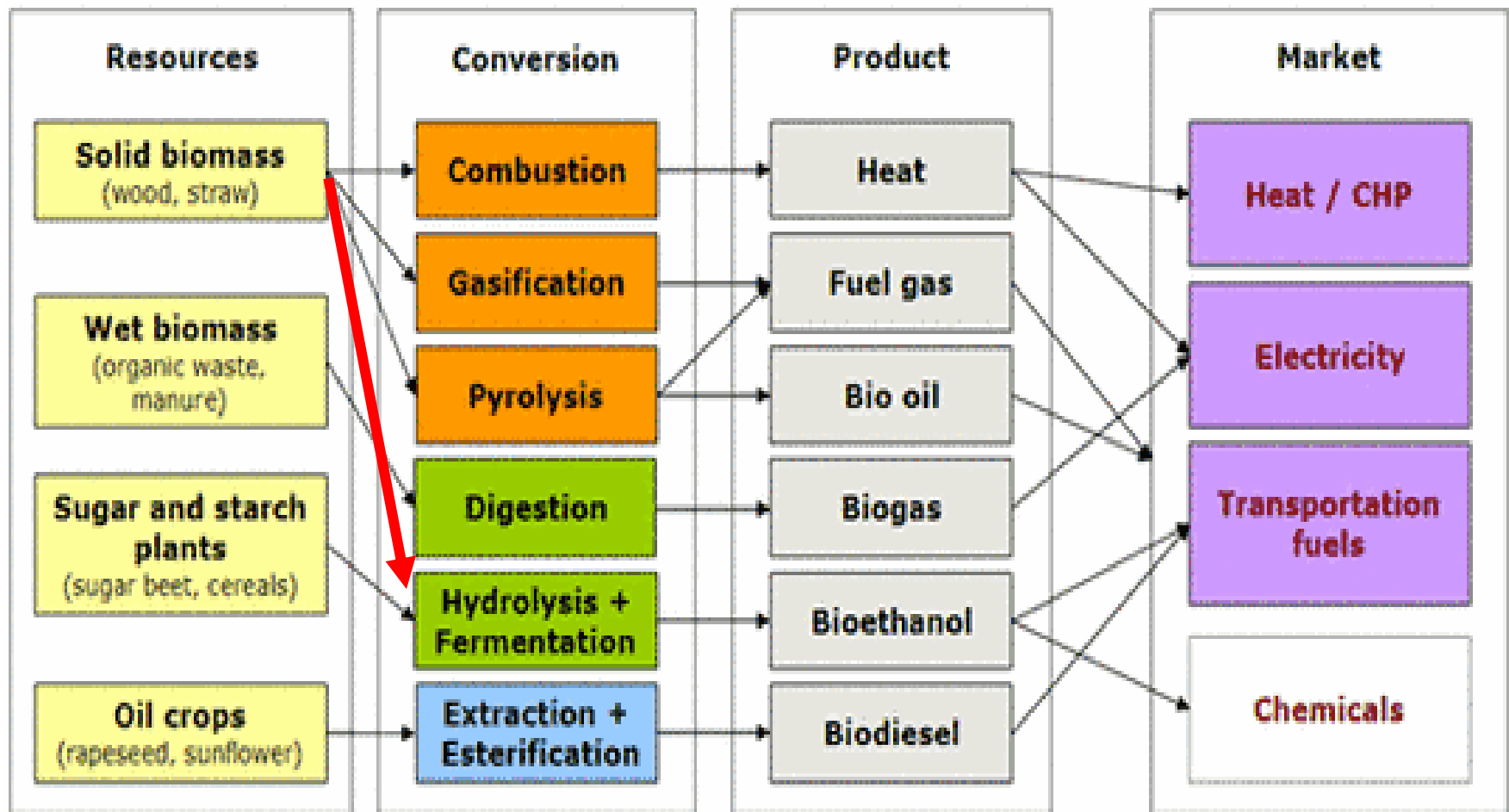
Ashes $\leq 1\%$



Plant cell wall

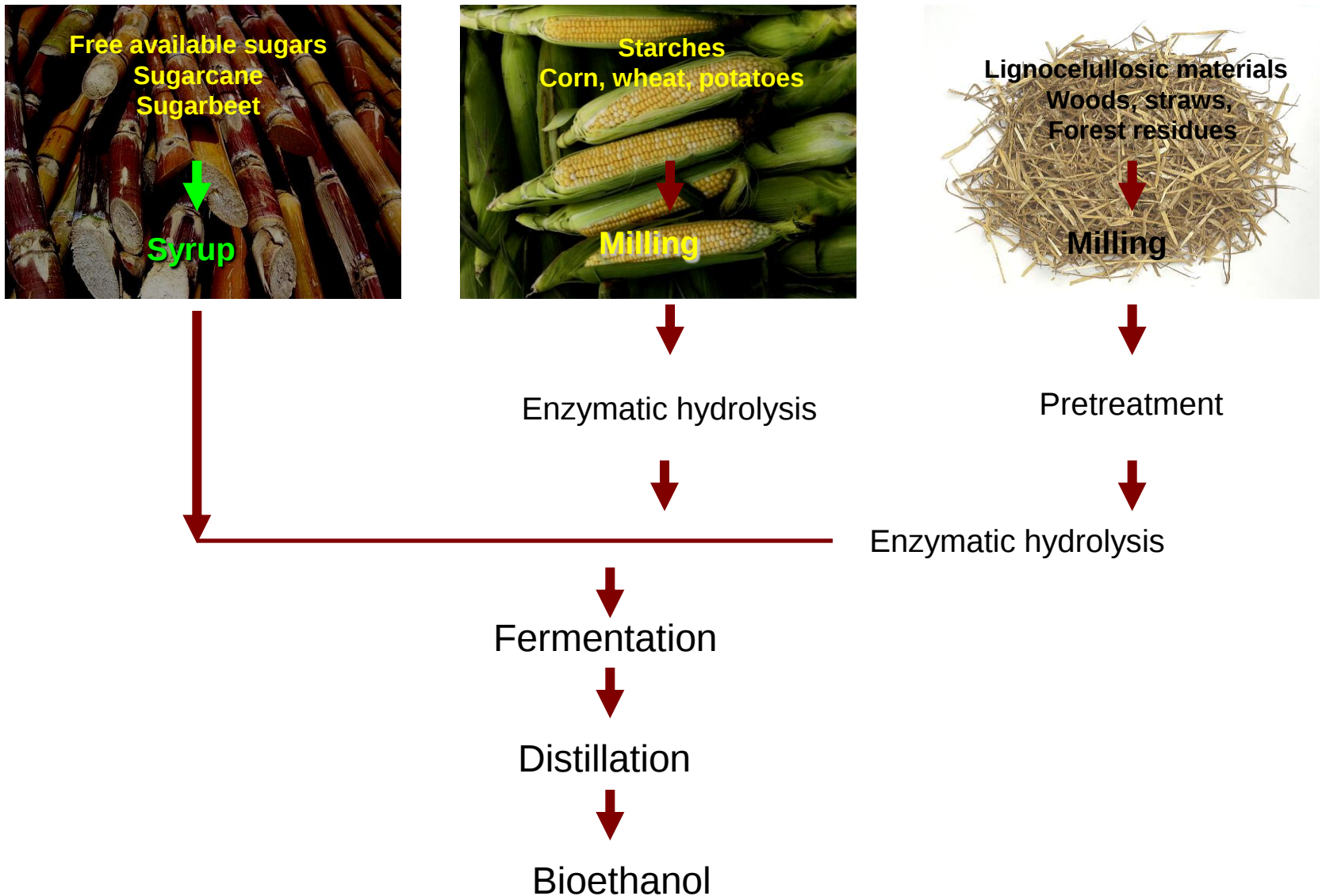


Options for processing biomass to obtain energy



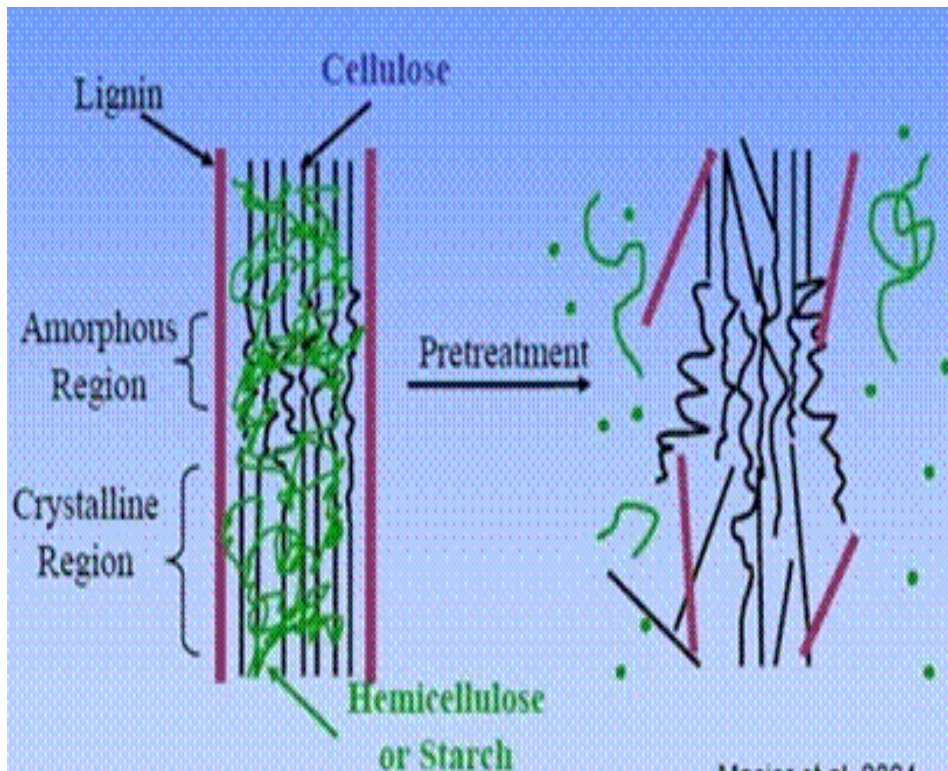
BIOETHANOL

Bioethanol obtainment



Pretreatment

Objective: release of cellulose from the cell wall complex

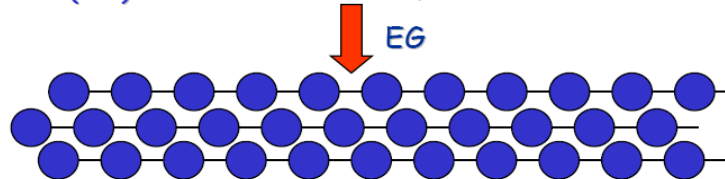


- **Physical mechanic disruption**
- **Chemical (based on acids or alkali, organosolv, oxidative lignin removal, ionic liquids)**
- **Physical-chemical (steam explosion, NH_3 or CO_2)**
- **Biological (White rot fungi)**

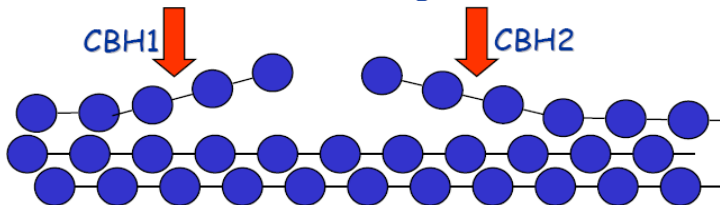
Cellulose hydrolysis mechanisms

T. reesei Cellulase Components

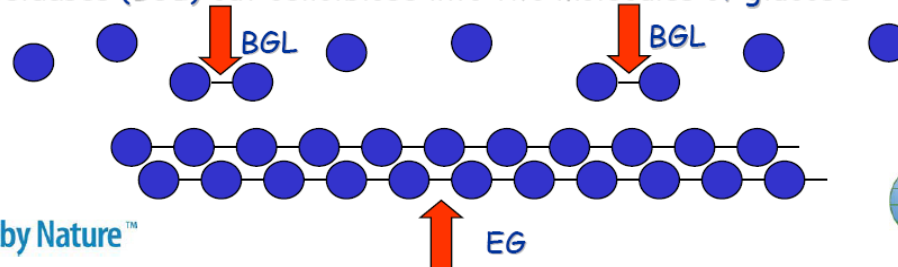
- Endoglucanases (EG) cut in the middle of the chain.



- Cellobiohydrolases (CBH) cut cellobiose (DP_2) from either end

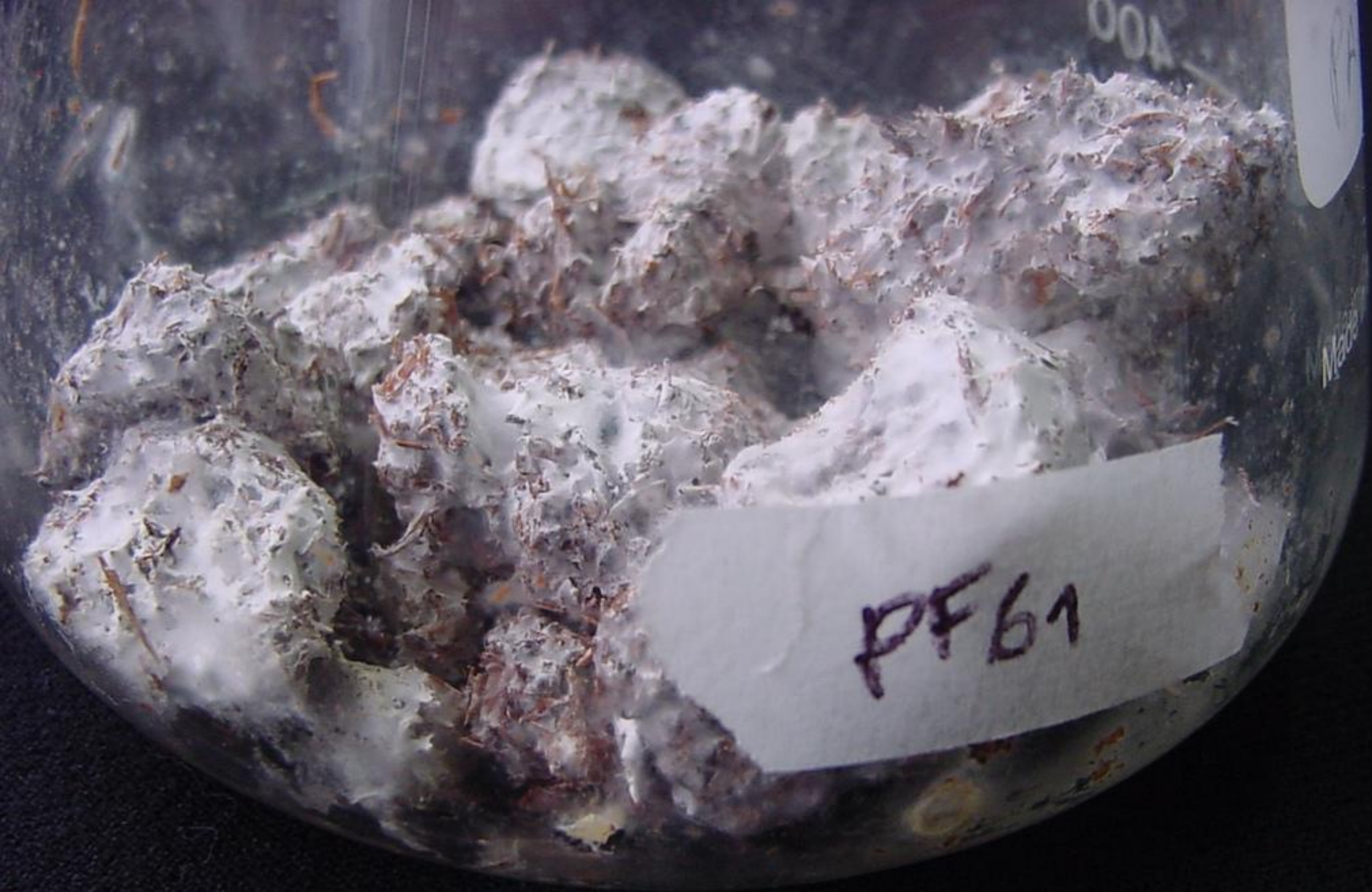


- β -glucosidases (BGL) cut cellobiose into two molecules of glucose



White rot fungi





Residues bioaugmentation

Protein engineering







Dra. María Elena Lienqueo, FCFM, U. de Chile



Dra. Oriana Salazar, FCFM, U. de Chile



Dr. Juan Asenjo, FCFM, U. de Chile



Prof. René Carmona, Fac. Cs. Forestales

Related projects

- 2007. “ASISTENCIA A EXPOBIOENERGÍA – II FERIA INTERNACIONAL DE BIOENERGÍA”, EN VALLADOLID, ESPAÑA”. Fundación para la Innovación Agraria.
- 2008 – 2010. “OPTIMIZACIÓN DEL PROCESO DE TRATAMIENTO DE LIGNOCELULOSAS CON MIRAS A LA OBTENCIÓN DE ETANOL”. Programa Domeyko Energía, Vicerrectoría de Investigación y Desarrollo, Universidad de Chile.
- 2008 – 2010. “OPTIMAL TREATMENT PROCESSES OF LIGNOCELLULOSES FOR BIOETHANOL PRODUCTION: OPTBIO CONSORTIUM”. Fuente de Financiamiento: CONICYT – Academia de Finlandia, Apoyo al Desarrollo de la Cooperación Internacional para la Investigación de Excelencia.
- 2010 – 2012. “CARACTERIZACIÓN FÍSICO-QUÍMICA DE BIOMASA Y PRETRATAMIENTOS PARA PRODUCIR BIOCOMBUSTIBLES” como parte del Consorcio BIOCOMSA, financiado por Innova-Chile.
- Prestación de servicios para Consorcio BIOENERCEL

First Chile – Finland Meeting



Thesis works

- Pretreatment and biomass characterization:
 - Felipe Villaseñor
 - Carolina Vicuña
 - Consuelo Fritz
 - Victoria Cortínez
 - Ricardo Pezoa
 - Pablo Santibáñez
 - Stephanie Oyaneder
 - Waldo Aracena
 - Sebastián Juri
 - Leonardo Stari
- Economic evaluations of biofuels plants:
 - Diego Schneuer
 - Roberto Sotomayor
 - Carlos Véjar
- Cloning and enzymes engineering:
 - Alejandra Guerrero
 - Alejandro Salinas
 - Marcela Vega
 - Iván Gajardo
 - Javier Jofré
 - Patricia Lozada
- Fermentation:
 - Tomás Niklitschek

Publications

- CARMONA, René, LIENQUEO, María Elena, SALAZAR, Oriana & GARCIA, Alejandro. 2009. ***Bioenergy II: Biological pretreatment with fungi as a tool for improvement of the enzymatic saccharification of Eucalyptus globulus Labill to obtain bioethanol.*** International Journal of Chemical Reactor Engineering. Vol. 7: A77. (<http://www.bepress.com/ijcre/vol7/A77>).
- CARMONA, René & GARCIA, Alejandro. 2009. ***Biocombustibles líquidos en Chile.*** Pp. 87-106 In: Biocombustibles líquidos en Latinoamérica. Red Iberoamericana de Biocombustibles, Red CYTED 306RT0279. ISBN 987652-043-1. Más anexos.
- ***The current status of liquid biofuels in Chile:***. Energy. Energy -Elsevier Publishers, Manuscript EGY-D-09-00528, in press (PII: S0360-5442(10)00319-1; DOI: 10.1016/j.energy.2010.06.005).
- PEZOA, Ricardo, CORTINEZ, Victoria, HYVÄRINEN, Sari, REUNANEN, Markku, HEMMING, Jarl, LIENQUEO, María Elena, SALAZAR, Oriana, CARMONA, René, GARCIA, Alejandro, MURZIN, Dmitry, MIKKOLA, Jiry-Pekka. 2010. ***The use of ionic liquids in the pretreatment of forest and agricultural residues for the production of bioethanol.*** Cellulose Chem. Technol., 44 (4-6), 165-172.

Publications

- Salmi, T., Wårnå, J. and Mikkola, J.-P., Chemical ***Reactor and Reaction Engineering***, Taylor & Francis, ISBN10: 1420092685 (book)
- Pasi Virtanen, Tapio O. Salmi, Jyri-Pekka Mikkola, ***Supported Ionic Liquid Catalysts (SILCA) for Preparation of Organic Chemicals***, ORCS 2010, Topics in Catalysis, vol.35, 15, 2010, 1096.
- S. Hyvärinen, P. Virtanen, D. Yu. Murzin, J.-P. Mikkola, ***Towards Ionic Liquid Fractionation of Lignocellulosics for fermentable sugars***, Cellulose Chemistry and Technology 2010 44 (1-3)
- Pia Damlin, Jyri-Pekka Mikkola, Tapio Salmi, ***Characterization of hardwood-derived carboxymethylcellulose by high-pH anion-exchange chromatography using pulsed amperometric detection***, Cellulose Chem. Technol., 44 (1-3), 65-69 (2010)
- P.Mäki-Arvela, I. Anugwom, P. Virtanen, R. Sjöholm, J.P. Mikkola, ***Dissolution of lignocellulosic materials and its constituents using ionic liquids—A review***, (Industrial Crops and Products) Ind. Crops and Prod. 32 (2010) 175-201, doi:10.1016/j.indcrop.2010.04.005
- Pia Hara, Jyri-Pekka Mikkola, Dmitry Yu. Murzin and Liisa Kanerva, ***Supported Ionic Liquids in Burkholderia cepacia Lipase-Catalyzed Asymmetric Acylation***, J.Mol.Cat. B, Enzymatic, 2010 MOLCAB2112P11: S1381-1177(10) 00202-X DOI: 10.1016/j.molcatb.2010.07.018

Publications

- Pia Hara, Jyri-Pekka Mikkola, Dmitry Yu. Murzin and Liisa Kanerva, ***Supported Ionic Liquids in Burkholderia cepacia Lipase-Catalyzed Asymmetric Acylation***, J.Mol.Cat. B, Enzymatic, 2010 MOLCAB2112PII: S1381-1177(10) 00202-X DOI: 10.1016/j.molcatb.2010.07.018
- Murzin, Dmitry; Grenman, Henrik; Warna, Johan; Mikkola, J-P; Sifontes, Victor; Fardim, Pedro; Salmi, Tapio, ***Modelling the influence of wood anisotropy and internal diffusion on delignification kinetics***, Ind.Eng.Chem.Res. 2010, Ind. Eng. Chem. Res. 2010, 49, 9703–9711, doi: 10.1021/ie101215a
- .V. Tokarev, A.V. Kirilin, E.V. Murzina, K. Eränen, L.M. Kustov, D.Yu. Murzin, J.-P. Mikkola, ***The role of bio-ethanol in aqueous phase reforming to sustainable hydrogen***, Int.J.Hydr.En., 35 (2010) 12642 – 12649 doi:10.1016/j.ijhydene.2010.07.118

Conference presentations

- a) 2009: ***The current situation of biodiesel and bioethanol in Chile.*** 5th Dubrovnik Conference on Sustainable Development of Energy, Water and Environments Systems, Dubrovnik, Croatia.
- b) 2009: ***Biological pretreatment with fungi as a tool for improvement of the enzymatic saccharification of Eucalyptus globulus Labill to obtain bioethanol.*** Bioenergy II Fuels and Chemical from Renewable Resources, Río de Janeiro, Brasil.
- c) 2010: ***Rendimiento de azúcares fermentables hidrolizados enzimáticamente a partir de residuos de Lenga y Eucalipto pretratados con HPB y ácido diluido*** (aceptada). V Congreso Chileno de Ciencias Forestales, Temuco, Chile.
- d) 2010: ***Use of ionic liquids for the production of second generation bioethanol.*** Aceptada para su presentación en ICERE 2 2010. International Conference and Fair on Education, Research & Employment in the Renewable Energy Sector. Santiago, Chile, 11th-12th November.
- e) 2010: ***Heterologous expression and characterization of novel cellulases from white rot fungi.*** 14th International Biotechnology Symposium and Exhibition. Biotechnology for the Sustainability of Human Society, 14th-18th September 2010, Rimini, Italy.

- a) 2010: ***Comparison of SHF and SSF processes from forest residues pretrated with ionic liquid to obtain bioethanol.*** UK-Brazil-(Chile) Frontiers of Science, Itatiba, Sao Paulo, August 27th-30th.
- b) 2009: ***Use of ionic liquids in the pre-treatment of lignocellulosic materials for production of second generation bioethanol.*** II Latin American Congress on Bio-refineries: Materials and Energy, Concepción, Chile.
- c) 2009: ***A chromatography approach for the biological pretreatment of lignocellulose to obtain bioethanol,*** II Latin American Congress on Bio-refineries: Materials and Energy, Concepción, Chile.
- d) 2009: ***Estudio del efecto del pretratamiento con hongos de pudrición blanca (HPB) sobre madera de Lenga (Nothofagus pumilio (Poepp. Et Endl.) Krasser en el rendimiento de azúcares para producir etanol.*** II Latin American Congress on Bio-refineries: Materials and Energy, Concepción, Chile.
- e) 2009: ***A chromatography approach applied to the biological pretreatment of lignocelluloses in order to produce bioethanol.*** 1st EPNOE Conference "Polysaccharides as a Source of Advanced Materials", Turku, Finlandia.
- f) 2009: ***Reducing sugars yields and released glucose from Nothofagus pumilio (Poepp. et endl.) Krasser wood pieces subjected to a biological pretreatment to produce bioethanol.*** 1st EPNOE Conference "Polysaccharides as a Source of Advanced Materials", Turku, Finlandia.
- g) 2009: ***Identification and cloning of novel cellulase genes from white rot fungi.*** 14^o European Congress on Biotechnology; Symbiosis: Science Industry and Society, September 13-16 Barcelona, España. Abstract publicado en New Biotechnology, Volume 25, page 95.

- a) Virtanen, P., Mikkola, J.-P., Salmi, T., ***Kinetics of Cinnamaldehyde Hydrogenation over Supported Ionic Liquid Catalysts (SILCA)***, CHISA, Prague, Czech Rep., 2008
- b) Salmi, T., Wärnå, J., Mikkola, J.-P., Kuusisto, J., ***Detailed Kinetic Analysis Reveals the True Reaction Path: Hydrogenation, Hydrolysis and Isomerization of Lactose***, 22nd Conf. on Cat.Org.React., March 30-April 3, Richmond, Virginia, USA 2008.
- c) Aho, A., Eränen, K., Kumar, N., Salmi, T., Hupa, M., Mikkola, J.-P., Murzin, D.Yu, ***Catalytic Upgrading of Pyrolysis Vapours in a Dual-fluidized Bed Reactor***, Nordic Wood Biorefinery Conference, Stockholm, 11-14.03.2008, Sweden.
- d) Virtanen, P., Mikkola, J.-P., Salmi, T., ***Kinetics of cinnamaldehyde hydrogenation over supported ionic liquid catalysts (SILCA)***, CHISA 2008, Aug.24-28, Praha, Czech Rep.
- e) Toukoniitty, E., Mikkola, J.-P., ***Towards Next Generation Biofuels***, 1st Nordic Wood Biorefinery Conference, Stockholm, 11-14.03.2008 Sweden.
- f) Toukoniitty, B., Mikkola, J.-P., Tuuf, J.-C., Kirilin, A., D.Yu.Murzin, Salmi, T., ***Ultrasound Enhancement of Cellulose Processing in Ionic Liquids***, ESS11:European Society of Sonochemistry 11th Meeting, La Grande Motte, France, 1-5 June 2008.
- g) Eva Pongrácz, Jyri-Pekka Mikkola, Jouni Korhonen, Riitta Keiski, ***The social life-cycle of waste Evolution of perceptions of CO₂***, 14th Annual International Sustainable Research Development Conference, New Delhi, India, 21-23 Sept. 2008-10-12.

- a) Dipak Kumar Madnani, Esa Toukoniitty and Jyri-Pekka Mikkola, ***Valorization of Bioethanol to 1-butanol***, 13th Nordic Symposium on Catalysis, 5-7 October, 2008, Göteborg, Sweden.
- b) Report 333: ***Sustainable Production and Energy: Catalysis by nanomaterials, Catalytic microreactors*** COST 543 Training School, ISBN 978-951-42-8991-0; ISSN 1458-6177, Univ. of Oulu 2008.
- c) Toukoniitty, E., Kumar Madnani, D., Kordas, K., Mikkola, J.P., ***Conversion of Bioethanol to 1-Butanol – A Step Towards Sustainable Transportation Fuels***, 21st North American Catalysis Society Meeting, 7-12.6.2009, San Francisco, California, USA..
- d) Jyri-Pekka Mikkola, Jean-Christoffer Tuuf, Alexey Kirilin, Pia Damlin and Tapio Salmi, ***Ionic liquid-aided carboxymethylation of Kraft pulp***, 8th World Congress of Chemical Engineering (WCCE8), Montréal, Canada August 23 to 27, 2009 (oral talk and session chairman).
- e) S. Hyvärinen, P. Virtanen, J. Hemming, M. Reunanen, A.S. Leppänen, D. Yu. Murzin, J.-P. Mikkola, ***Ionic Liquid Fractionation of Lignocellulosics***, 2nd Nordic Wood Biorefinery Conference, Helsinki, 02-04.09.2009, Finland.
- f) V.Cortinez, S. Hyvärinen, M. Reunanen, J. Hemming, M.E. Lienqueo, D. Yu. Murzin, J.-P. Mikkola, ***Evaluation of ionic liquid mediated pretreatment for the enzymatic hydrolysis of forest residues to obtain bioethanol***, 2nd Nordic Wood Biorefinery Conference, Helsinki, 02-04.09.2009, Finland.
- g) R. Pezoa, S. Hyvärinen, M. Reunanen, J. Hemming, M.E. Lienqueo, D. Yu. Murzin, J.-P. Mikkola, ***Evaluation of ionic liquid mediated pretreatment for the enzymatic hydrolysis of forest residues to obtain bioethanol***, 2nd Nordic Wood Biorefinery Conference, Helsinki, 02-04.09.2009, Finland.

- a) P.Damlin, J.-P. Mikkola, T. Salmi, ***Characterization of softwood-derived carboxymethylcellulose by high-pH anion-exchange chromatography using pulsed amperometric detection***, 2nd Nordic Wood Biorefinery Conference, Helsinki, 02- 04.09.2009, Finland.
- b) V. Cortinez ,S. Hyvärinen, M. Reunanen, J. Hemming, D. Yu. Murzin, J.-P. Mikkola, ME. Lienqueo, ***Pretreatment with ionic liquids of Lenga (Nothofagus pumilio) and Eucalyptus (Eucalyptus nitens) residues for producción of second generation bioethanol***, XVII Congreso de Ingeniería Química,Viña del Mar, 25-28 Octubre 2009.
- c) R. Pezoa ,S. Hyvärinen, M. Reunanen, J. Hemming, D. Yu. Murzin, J.-P. Mikkola, ME. Lienqueo, ***Use of ionic liquids in the pretreatment of agronomic residues for production of second generation of bioethanol***, XVII Congreso de Ingeniería Química,Viña del Mar, 25-28 Octubre 2009.
- d) Sari Hyvärinen, P. Virtanen, S. A. Pranovich, A.-S. Leppänen, J. Hemming, M. Reunanen, Willför, D. Yu. Murzin, J.-P. Mikkola, ***Towards improved fractionation of lignocellulosics via integrated ionic liquid-thermal pretreatment The analysis challenge***, XVII Congreso de Ingeniería Química,Viña del Mar, 25-28 Octubre 2009.
- e) J. Hajek, J.-P. Mikkola, T. Salmi, ***Isomerisation of saccharides***, CHISA 2010, August, Prague, Czech Republic.
- f) T. Salmi, P. Damlin, J-P. Mikkola, M. Kangas, ***Modelling of complex liquid-solid reactions: cellulose substitution kinetics***, CHISA 2010, August, Prague, Czech Republic.
- g) T.Salmi, P.Damlin, J-P Mikkola, M.Kangas, ***Modelling of complex liquid-solid reactions: cellulose substitution kinetics***, CHISA 2010, August, Prague, Czech Republic, CHISA 2010, August, Prague, Czech Republic.

- a) J.Hajek, J-P Mikkola, T.Salmi, ***Isomerization of Saccharides***, CHISA 2010, August, Prague, Czech Republic.
- b) H. Grénman, T. Salmi, P. Fardim, J.-P. Mikkola and D. Yu. Murzin, ***Towards new applications of chemical engineering: delignification***, CHISA 2010, August, Prague, Czech Republic.
- c) Johan Ahlqvist, Ajaikumar Samikannu, Jyri-Pekka Mikkola, ***Catalytic Conversion of Lignocellulosic Materials***, CHISA 2010, August, Prague, Czech Republic.
- d) John Gräsvik, Jyri-Pekka Mikkola, ***Biomaterials Dissolution Using Green Ionic Liquids***, CHISA 2010, August, Prague, Czech Republic.
- e) Alexey Kirilin, Anton Tokarev, Dmitry Yu. Murzin and Jyri-Pekka Mikkola, ***Aqueous phase reforming of biomass derived oxygenates for selective production of hydrogen and fuel components***, COST Action 543 Second Training School, UNIVERSITY of CALABRIA, Italy, April 28-29, 2010.
- f) Toni Riittonen and Jyri-Pekka Mikkola, ***Catalytic Valorization of Bioethanol to Biobutanol***, COST Action 543 Second Training School, UNIVERSITY of CALABRIA, Italy, April 28-29, 2010.
- g) J-P Mikkola, L. Jönsson and S. Marklund, ***Bio4Energy – the Swedish quest for sustainable society, INTERNATIONAL CONFERENCE in CATALYSIS FOR RENEWABLE SOURCES: FUEL, ENERGY, CHEMICALS***, Tsars Village, St.Petersburg, June 28 – July 2, 2010 Russia (Keynote talk).
- h) Toni Riittonen and Jyri-Pekka Mikkola, ***Catalytic Valorization of Bioethanol to Biobutanol***, 1st International Conference on Materials for Energy 04.07.2010 - 08.07.2010, Karlsruhe, Germany (oral contribution).

Possible future proposals

- APOYO A LA FORMACIÓN DE REDES INTERNACIONALES ENTRE CENTROS DE INVESTIGACIÓN (CONICYT):
 - BIOCOMSA - Bioproducts Discovery & Development Centre (BDDC)- Universidad de Guelph - Forest Products Biotechnology/Bioenergy Research Group of University of British Columbia.
 - BIOCOMSA – Process Chemistry Centre, Åbo Akademi University, Turku.
- VIII CONCURSO NACIONAL DE PROYECTOS DE DESARROLLO DE RECURSOS NATURALES FUNDACIÓN COPEC - UNIVERSIDAD CATÓLICA:
 - Mejoramiento de pretratamiento de materiales lignocelulósicos para la producción de bioetanol de segunda generación: uso de líquidos iónicos y celulasas mejoradas.