Biorefinery I: Chemicals and Materials From Thermo-Chemical Biomass Conversion and Related Processes

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Conference Program and Abstracts

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Biorefinery I: Chemicals and Materials from Thermo-Chemical Biomass Conversion and Related Processes

September 27 - October 2, 2015

Crete, Greece

Conference Co-Chairs

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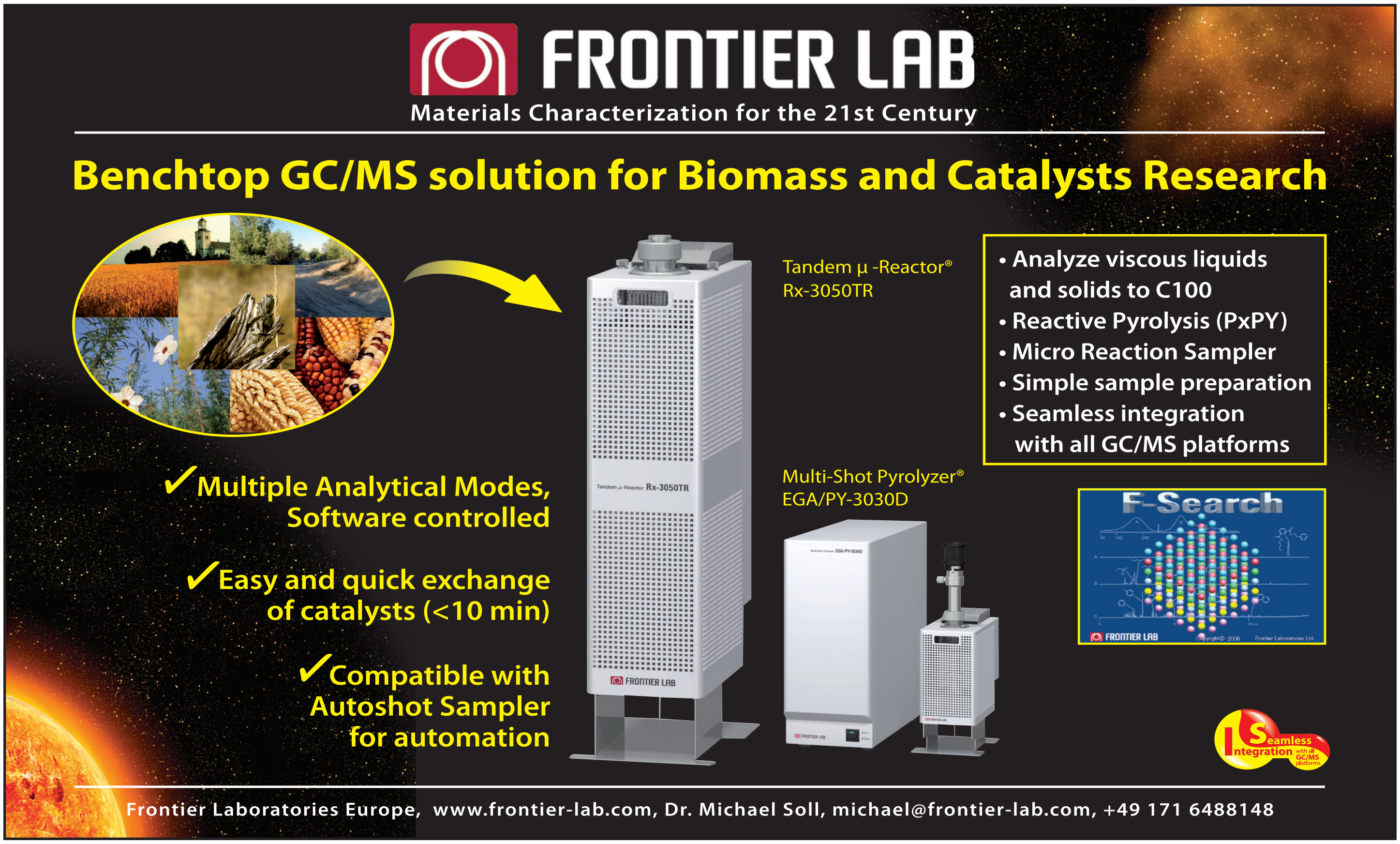

Sunday, September 27, 2015

17:00 – 18:30 Conference check-in (Rosa Conference Room Foyer)

18:30 – 19:00 Welcome Drink (Rosa Conference Room Foyer)

19:00 – 20:30 Dinner

NOTES

- Technical sessions and poster sessions will be held in the Rosa Conference Room.
- Posters can be hung on the walls of the meeting room.
- All meals, except the banquet, will be in the Artemis Restaurant. The location of the conference banquet on Thursday will be announced on site.
- Audiotaping, videotaping and photography of presentations are strictly prohibited.
- Speakers – Please leave at least 5 minutes for questions and discussion.
- Please do not smoke at any conference functions.
- Turn your cellular telephones to vibrate or off during technical sessions.
- Please write your name in the front of this booklet in case it is misplaced.
- Be sure to check the participant list in this booklet to confirm that your listing is correct. If there are changes or updates, please login to the ECI website and update your listing so that the list that ECI will send to all participants after the conference will be correct.

Monday, September 28, 2015

07:30 - 08:30	Breakfast
08:30 - 08:45	Welcome and Conference Overview Conference Chairs, ECI Liaison
	Session 1: Light oxygenates, phenols and aromatics
08:45 - 09:15	**Plenary**: Feedstocks Matter Ralph P. Overend, Nextfuels LLC
09:15 - 09:30	Pure aromatics from biomass Matti Reinikainen, VTT, Finland
09:30 - 09:45	Biomass into chemicals: Green chemical conversion of carbohydrates (fructose, sucrose and glucose) into 5-hydroxymethylfurfural in pyridinium dicationic ionic liquid Hern Kim, Myongji University, South Korea
09:45 - 10:00	Monomeric phenols from lignin - formic acid assisted hydrous liquefaction Mike Kleinert, University of Bergen, Norway
10:00 - 10:15	Structure characterization of bio-oil and solid fractions from near-critical water depolymerization of LignoBoost© Kraft lignin Cecilia Mattsson, Chalmers University of Technology/Forest Products and Chemical Engineering, Sweden
10:15 - 10:45	Coffee break/Networking
10:45 - 11:00	BIORECOVER: Biomass residues conversion and valorization for an economic refinery Paul De Wild, Energy Research Centre of the Netherlands (ECN), The Netherlands
11:00 - 11:15	Platform chemicals from biorefinery waste streams Hero Jan Heeres, University of Groningen, The Netherlands
11:15 - 11:30	Fluidized bed pyrolysis of lignocellulosic biomass: A modeling approach Ernst-Ulrich Hartge, Hamburg University of Technology, Germany
11:30 - 11:45	Catalytic pyrolysis of forestry and agricultural residual biomass for production of renewable chemicals Angelos Lappas, CPERI/CERTH, Greece
11:45 - 12:00	Olive mill wastewater biorefinery: treatment in a rhizodegradation pilot Margarita Petoussi, Technical University of Crete, Greece
12:00 - 12:15	Biodiesel from vegetable oils: Effects of feedstock composition and reaction conditions Ajay Dalai, University of Saskatchewan, Canada
12:15 - 12:30	Two-stage thermochemical conversion of lignin into aromatic chemicals Paul De Wild, Energy Research Centre of the Netherlands (ECN), The Netherlands
12:30 – 12:45	Stirred and unstirred lignin solvolysis with formic acid in aqueous or ethanolic solvents by using 5-L reactor Mike Kleinert, University of Bergen, Norway
12:45 - 14:15	Lunch
14:15 - 18:00	Free time/*ad hoc* sessions

Monday, September 28, 2015 (continued)

Sessions 2 and 3: Adhesives and lubricants / Feed / Food and Additives

18:00 – 18:15	Fungal bio-refinery of citrus wastes for pectin, chitosan, oil, and protein production Behzad Satari, Högskolan i Borås, Sweden
18:15 - 18:30	Autothermal fast pyrolysis of wood residues for wood adhesives Dongbing Li, ICFAR, Western University, Canada
18:30 - 18:45	Gasification of fructose in supercritical water for production of hydrogen enriched syngas Ajay K. Dalai, University of Saskatchewan, Canada
18:45 - 19:00	Induction heating fluidized bed reactor (IHFBR) and its applications for combustion and gasification of biomass based feedstocks Jamal Chaouki, Ecole Polytechnique of Montreal, Canada
19:00 – 19:15	Characterization and upgrading of bio-oil distillation residues into coproducts Yaseen Elkasabi, U.S. Department of Agriculture, USA
19:15 - 20:30	Dinner
20:30 - 21:30	Poster Session and Social Hour

Tuesday, September 29, 2015

07:30 - 08:30	Breakfast
	Session 4: Specialties, pharmaceuticals, fine chemicals and fibrous products
08:30 - 09:00	**Plenary**: Advanced lipid-based chemicals: renewables in the shadow of the Canadian oil sands David Bressler, University of Alberta, Canada
09:00 - 09:15	Extractive bioconversion of gamma-cyclodextrin by cyclodextrin glycosyltransferase in alcohol/salt aqueous two-phase system Tau Chuan Ling, University of Malaya. Malaysia
09:15 - 09:30	Organosolv pretreatment as a major step of lignocellulosic biomass refining Dimitrios Sidiras, University of Piraeus, Greece
09:30 - 09:45	Dehydration of glycerol to acrolein in fluidized bed reactor Marjan Dalil, Ecole Polytechnique of Montreal, Canada
09:45 - 10:00	Production of crude bio-oil and stabilizer for photosensitive materials via hydrothermal liquefaction of spent coffee grounds Quan (Sophia) He, Dalhousie University, Canada
10:00 - 10:30	Coffee Break / Networking
10:30 - 11:00	**Plenary**: A review of microwave pyrolysis of biomass and waste for energy and fuels Jamal Chaouki, Polytechnique Montreal, Canada
11:00 - 11:15	Selective hydrogenolysis of glycerol to 1, 3-propanediol in a fluidized bed Marjan Dalil, Ecole Polytechnique of Montreal, Canada
11:15 - 11:30	Upgraded production of a hydroxylactone anhydro-sugar by cellulose pyrolysis and its application in the synthesis of biologically active compounds Daniele Fabbri, University of Bologna, Italy
11:30 - 11:45	Pyrolysis of napier grass and phragmite reeds pretreated with acidic pyrolytic Water Charles Greenhalf, ICFAR, University of Western Ontario, Canada
11:45 - 12:00	Study of the presence of added-value chemical compounds in sewage sludge pyrolysis liquids: Extraction, identification and quantification Isabel Fonts, Thermochemical Processes Group - Universidad Zaragoza, Spain
12:00 - 12:15	Upgrade of flash pyrolysis condensate by esterification with higher alcohols Tim Schulzke, Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Germany
12:15 - 12:30	Sugar production via pyrolysis Roel J. M. Westerhof, University of Twente, the Netherlands
12:30 – 12:45	Upgrading of solid fast pyrolysis byproducts for material use with high value Axel Funke, Karlsruhe Institute of Technology, Germany
12:45 - 14:15	Lunch
14:15 - 17:45	Free time/*ad hoc* sessions

Tuesday, September 29, 2015 (continued)

Session 5: Synthetic fuels, charcoal (derivatives) and other commodity chemicals

17:45 – 18:00	Advanced carbonized biomass materials for biosensor applications Mauro Giorcell, Politecnico di Torino, Italy
18:00 - 18:15	Biomass fast pyrolysis: Influence of biomass nature on products yield Francis Billaud, CNRS UPR 3349, France
18:15 - 18:30	Hydrogen production from intermediate pyrolysis biochars for use in solid oxide fuel cells Anwar Sattar, Fraunhofer Institute UMSICHT, United Kingdom
18:30 - 18:45	Generation of hydrogen, methane and recovery of phosphorus from biomass Nikolaos Boukis, Karlsruhe Institute of Technology, Germany
18:45 - 19:00	Bio-hydrocarbons through catalytic pyrolysis of used cooking oils: Towards sustainable jet and road fuels Andrea Maria Rizzo, RE-CORD, Italy
19:00 - 19:15	Lignocellulosic butanol production from corn-cobs, switchgrass and phragmites Kai Gao, Western University, Canada
19:15 - 20:30	Dinner
20:30 - 21:30	Poster Session and Social Hour

Wednesday, September 30, 2015

07:30 - 08:30	Breakfast
	Session 5 (continued): Synthetic fuels, charcoal (derivatives) and other commodity chemicals
08:30 - 09:00	**Plenary**: Separation technology: Making a difference in biorefineries Anton A. Kiss, Akzo Nobel Research, Development & Innovation, Process technology SRG, The Netherlands
09:00 - 09:15	Production of activated carbons from pyrolytic biochar Franco Berruti, Western University, Canada
09:15 - 09:30	Manipulating the production of solvents versus 1,3-propanediol in *C. pasteurianum* fermentation using redox balance and pH strategies Erin Johnson, Western University, Canada
09:30 - 09:45	On-line analysis of catalytic biomass products using a high pressure tandem micro-reactor GC/MS Michael Soll, Frontier Laboratories Europe, Germany
09:45 - 10:00	Evolution of palm oil mills into bio-refineries: Technical and environmental assessment of six bio-refinery options Jesus A. Garcia, Cenipalma, Columbia
10:00 - 10:30	Coffee Break and Networking
10:30 - 10:45	Biochar from TCR-process - an option for digestate utilization and nutrient management Fabian Stenzel, Fraunhofer UMSICHT, Germany
10:45 - 11:00	Biodiesel synthesis from domestic used coking oil in Southern Europe. Evaluation of the fuel quality Theocharis Tsoutsos, Technical University of Crete, Greece
11:00 - 11:15	Modeling of pollutant adsorption on novel modified biomass as a means of seawater decontamination Dimitrios Sidiras, University of Piraeus, Greece
11:15 – 11:30	Production of biodiesel by the esterification of oleic acid while using Amberlyst 15 as catalyst Aleksander Hykkerud, Norwegian University of Life Sciences, Norway
11:30 - 12:30	Poster Session
12:30	Pick up boxed lunch
12:45 - 19:30	Depart for Excursion to Agia Sofia and Elafonissi
	Schedule 12.45 Board buses 13.25 First stop Cave of Aghia Sofia 14.00 Departure from the Cave of Aghia Sofia for Elafonissi 15.00 Arrival at Elafonissi 17.20 Departure from Elafonissi 18.20 Photo stop at the canteen after the tunnel 19.30 Arrive back at the hotel
19:45 - 21:15	Dinner

Thursday, October 1, 2015

07:30 - 09:00 Breakfast

Session 5 (continued): Synthetic fuels, charcoal (derivatives) and other commodity chemicals

09:00 - 09:30 **Plenary**: Intermediate pyrolysis as an alternative to fast pyrolysis
Andreas Hornung, Aston University (EBRI and Fraunhofer), United Kingdom

09:30 - 09:45 Carbon surface engineering for control of emission of various global atmospheric pollutants
Ajay Dalai, University of Saskatchewan, Canada

09:45 – 10:00 Biorefinery for greenhouse tomato plant residues
Mohammad M. Hossain, ICFAR-Western University, Canada

10:00 - 10:15 A review on plasma technologies applied to thermo-chemical biomass conversion
François Gitzhofer, Université de Sherbrooke, Canada

10:15 - 10:30 A new two-dimensional pyrolysis process for concentrating and separating high-value liquid products from plant biomass
Mohammad M. Hossain, ICFAR-Western University, Canada

10:30 - 11:00 Coffee Break/Networking

Session 6: Plastics and Synthetic Fuels

11:00 - 11:15 Fractionation of flash pyrolysis condensates by staged condensation
Tim Schulzke, Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Germany

11:15 - 11:30 Advanced fuels and coproducts from tail-gas reactive pyrolysis (TGRP) bio-oil
Yaseen Elkasabi, U.S. Department of Agriculture, Agricultural Research Service, USA

11:30 - 11:45 Synthetic fuels from 3- φ Fischer-Tropsch Synthesis using bio-derived gas feed and novel nanometric catalysts
Nicolas Abatzoglou, Université de Sherbrooke, Canada

11:45 - 12:00 Process concepts for conversion of sugar cane residue to value added products
Stavros Michailos, University of Manchester, United Kingdom

12:00 – 12:15 Electrical characterization of different carbon based polymer composites
Mauro Giorcelli, Politecnico di Torino, Italy

12:15 – 12:30 Castor bean cake upgrading via thermal and catalytic pyrolysis
Kostas Kalogiannis, CPERI/CERTH, Greece

12:30 - 13:45 Lunch

13:45 - 18:30 Free Time / *ad hoc* sessions

18:30 - 19:30 Poster Session and Social Hour

19:45 - 21:45 Conference Banquet

Friday, October 2, 2015

07:30 - 09:00	Breakfast
09:00 – 10:00	Roundtable Discussion Topics: Introduction: Discussion of existing examples of biorefineries in different countries -Is it possible to build and operate in a sustainable way biorefineries or only industrial units dedicated to one or a limited number of bioproducts? Justify the ‘YES’ or propose ‘Schemes’ for the ‘NO’ -List and rank the most promising chemicals (commodity, platform and specialty) that can be derived from biomass, the biomass sources (type, logistics and availability) and the best production routes.
10:00 – 10:30	Discussion, feedback, what is next, concluding remarks and closing of conference
10:30 – 11:00	Coffee Break
12:00	Lunch and departures

Abstracts

Biorefinery I: Chemicals and Materials from Thermo-Chemical Biomass Conversion and Related Processes

September 27-October 2, 2015

Crete, Greece

Engineering Conferences International

FEEDSTOCKS MATTER

Ralph P. Overend, Nextfuels LLC

Monday, September 28, 2015 Plenary

PURE AROMATICS FROM BIOMASS

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Pekka Simell, VTT Technical Research Centre of Finland Ltd

Key Words: Catalysts, BTX, Biomass, Aromatic, Syngas

New processes for the production of renewable transport fuels from biomass have been actively developed. At the same time the demand for chemicals from renewable sources has increased rapidly and there is an urgent need for alternative, preferably “green” production routes. For instance the production of bio-based pure aromatic compounds (BTX) essential to the fine chemical and pharma industry have so far been elusive. In this paper we provide a feasible and highly selective concept for their manufacture from woody biomass.

Synthesis gas (syngas) produced by biomass gasification is used as the raw material. Light aromatics formed in the gasification are separated and combined with the synthesis product. In the first synthesis step a product mixture rich in olefins and oxygenates is produced from synthesis gas over an iron catalyst promoted by silicon, copper and potassium. In the second stage, the whole product from the first step reacts further to a mixture of aromatic hydrocarbons over a ZSM-5-catalyst modified with lanthanum and zinc. The principle of the reactor setup is depicted in Figure 1. A hydrocarbon product with an exceptionally good selectivity to benzene, toluene, and xylenes is formed. Typical product composition of the aromatic fraction is illustrated in Figure 2. To our knowledge this is the first example of a process capable of producing BTX-components with such a high selectivity from biomass.

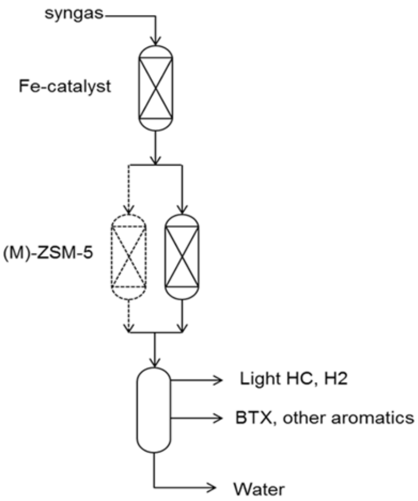

Figure 1. Reactor setup.

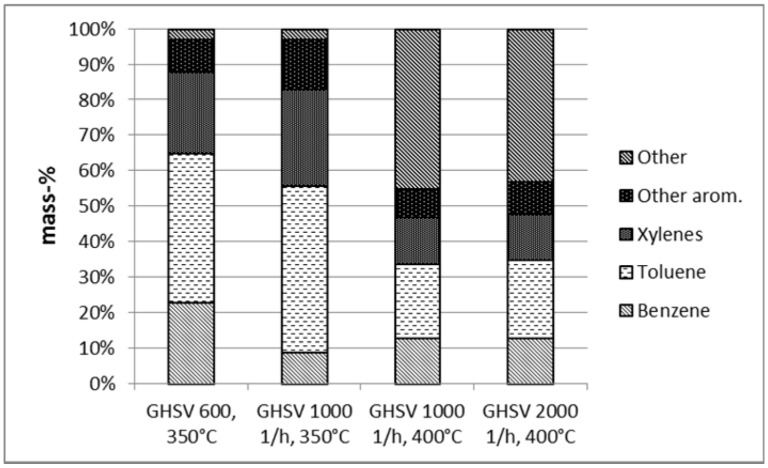

Figure 2. Product distribution.

The crude BTX-product was purified by atmospheric Vigreux distillation and crystallization. Pure BTX components could be isolated in a high purity (>80%) with over 85 % of the available benzene obtained with greater than 90 % purity with the impurity being toluene. With pure benzene and toluene having been isolated in good recovery (over 49 % of the total available product) from the BTX mixture the next step is to valorize the material into a valuable bio-based compound. For this purpose bio-paracetamol is being prepared *via* the oxidation of benzene to phenol. After this literature methods will allow for rapid development. The overall process shall be developed further to produce more benzene and thus enhance the yield further.

Aspen plus simulation tool was used to simulate the process from biomass gasification gas to pure BTX-components. Experimental activity and selectivity data was used in the selection and dimensioning of the unit operations of the process. The calculations were done for a 25 000 t/a bio-BTX plant (90 MW thermal). As a first estimate the price of bio-BTX would be about 40 % higher than that of fossil aromatics.

BIOMASS INTO CHEMICALS: GREEN CHEMICAL CONVERSION OF CARBOHYDRATES (FRUCTOSE, SUCROSE AND GLUCOSE) INTO 5-HYDROXYMETHYLFURFURAL IN PYRIDINIUM DICATIONIC IONIC LIQUID

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Keywords: pyridinium ionic liquids, sugars, 5-Hydroxymethylfurfural, dehydration, biomass conversion.

Biomass is considered to be an important renewable source for securing future energy supply, production of fine chemicals and sustainable development. There are currently a number of catalysts that are active in the dehydration of sugars to form 5-hydroxymethylfurfural (HMF). However, most of them also promote side reactions that form undesired by-products, and rehydrate HMF to form levulinic acid and formic acid. A simple and an efficient method to produce pure HMF from abundant renewable carbohydrates in high yield at low energy cost must be developed before a biorefinery platform can be built on the basis of this substrate. Demands by green chemistry, the development of new environmentally friendly solvents has created a fast-growing interest. During the past decades, design and synthesis of new multifunctional ionic liquids (ILs) attracted attention due to their interesting properties compared with traditional molecular solvents, such as undetectable vapour pressure, wide liquid temperature range special solubility for many organic or inorganic compounds, and favourable environments. In this work the dehydration of sugars has been studied with different kinds of pyridinium based dicationic ionic liquids. So far many researchers were used ionic liquid as solvent and metal chlorides or other additives as a catalyst for the conversion of sugars. However, in these reported works, the ILs mainly played a role as the solvent and was consumed in considerably large amounts. In this work, we used catalytic amount of different kinds of pyridinium dicationic ionic liquids with dimethyl sulfoxide (DMSO) and without DMSO. They have shown good performance and gave excellent yield for 5 HMF. The results strongly suggested that an ionic liquid can play an important role in exploring new efficient and easy to use processes for the production of 5 HMF. The ionic liquids used in this study will benefit many biofuel-related applications.

Acknowledgment
This study was supported by National Research Foundation of Korea (NRF) – Grants funded by the Ministry of Science, ICT and Future Planning (2014R1A2A2A01004352) and the Ministry of Education (2009-0093816), Republic of Korea.

MONOMERIC PHENOLS FROM LIGNIN – FORMIC ACID ASSISTED HYDROUS LIQUEFACTION

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Key Words: Hydrous pyrolysis, Lignin-to-Liquid, phenols, biogenic platform chemicals, derivatisation.

Lignin has long been recognised as a promising and potential source material for the production of biogenic chemicals, fine chemicals, materials, bio-fuels and fuel blending constituents due to its broad availability potential and its chemical structure. On the other hand, extensive research over a long period of time has revealed the challenges connected to lignin liquefaction. However, a thermochemical solvolytic process based on a cheap and environmental friendly solvent system consisting of formic acid (FA) and water only now provided an efficient lignin liquefaction concept.

A lignin-derived bio-liquid is formed in high yield and with excellent reproducibility and an almost quantitative material balance has been accomplished for this liquefaction process leaving behind the formerly laborious product workup procedure (Fig 1).

Qualitative analyses revealed that the produced liquid consisted of a wide variety of monomeric phenols in addition to minor amounts of a non-polar hydrocarbon fraction. The phenolic fraction could be isolated and quantified. The carbon mass balance in terms of a yield ratio “carbon of liquid product” per “carbon of lignin input” is over 70% depending on chosen feedstock and conditions.

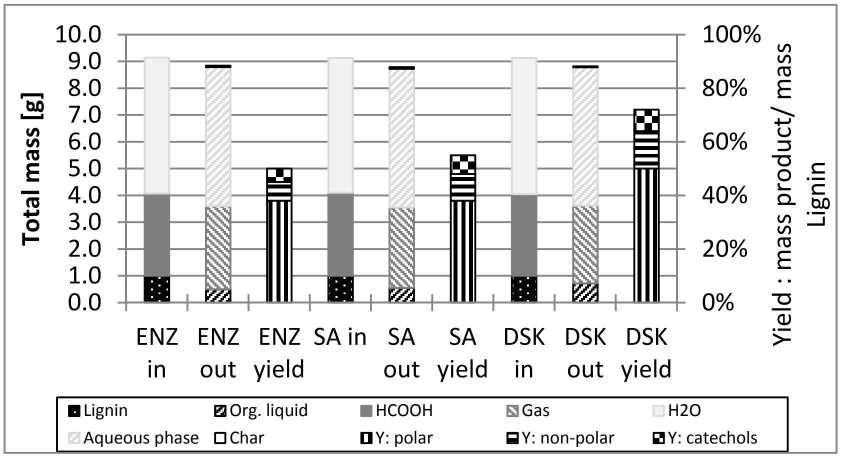

Figure 1 – Overall mass balance of LtL conversion of different industrial lignins. LtL-oil yield (Y) per lignin input reaches over 70%.

Quantitative analyses then went even deeper and were made possible by silylation of the polar phenolic hydroxyl groups with *N,O*-Bis(trimethylsilyl)trifluoroacetamide. Only by this approach a reliable and reproducible GC quantification was possible. All the relevant model compounds were prepared in the silylated form in order to be able to calibrate the system. Fig. 2 showns the selected phenols which all were of high industrial value, catechol, vanilin and propofol in particular. Accordingly, >40% of the entire LtL oil could be assigned safely.

This approach facilitates the more target-oriented research of the utilisation of world’s second largest biomass resource, lignin, towards the production of high-value platform chemicals. Design of Experiment studies towards best conversion conditions will be presented. Also, the effect of feedstock impurities such as residual carbohydrates will be addressed and an innovative consecutive Organosolv-LtL-conversion will be introduced.

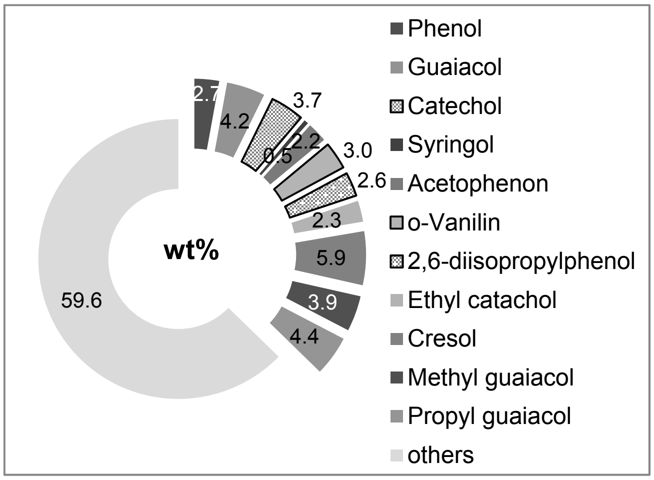

Figure 2 – Detailed quantification of selected target phenols in LtL-oil (after silylation for GC applicability).

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- M. Kleinert, J.R. Gasson, I. Eide, A.-M. Hilmen, T. Barth, *Cellulose Chem. Technol.*, **2011,** *45*, 3.
- B. Holmelid, M. Kleinert, T. Barth, *JAAP* **2012**, *98*, 37.

STRUCTURE CHARACTERIZATION OF BIO-OIL AND SOLID FRACTIONS FROM NEAR-CRITICAL WATER DEPOLYMERIZATION OF LIGNOBOOST© KRAFT LIGNIN

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Key Words: Kraft Lignin, bio-oil, 2D NMR, GPC, depolymerization

Lignin is a renewable heterogeneous aromatic biopolymer based on phenyl-propane structures which today is used mainly for generating heat. It is also an important source for generating small aromatics which further on could be used for fine chemicals or fuels. One strategy for depolymerization of the lignin is by using near-critical water with or without catalysts generating bio-oil. For a better understanding of the lignin depolymerization process structure analysis of the bio-oil is needed. This work is focused of the elucidation of the composition of the different fractions from LignoBoost© kraft lignin after base catalyzed subcritical water depolymerization. LignoBoost© kraft lignin (5.5 wt.%) from softwood was depolymerized in continues high-pressure pilot plant catalytic reactor over ZrO_2 pellets into bio-oil, water soluble organics and char in near-critical water [phenol (4.1 wt.%), K_2CO_3 (1.6 wt.%), KOH (0.2 wt.%), 350 °C, 25 MPa]. The depolymerization yielded good conversion to bio-oil and water soluble organics in 64% yield.[1, 2] The bio-oil was separated by liquid fractionation and yielded: light oil (diethyl ether soluble fraction), heavy oil (tetrahydrofuran soluble fraction) and suspended solids (insoluble residue). These different fractions were investigated further for their structural composition by gas chromatography-mass spectrometry (GC-MS), ^1H and ^{13}C nuclear magnetic resonance (NMR) and 2D NMR (heteronuclear single-quantum correlation, HSQC), molecular weight distribution by gel permeation chromatography (GPC) measurements and their elemental composition. The light oil was found to be a monomeric/dimeric fraction with low molecular weight and composed of simple phenolic like compounds *i.e.* phenol, anisole, catechol and guaiacol derivatives mainly substituted with small alkyl chains *i.e.* methyl and ethyl (GC-MS). This monomeric fraction was found both in light oil and also transported into the water phase (water soluble organics). However, the presence of unpolar compounds like polyaromatic hydrocarbons is very low or non-existent. By various NMR analysis it was confirmed that the signals from aliphatic lignin inter-unit linkages *i.e.* β-O-4', α-O-4', β-β', β-1' and β-5' has disappeared in all bio-oil fractions. This means that both aliphatic carbon-oxygen and carbon-carbon bonds in LignoBoost© kraft lignin have been broken. Another important finding was the difference in aromatic units for the different fractions. The light oil was found to be a 2.4:1 mixture of phenol and guaiacol like aromatic units. However, the heavy oil and suspended solids was found to be repolymerized polymers (5.4 kDa resp. 19.5 kDa) with new structural network based on the guaiacol/disubstituted aromatic ethers. Furthermore, all three lignin-oil fractions show new structural pattern compared with LignoBoost© kraft lignin (16.7 kDa). In the subcritical phase, deoxygenation reactions will take place and yield phenolic based bio-oil with low atomic oxygen content (15 wt.%). However, at the same time competing repolymerization reactions occur *i.e.* deoxygenation, aromatization and condensation generating suspended solids with lower H/C atomic ratio (0.70) than LignoBoost© kraft lignin (0.87). In summary, the elucidation of NMR, GC-MS and GPC studies has yielded a better understanding of the different structures of the fractionated bio-oil. It has also been confirmed that important aliphatic lignin inter-unit linkages have been broken and generated phenolic like monomers and new repolymerized polymers with low oxygen count compared to LignoBoost© kraft lignin.

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BIORECOVER: BIOMASS RESIDUES CONVERSION & VALORISATION FOR AN ECONOMIC REFINERY

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Key Words: Biorefinery, Lignin, Solvolysis, Pyrolysis, Phenols, Fuels.

Our society is unsustainable because it heavily depends on limited fossil resources for chemicals, fuels, materials and energy. Biomass is the only renewable source from which chemicals, fuels and performance materials can be made, e.g. via the biorefinery concept. Most lignocellulosic biomass consists of 60 – 70% carbohydrates that can be converted into ethanol via proven biorefining technologies while the residual content, including most of the lignin, ends up as a side stream that is nowadays mostly combusted to generate process heat. Enabling higher added value applications for these lignin-rich biorefinery residues is important to ensure better sustainability and cost efficiency of the whole biorefinery concept. However, the high recalcitrance and impurity of the residues precludes a cost-effective valorisation. In general, biorefinery residues are very heterogeneous and require tailor-made solutions for an efficient valorisation.

It is envisaged that this can be achieved via a flexible thermochemical cascade approach that progressively converts the biorefinery residue and is mainly targeted at the production of a high-quality pure lignin and/or phenolic fractions thereof with concomitant treatment of process-derived liquid and solid (waste) streams using existing technologies such as combustion in a recovery boiler and anaerobic digestion in a waste-water treatment facility. The cascading approach involves a staged process by which the lignin-rich stream is consecutively fractionated, separated, purified (e.g. by aquathermolysis, organosolv and/or other solvolysis technologies [1]) and depolymerised by fast, intermediate or slow pyrolysis methods, depending on the desired product slate. The cascading approach is flexible and can be adjusted to industry needs. E.g. when it is opportune to directly convert the recalcitrant residue into a liquid fuel, a (fast) pyrolysis might be a one-stage option. In case the residue is prone to fractionation, the extraction and purification of pure lignin for application such as a phenol-substitute in phenol-formaldehyde resins and adhesives is a two-stage possibility. Moreover, when it is also desired to produce bio-based oxygenated aromatic fuel (additives) or phenolic chemicals, dedicated pyrolysis protocols and corresponding down stream processing methods might be added as third or higher process stages. In general, lignin pyrolysis oil from pure lignin is an interesting candidate for further upgrading towards phenols and/or other oxygenated aromatics [2]. The lignin char can be deployed as a solid fuel or –depending on its characteristics- put to use for agricultural uses such as soil improvement or crop-growth enhancer.

The presentation will discuss experimental results from conversion trials with wheat straw and corn stover – derived biorefinery residues and from pyrolysis trials with pure wheat straw and corn stover lignins. Industrial application trials with residue-derived pyrolysis oils will be highlighted and an outlook will be provided of potential end-uses for the biorefinery residue conversion products and their side-streams.

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PLATFORM CHEMICALS FROM BIOREFINERY WASTE STREAMS

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Key Words: biobased chemicals, sugar beet biorefinery, sucrose, levulinic acid

The development of efficient chemical processes for biomass conversions to biobased chemicals is high on the global research agenda [1,2]. Examples of very attractive biobased chemicals are 5-hydroxymethylfurfural (HMF) and levulinic acid (LA). For instance, HMF is an excellent starting material for polymer precursors to allow the synthesis of renewable plastics (e.g. PET replacements). LA and HMF synthesis is possible by reaction of the C6 sugars in the biomass source (e.g. D-glucose and D-fructose) in water using Bronsted acids. For the development of economically viable processes, the use of a cheap feedstock is essential. Potentially very attractive feeds for both platform chemicals are intermediate streams in conventional sugar beet refineries with a high content of sucrose (thick and thin juice). Sucrose, a dimeric sugar consisting of glucose and fructose units, is known to be a good feed for LA and HMF production [2]. However, detailed kinetic studies for LA and HMF formation from sucrose are lacking, hampering process development studies and selection of optimum reactor configurations.

We here report a kinetic study on the conversion of sucrose in water using sulfuric acid (H_2SO_4) as the catalyst in a batch set-up. A total of 25 experiments were performed at T= 100–180°C with C_{H2SO4} (0.05–0.5 M) and an initial sucrose intake between 0.05–0.5 M. Glucose, fructose and 5-hydroxymethylfurfural (HMF) were detected as the intermediate products. The maximum LA yield was 65 mol% (C_{H2SO4} = 0.5 M, $C_{SUC,0}$ = 0.1 M, 140°C), the maximum HMF yield was 24 mol% (C_{H2SO4} = 0.05 M, $C_{SUC,0}$ = 0.1 M, 160°C). The experimental data were modeled using a first order approach and agreement between experiment and model was satisfactorily.

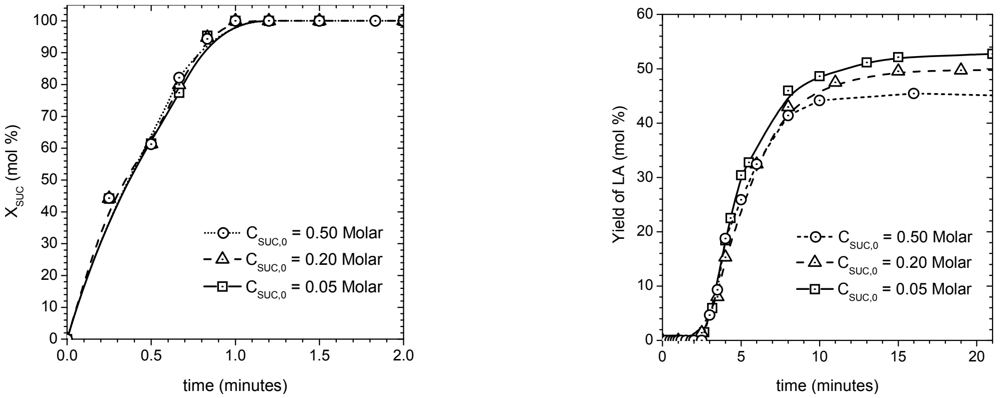

Figure 1. Conversion of sucrose (left) and yield of levulinic acid (right) at different $C_{SUC,0}$ ($C_{H_2SO_4}$*= 0.50 M, 180°C)*

The implications of these findings for further process development on LA and HMF synthesis will be discussed. In addition, the results for a representative sugar beet biorefinery stream will also be provided.

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FLUIDIZED BED PYROLYSIS OF LIGNOCELLULOSIC BIOMASS – A MODELING APPROACH

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Key Words: Lignocellulosic biomass, Pyrolysis, Fluidized bed, Modeling, CFB.

Dwindling resources necessitate a substitution of crude oil as source for many chemicals. Therefore, pyrolysis of biomass becomes a promising process for the future. In the prospect of achieving high liquid product yields, fluidized bed reactors are a choice. However, the large variation of biomass composition is a major issue, which makes it hard to predict process performance. Therefore, the authors suggest a fluidized bed model for lignocellulosic biomass pyrolysis – considering separately cellulose, hemicellulose and lignin.

The fluid dynamics of the fluidized bed are described by a two-phase dense bottom zone and a gas solid suspension in the upper part of the fluidized bed. In the bottom bed a suspension phase with high solids concentrations coexist with a solids free bubble phase. The mass transfer of gaseous components between the phases is implemented. The gas flow is described as plug flow through bubble and suspension phases, respectively. The solids are assumed to be ideally mixed. The freeboard is modeled as a suspension with decreasing solids concentration with height. Here, plug flow is assumed for both gas and solids. *(Werther and Hartge, 2004)*

The reactions are modeled according to a kinetic scheme of *Miller and Bellan (1997).* It combines the reactions for cellulose, hemicellulose and lignin proportionately to their content in the fed biomass. The scheme is composed of primary reactions from biomass to solid, liquid and gaseous products, with subsequent secondary reactions from oil to gas.

Validation of the model is carried out by comparing the yield of diverse fluidized bed biomass pyrolysis reactors and lignocellulosic feedstock with the model yield: 1) Circulating fluidized bed pyrolysis of lignin (authors' group), 2) Circulating fluidized bed pyrolysis of pine wood by *Boukis et al (2007)*, 3) Bubbling fluidized bed pyrolysis of a) wheat straw, b) aspen wood and c) maple wood by *Scott and Piskorz (1984)*. In this broad range of operating conditions (e.g. superficial velocities in the range of 0.5 to 5 m/s, wide feedstock variety) the yields calculated by the model are in good agreement with the experimental data.

Exemplary, for the pyrolysis of aspen wood in a bubbling fluidized bed, the comparison of model conversion and oil, char and gas yields with the experimental data of *Scott and Piskorz (1984)* is shown in *Figure 1*.

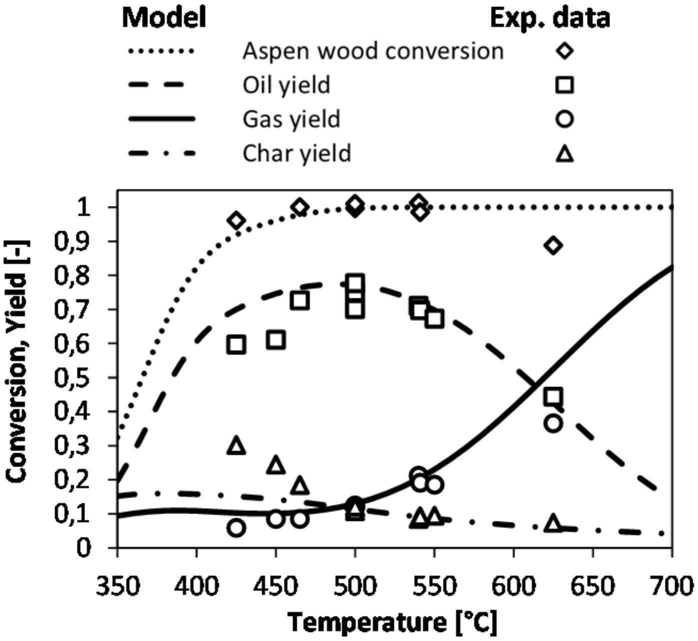

Figure 1 – Model conversion and char, gas and oil yields in comparison with experimental data (Scott and Piskorz, 1984).

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CATALYTIC PYROLYSIS OF FORESTRY AND AGRICULTURAL RESIDUAL BIOMASS FOR PRODUCTION OF RENEWABLE CHEMICALS

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Key Words: Biomass Catalytic pyrolysis, agricultural residues, ZSM-5, phenols, aromatic hydrocarbons.

The biomass catalytic pyrolysis process produces an energy carrier (catalytic pyrolysis oil-CPO) that can be used as bio-crude in a refinery for further upgrading towards production of transportation fuels. The use of CPO as a source of renewable chemicals has also gained significant attention the last years. The properties of the CPO and its chemical composition depend on several parameters among which the most important are considered to be the catalyst type, the feedstock and the process conditions. In the frame of the EU FP7 BioBoost project, an in depth analysis of the production process of the CPO, with the technology of the circulated fluidized bed, has been performed taking into account the overall process yield, the deoxygenation degree and CPO quality. Details of the technology can be found elsewhere [1]. To this end, different catalysts and feedstocks were tested and the produced CPOs were chromatographically characterized via advanced techniques such as GC-MS and 2DGC-TOFMS.

Catalyst selection proved to be the most important parameter in controlling both the efficiency of the process towards CPO production and achieving high selectivities towards specific chemical groups such as aromatic hydrocarbons (AH) and phenols. The catalysts used were both novel materials, produced during the Bioboost project and commercially available samples. The catalysts differed significantly in their main parameters such as type of active component (Y or ZSM-5 zeolites), surface area, matrix type etc. The CPO produced from all these catalysts were quantitatively analyzed based on 2DGC-TOFMS. The main focus was on the identification of aromatics and phenolics compounds.

Catalysts based on UCY zeolite appear to promote the formation of phenols since phenol and cresols, are among the primary compounds, instead of aromatic compounds. On the other hand catalysts based on silica resulted in a bio-oil rich in furfural and cyclopentanone derivatives. The ZSM-5 based catalysts resulted in CPO with increased aromatic and polyaromatic hydrocarbons content while phenolic compounds are produced as well. The aromatic compounds with the highest concentration are p-xylene, toluene and 1,2,3-trimethylbenzene. The phenolic compounds produced at higher concentration are phenol and cresols.

The effect of biomass type on chemical composition of biomass was also studied. Two types of biomass (woody vs. agricultural residue) were tested with the same catalyst and the CPOs were fully analyzed. Although the different biomass type affects strongly the yield of the pyrolysis products the composition of the CPO is not significantly affected. It seems that catalyst has more effect on the production of chemicals in biomass catalytic pyrolysis rather than the biomass type.

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OLIVE MILL WASTEWATER BIOREFINERY: TREATMENT IN A RHIZODEGRADATION PILOT

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Key Words: Olive mill wastewater, Rhizodegradation, Modeling, Antioxidants

Olive mill wastewater (OMW) constitutes an important environmental problem, especially in Mediterranean countries, where enormous quantities of the order of 30×10^6 m^3 are produced every year in short periods of time. OMW is considered phytotoxic due to the high concentration of phenolic compounds. However, OMW should also be regarded as a precious resource for the recovery of useful, added-value chemicals after either direct recovery or chemical/ biological transformation. More specifically, the presence of significant concentrations of high priced antioxidants, tyrosol and hydroxytyrosol in OMW, makes the latter an important resource.

From a biorefinery point of view, we have developed an integrated approach based on (1) use of self-cleaning filter to remove solids in OMW, (2) removal of antioxidants from OMW, (3) phytoremediation of the antioxidant-free wastewater with biomass production, (4) reuse of treated wastewater in irrigation.

In this presentation we focus on step #3 where the OMW is treated in a rhizodegradation pilot.

A pilot unit containing three *Tamarix Parviflora* plants has been operated over a period of 12 months treating OMW of various strengths (ranging from 1,000 to 50,000 mg/L COD). Several experimental runs have been conducted and the dynamics of the OMW degradation process have been monitored by frequent sampling and chemical analysis. Subsequently, the dynamics of the process have been modeled with MATLAB.

Experimental data indicate that the process is very effective and a COD reduction of the order of 98% can be accomplished within a period of 28 days when the starting concentration of COD is 10,000 mg/L. These runs were performed without removing the polyphenols from the wastewater. This is a more stringent test of the efficacy of the treatment method, as it can also be used directly without the antioxidant removal step.

Hence, the proposed treatment method can be employed also as a low cost method for the treatment of OMW with the additional benefit of biomass production.

BIODIESEL FROM VEGETABLE OILS: EFFECTS OF FEEDSTOCK COMPOSITION AND REACTION CONDITIONS

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Biodiesel has achieved worldwide recognition for many years due to its renewability, lubricating property, and environmental benefits. Biodiesel is produced from triglycerides (major constituents of oils or fats) through transesterification or from free fatty acids through esterification. Vegetable oils may vary in compositions depending on the species, geographic locations and weather conditions. To find out the effects of feedstock compositions and reaction conditions data mining method is used. Data mining is the branch of computer science used to extract useful information or knowledge which is very difficult to observe. The estimation methods are used to capture the general trends or to make predictions. Artificial Neural Networks (ANN) is among the most-effective tools for estimation. In this study, the data mining technique was utilized for the first time to find out the effects of feedstock composition and reaction conditions variation on biodiesel production process. For data mining purposes, feedstock (vegetable oil) structures are converted in some sort of common mathematical formulation. Based on the converted mathematical data an Artificial Neural Network (ANN) is built and STATISTICA 12 data mining toolbox is used for this purpose. A multi-layer perceptron (MLP) with feed-forward back propagation method was used to correlate the inputs and outputs. The optimal MLP structure obtained was with three layers: the first layer with 16 inputs, the second layer with 16 hidden units and the third layer with 2 outputs. The study reveals that the vegetable oil carbon chain length, degree of unsaturation, along with the reaction conditions affect the biodiesel production process. The model is developed in such extent that it can predict the effects of composition of a new feedstock and reaction conditions.

TWO-STAGE THERMOCHEMICAL CONVERSION OF LIGNIN INTO AROMATIC CHEMICALS

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Key Words: Bio-based industries, Lignin, Pyrolysis, Hydrodeoxygenation, Aromatic chemicals, Phenols.

Bio-based industries such as the pulp- and paper sector and lignocellulosic biorefineries (will) generate vast amounts of lignin as their largest side-stream. To date, this stream is mostly regarded as waste that is combusted for the generation of process heat. This is a waste of money, because as a phenolic biopolymer, lignin should be exploited as a source for valuable aromatic chemicals, thereby enhancing the profitability of sustainable bio-based industries [1]. Unfortunately, lignin is a very heterogeneous material which makes a direct commercial application cumbersome. Also, conversion into (precursors for) value added products is difficult. There is ample need for cost-effective technology to better exploit lignin's potential. Industrial lignins are highly variable in composition because they originate from different types of biomass feeds and fractionation technologies. Examples are Kraft, soda, organosolv and hydrolysis lignins. Especially, organosolv lignin seems an interesting candidate for valorisation as aromatics because of its high purity (i.e., low in residual carbohydrates and ash).

The purpose of this work is to explore the potential of a two-stage conversion as a versatile method to thermochemically produce value-added aromatics from lignin. First, lignin is (partially) depolymerised by a relatively simple and cost-effective pyrolysis technique into a lignin pyrolysis oil (LPO) that consists of a mixture of mono- and oligophenolic fragments. In the next step, the LPO is further processed by dedicated catalytic hydrodeoxygenation (HDO), possibly requiring less severe conditions when compared to the direct HDO of the original lignin [2].

At ECN, a (catalytic) pyrolysis approach has been developed to effectively pyrolyse any type of lignin into a phenolic bio-oil and biochar using a specific clay additive in combination with appropriate feeding, pyrolysis and product recovery protocols. The process can be operated continuously and performs robust and flexible with respect to the specific lignin type. RUG has developed (continuous) catalytic HDO technology to convert lignin and LPO into aromatic chemicals. Catalytic HDO is a promising technology that offers a flexible route to hydrotreat lignin to aromatic chemicals in relatively high yields. To enhance the cost-effectiveness of the HDO technology, current research focuses on process optimisations such as (the development of efficient) continuous operation, catalyst activity, stability and regenerability.

Clay-promoted Kraft softwood lignin, soda wheat straw lignin, organosolv poplar, wheat straw and spruce lignins were pyrolysed at 450°C in a bubbling fluidised bed reactor system and the resulting lignin pyrolysis oil samples were hydrodeoxygenated. Pyrolysis of the lignins typically yielded 50% of a liquid phenolic fraction, 35% biochar and 15% combustible gas. The Kraft, soda wheat straw, organosolv poplar, straw and spruce LPO samples as well as their corresponding lignins were hydrodeoxygenated in a batch-type autoclave reactor system at 350 °C, 100 bar hydrogen initial intake and a $NiMo/Al_2O_3$ catalyst. HDO of the organic part of the lignin pyrolysis oils yielded primarily alkylated phenolics (21 wt% on lignin oil intake) and aromatics (6 wt% on lignin intake) with a very low solid formation (< 3 wt% on lignin oil intake). In comparison with the direct HDO-route, starting with the solid lignin, it appears that using a 2-stage system leads to higher amount of alkylated phenolics (21 wt% vs. 10 wt% for the direct HDO route) and produces lower amounts of solids (3 wt% vs. 21 wt%). The proof – of – concept for the 2-stage production of value-added aromatic chemicals via the pyrolysis – HDO route was achieved for various lignin types.
The presentation will address the pyrolysis results for Kraft lignin, soda lignin and three organosolv lignin varieties as well as the intricacies of the combination lignin pyrolysis – lignin pyrolysis oil recovery – lignin pyrolysis oil hydrotreating. Finally, the techno-economic implications of the incorporation of the 2-stage process lignin pyrolysis – hydrodeoxygenation in a lignocellulose biorefinery will be discussed.

This research has been performed within the CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science.

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STIRRED AND UNSTIRRED LIGNIN SOLVOLYSIS WITH FORMIC ACID IN AQUEOUS OR ETHANOLIC SOLVENTS BY USING 5-L REACTOR

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Work objective: Lignin is a low-cost renewable by-product from paper- and pulp and bio-ethanol production which has a high potential for further development as a raw material. Previously, we have developed a solvolytic conversion process with formic acid as a hydrogen donor where lignin is hydrodeoxygenated in a one-step conversion to low molecular weight bio-oils. The thermal decomposition of formic acid gives active hydrogen species that are more reactive than molecular hydrogen at the same conditions. The resulting product is a bio-oil which is a mixture of monomeric phenols and more hydrogenated products. Ongoing research is addressing the upscaling of the process and testing of the final products. We will report results from lignin solvolysis in a 5-L stirred and unstirred batch reactor.

Methodology: Lignin conversion is performed at 320-350 ºC in aqueous or ethanolic solvents. Different levels of loading in the reactor have been tested under stirred and unstirred conditions. Mass and elemental composition balance data for oil and coke yields relative to the input of lignin and formic acid are determined. Experimental designs are used to systematically explore the relationship between the oil and coke yields and the reaction conditions.

Results: Oil yields differ with type of the solvent, stirred condition and operating temperature. Overall, ethanolic solvent together with high level of loading in the reactor result in highest oil yield. More than 40% weight of the lignin can be directly recovered as oil at 320 °C by using stirring, regardless of solvent type. The increased oil yield can be because of the efficient stirring and/or higher operating pressure when higher level of the reactor is loaded. Compositional data for the bio-oil will also be presented and discussed in the perspective of identifying value-added products. Multivariate statistical models based on the experimental designs provide equations describing the relationship between the reaction conditions and the oil yields.

FUNGAL BIO-REFINERY OF CITRUS WASTES FOR PECTIN, CHITOSAN, OIL, AND PROTEIN PRODUCTION

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Key Words: Chitosan; enzymatic hydrolysis; *Mucor indicus*; oil; orange wastes; pectin; protein; *Rhizopus oryzae*.

In this study, orange wastes (OWs) from Brämhults Juice AB in Sweden were used for the production of pectin as well as fungal chitosan, oil, and proteins. The performance of two stains of zygomycetes fungi, i.e., *Mucor indicus* and *Rhizopus oryzae*, were compared in this biorefinery. Free sugars were extracted from OWs and the sugar free solid residue was utilized for pectin production. Pectin was extracted from this residue using hot dilute nitric acid. At the best obtained conditions (pH 1.8, 80 ºC, and 2 h), 45.5 % pectin (based on dry weight of the residue) was obtained. The free sugars solution was used for the fermentation of the fungi in an airlift bioreactor without supplementation of any extra nutrient. Biomass yields of 0.28 and 0.25 g/g consumed sugars were obtained for *R. oryzae* and *M. indicus*, respectively. Chitosan, oil, and proteins were the valuable ingredients of the obtained fungal biomass, (in correspond averages 180, 70, and 455 mg/g biomass). The remaining pectin-free residue of citrus wastes was hydrolyzed enzymatically and the liberated sugars were fermented by the fungi. On average, 180, 8, 3, and 16 g pectin, chitosan, oil, and protein was obtained from each kg of the orange wastes (based on dry weight), respectively.

AUTOTHERMAL FAST PYROLYSIS OF WOOD RESIDUES FOR WOOD ADHESIVES

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Key Words: Fast pyrolysis, autothermal operation, dry bio-oil, phenol formaldehyde resin, wood adhesive.

Autothermal fast pyrolysis of wood residues with a high lignin content, such as hydrolysis lignin, Kraft lignin, birch bark and birch wood, provides oils that can be substituted for phenol in phenol-formaldehyde resins. Fast pyrolysis was performed in a dedicated fluidized bed pyrolyzer that incorporated two crucial innovations. A fractional condensation train provided dry bio-oils with ~1 % of moisture and much reduced acidity. Autothermal pyrolysis with partial oxidation reduces operating and capital costs, as well as increasing the quality of the dry bio-oil. With autothermal pyrolysis, external heating is not required, which simplifies the reactor design and reduces energy costs. Autothermal pyrolysis provides a dry bio-oil with lower acidity, reduced pyrolytic lignin and a higher concentration of the desirable, low molecular weight phenolics. The dry bio-oil yields were 31 wt% and 29 wt% for birch bark and Kraft lignin, respectively. Dry bio-oil obtained from autothermal fast pyrolysis of hydrolysis lignin, birch bark or birch wood can be used to substitute up to 65 % of phenol in reacting with formaldehyde to produce wood adhesives that met the ASTM standards, including the boil test. With dry bio-oil from Kraft lignin, the substitution level can be as high as 80 % (Figure 1). The mechanical strength of the bonded plywood is affected by the phenol substitution ratio and total phenolics content of the dry bio-oil. Results are summarized in Table 1.

Figure 1 – Plywood panels bonded with adhesive made with dry bio-oil from Kraft lignin pyrolysis.

Biomass	Bed material	Autothermal operation?	Mechanical shear strength (MPa)					
			Bio-oil subst.: 50 %		**Bio-oil subst.: 65 %**		**Bio-oil subst.: 80 %**	
			Dry test	Boil test	Dry test	Boil test	Dry test	Boil test
Birch wood	Sand	N	1.5	1.6	1.3	1.6	Failed	Failed
Birch wood	Sand	Y	1.5	1.4	1.3	1.7	Failed	Failed
Birch bark	Sand	N	1.8	1.5				
Birch bark	Sand	Y	1.9	1.4				
Hydrolysis lignin	Sand	N	1.7	1.8				
Hydrolysis lignin	Sand	Y	1.9	1.8				
Kraft lignin	Lignin char	Y	2.0	2.5	1.9	2.0	1.4	1.5

* Pure phenol with 0 % of bio-oil substition: 3.6 MPa (dry), 3.1 MPa (boiled)

Table 1 – Summary of results

GASIFICATION OF FRUCTOSE IN SUPERCRITICAL WATER FOR PRODUCTION OF HYDROGEN ENRICHED SYNGAS

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Key Words: Fructose, supercritical water gasification, hydrogen, alkali catalyst, parametric study.

The experimental impacts of climate change via increased greenhouse gas emissions and overwhelming usage of fossil fuels are global. Substantial amounts of waste food are obtained globally that, via landfill, contribute majorly to the production of greenhouse gases such as CO_2 and CH_4. Currently, waste food materials are tossed in landfill for composting or anaerobic digestion to produce CH_4. Fructose is a ketonic monosaccharide predominantly found in fruits, berries and vegetables. Supercritical water (temperature > 374°C and pressure > 22.1 MPa) has found several applications in lignocellulosic biomass gasification for syngas production. With this objective of waste food conversion to biofuels, supercritical water gasification of fructose (as a model sugar compound for waste fruits/vegetables) was performed in this study. Different parameters influencing gasification of fructose were investigated that include temperature, feed concentration and residence time and catalyst concentration. The alkali-based homogenous catalysts, i.e. KOH and NaOH were employed in catalytic gasification of fructose for comparative evaluation of syngas yield and composition.

Fructose as a model sugar compound of fruits/vegetables was used as the feedstock in supercritical gasification in a custom-built continuous-flow stainless steel tubular reactor. The gasification apparatus consisted of feed pump, preheater, tubular flow reactor, water-cooled tube, filter, back-pressure regulator, gas-liquid separator, pressure gauges and thermocouples. Supercritical water gasification was performed at 25 MPa to study the impacts of temperature (550-700°C), feed (fructose) concentration (4-10 wt%) and residence time (30-75 s). Homogenous catalysts such as KOH and NaOH at varying concentrations (0.2-0.8 wt%) were used to relatively examine their impacts on syngas yield and composition. The gases were analyzed in an Agilent 7820A gas chromatography with TCD detector including three packed columns and one capillary column.

The effects of temperature, feed concentration and residence time were investigated for maximum gas yields for fructose gasification. Total gas yields, carbon gasification efficiency and maximum H_2 yields were recorded at the optimal temperature, feed concentration and residence time of 700°C, 4 wt% and 60 s, respectively. The total gas yield from fructose gasification was higher at 700°C (1.04 L/g of fructose) compared to that at 550°C (0.2 g/L of fructose). However, addition of alkali catalysts such as KOH and NaOH enriched the total gas yields to 2.01 L/g and 1.9 L/g, respectively. The H_2 yield at 700°C (3.4 mol/mol of fructose) was higher than that at 550°C (0.3 mol/mol of fructose). Lower feed concentration (4 wt% fructose) resulted in greater total gas yields of 1.04 L/g compared to that of 10 wt% fructose (0.8 L/g). Furthermore, 30 s of residence time resulted in lower total gas yields (0.4 L/g) compared to that at 60 s (1.05 L/g).

With the increase in catalyst concentration from 0.2 to 0.8 wt%, there was an increase in total gas yields and concentrations of H_2, CO_2 and CH_4. Maximum H_2 yields of 10.7 and 9.9 mol/mol of fructose were obtained with the addition of 0.8 wt% of KOH and NaOH, respectively. The increase in H_2 yield by alkali catalyst addition was due to enhanced water-gas shift reaction. In the non-catalytic gasification of fructose, the lower heating value (LHV) of syngas was higher at 700°C (2482 KJ/m^3) compared to that at 550°C (1281 KJ/m^3). However, the LHV of syngas generated at 700°C, 4 wt% fructose with 0.8 wt% KOH was greater (3630 KJ/m^3) than that of 0.8 wt% NaOH (3576 KJ/m^3).

Due to high carbohydrate content in waste fruits/vegetables, their gasification in supercritical water could potentially yield H_2-rich syngas and eliminate the cost of feedstock drying and pretreatment. KOH appears to be a promising catalyst in fructose gasification by enhancing the selectivity for H_2. Catalytic gasification has tremendous prospects to generate syngas from waste fruits and vegetables or discarded fruit-derived beverages. This process could supplement the increasing energy demand by producing H_2-rich syngas from waste fruits instead of emitting greenhouse gas CH_4 through their anaerobic digestion.

INDUCTION HEATING FLUIDIZED BED REACTOR (IHFBR) AND ITS APPLICATIONS FOR COMBUSTION AND GASIFICATION OF BIOMASS BASED FEEDSTOCKS

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Key Words: Biomass, Gasification and Combustion

The Induction Heating Fluidized Bed Reactor (IHFBR) was designed for screening the solid feedstocks with different formulations in high temperature reactions such as gasification and combustion.

Unique design of the reactor, despite conventional mini reactors, help mimic real scenario of solid feeding in industrial reactors: cold feedstock is injected within one second from a lift tube, then particles reach reaction temperature in less than 5 seconds in a reaction zone. The lift tube (9.5 cm diameter) is also gas distributor of the fluidized bed (2.5 cm diameter) so that the bed is completely fluidized with uniform gas distribution.

The IHFBR operates semi batch-wise, by which a complete test would be done within a few minutes; therefore, many tests for different feedstock samples can be performed over a short period of time while a considerable amount of time and cost is saved.

Biomass is a solid feedstock that has gained a significant attraction to be used an alternative fuel and renewable energy resource because of its oxygenated molecules and its low content of elements such as sulfur and nitrogen. Thermochemical conversion of biomass has been investigated extensively for production of liquid and gaseous products. However, since it comes from a variety of sources such as forestry and agricultural residues as well as municipal waste and the fact that formulation of biomass is very dependent on its primary source, operating conditions of the thermochemical process should vary for each biomass.

Fluidized bed reactors have been promising reactors for biomass thermochemical conversion. The IHFBR was utilized to investigate conversion of diverse biomass samples through gasification and combustion. Promising results were obtained that prove capability of the IHFBR for quick and reliable screening tests. In addition, it was discovered that the IHFBR could facilitate prediction of defluidization state, which is a common challenge in biomass thermochemical processes.

CHARACTERIZATION AND UPGRADING OF BIO-OIL DISTILLATION RESIDUES INTO COPRODUCTS

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Key Words: pyrolysis, bio-oil, distillation, coke

Renewable alternatives to petroleum-based co-products must be pursued for sustainability and environmental reasons. Fast pyrolysis of biomass generates bio-oil amenable to distillation and/or hydrotreatment into liquid hydrocarbons. Biorefineries must add value through parallel generation of co-products. We will present our most recent results from our utilization of bio-oil distillation residues. We distilled bio-oil (>380 ^{o}C) and characterized the residues with FTIR, elemental analysis, NMR, temperature programmed oxidation (TPO), and Py-GC-MS methods. Except for their high molecular weight, distillate bottoms are structurally similar to their representative bio-oils. Py-GC-MS experiments provided yields of specific compounds produced, char yield, and structural units present in the residuum. It was found that bio-oil residues from tail-gas reactive pyrolysis (TGRP)[1] produced valuable compounds like phenols and paraffins under py-GC-MS conditions.

As an application, distillate bottoms were subjected to devolatilizaiton and calcination at 1200 ^{o}C for >1 hr under N_2 atmosphere to produce calcined coke. The dry calcined product contained 96 – 99% carbon, trace sulfur (< 500 ppm), and contained 0.2 – 1.1% ash. Critical metals which often contaminate calcined coke anodes were found to be either in trace amounts (Ca, Na, K) or completely undetected (Ni, V). Gradual increases in crystallite size in certain cases were detected with XRD, for both devolatilization and calcination. FTIR spectroscopy showed a loss of functional groups after calcination, except two broad peaks representing C-C and C-O. TPO of the bottoms before and after calcination illustrates an increasing structural order via the increasing temperature(s) necessary to oxidize the samples. Bubbly morphologies similar to sponge coke were visualized with scanning electron microscopy (SEM). The electrical resistivity of calcined coke samples measured to be < 1.6 mΩ-m, which closely falls in line with specifications for carbon anodes. Biorenewable calcined coke is a valuable alternative to petroleum coke and can find application in carbon anodes, steel carburization, and graphite synthesis.

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ADVANCED LIPID-BASED CHEMICALS: RENEWABLES IN THE SHADOW OF THE CANADIAN OIL SANDS

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EXTRACTIVE BIOCONVERSION OF GAMMA-CYCLODEXTRIN GLYCOSYLTRANSFERASE IN ALCOHOL/SALT AQUEOS TWO-PHASE SYSTEM

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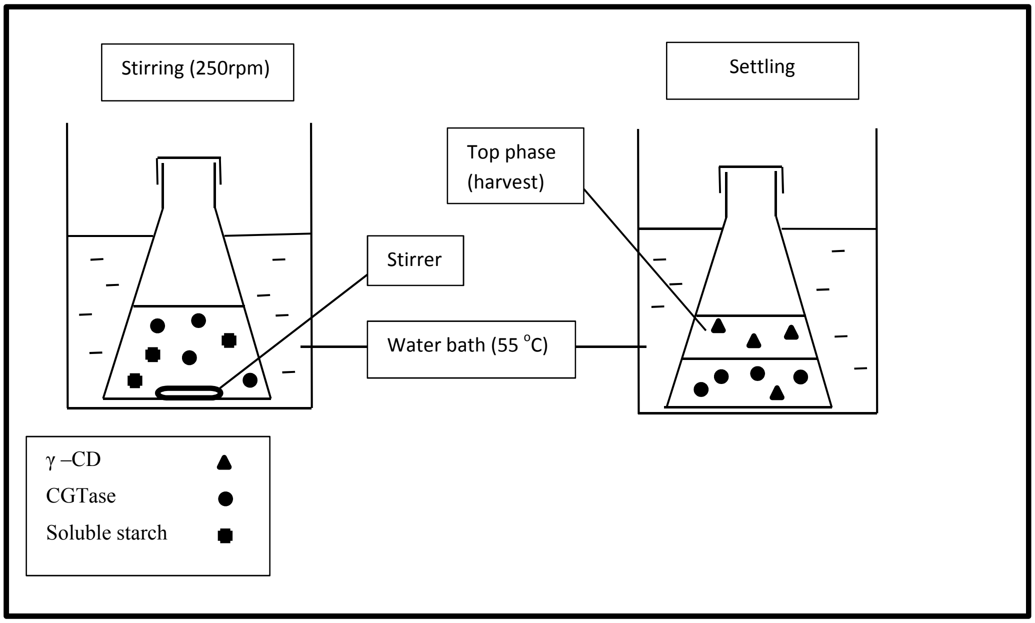
Key Words: aqueous two-phase system, extractive bioconversion, cyclodextrin, *Bacillus cereus*, cyclodextrin glycosyltransferease.

In this study, extractive bioconversion of gamma-cyclodextrin (γ-CD) from soluble starch with *Bacillus cereus* cyclodextrin glycosyltransferase (CGTase, EC 2.4.1.19) was performed in alcohol/potassium phosphate aqueous two-phase system (ATPS). The influences of alcohol-based top phase (ethanol, 1-propanol and 2-propanol) on CGTase bioactivity were investigated. The result showed that the optimum condition was achieved in ATPS composed of 24.0% (w/w) ethanol and 20.0% (w/w) potassium phosphate with 3.0% (w/w) sodium chloride. It demonstrated that the γ-CD was primarily partitioned to the top phase and the CGTase remained at salt-rich bottom phase of the ATPS. The result indicated that a relatively high concentration of γ-CD (2.28 mg/mL) was recovered in the top phase of ethanol/potassium phosphate ATPS after 1 hour bioconversion operation. Continuous repetitive batch (three times) bioconversion of soluble starch was performed successfully.



ORGANOSOLV PRETREATMENT AS A MAJOR STEP OF LIGNOCELLULOSIC BIOMASS REFINING

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Key Words: Organosolv, fractionation, delignification, lignocellulosic biomass.

The development of biorefineries from lignocellulosic biomass is expected to be an alternative to current reliance on non-renewable resources like carbon, crude oil and natural gas. Renewable lignocellulosic biomass can be utilized to produce biofuels and biochemicals. In order to make these biobased products more cost-competitive with fossil-derived conventional commodities, organosolv pretreatment of lignocellulosic biomass can become a key process involved in bioconversion of carbohydrates to inexpensive sugars (e.g. for ethanol production), adsorbent materials (as low-cost activated carbon substitutes) and pulp fibers (for the paper industry).

The key components of lignocellulosic biomass, i.e., cellulose, hemicelluloses and lignin, are closely associated with each other at the plant cell level. This close association, together with the partly crystalline nature of cellulose, reduces cellulose reactivity towards acid and enzymatic hydrolysis in native biomass. Thus, organosolv pretreatment is necessary to render the carbohydrate fraction to acid, enzymatic and microbial action.

Organosolv delignification was initially studied as a novel environmental-friendly method of producing chemical pulps for paper manufacture with substantially reduced capital costs compared with those for conventional processes. Moreover, this method has generated interest as a pretreatment of lignocellulosic raw materials to increase the hydrolysability of the cellulosic components to sugars.

Treatment with organic solvents involves the use of an organic liquid (e.g., methanol, ethanol, butanol, acetone, ethylene glycol, diethylene glycol, triethylene glycol etc.) and water, with or without addition of a catalyst agent (acid or base). This mixture partially hydrolyzes lignin bonds and lignin–carbohydrate bonds, resulting in a solid residue composed mainly by cellulose and some hemicellulose. Organosolv pretreatment efficiently removes lignin from lignocellulosic materials but most of the hemicellulose sugars are also solubilized by this process.

Moreover, a combined use of organosolv process with a previous stage of dilute-acid hydrolysis, separates hemicelluloses and lignin in two consecutive fractionation steps. Organosolv pretreatment produces a large amount of a high-quality lignin that is relatively pure, primarily unaltered, and less condensed than Kraft lignins. Such lignin is partially soluble in many organic solvents and could be applied in the fields of adhesives, films and biodegradable polymers.

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DEHYDRATION OF GLYCEROL TO ACROLEIN IN A FLUIDIZED BED REACTOR

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Keywords: Dehydration, Glycerol, Acrolein, WO_3/TiO_2, Fluidized bed

Acrolein is a valuable chemical that can be produced by the dehydration of glycerol. The value of glycerol, as the main co-product in the process of biodiesel synthesis, has dropped considerably due to a rapid increase in biodiesel production and a lack of market for such an enormous production capacity. Therefore, the dehydration of glycerol to acrolein is one of many reactions under development, which aims to convert low cost feedstock to more valuable products. Catalyst deactivation, on the other hand, which is caused by coke formation on the surface, is a serious issue for the commercialization of this process. In the case of glycerol dehydration, although acidic sites help to enhance the acrolein selectivity, they also accelerate catalyst deactivation. Acrolein could be a source of carbon build-up, as well.

Currently acrolein is produced in a single step oxidation of propylene in the presence of Bi/Mo catalyst. Most of the acrolein then converts to acrylic acid via another oxidation step in a fixed bed reactor. Replacing propylene with a bio-feedstock has been a priority for many industries due to a concern for the environment, high propylene prices and supply uncertainty as well as the low price of glycerol.

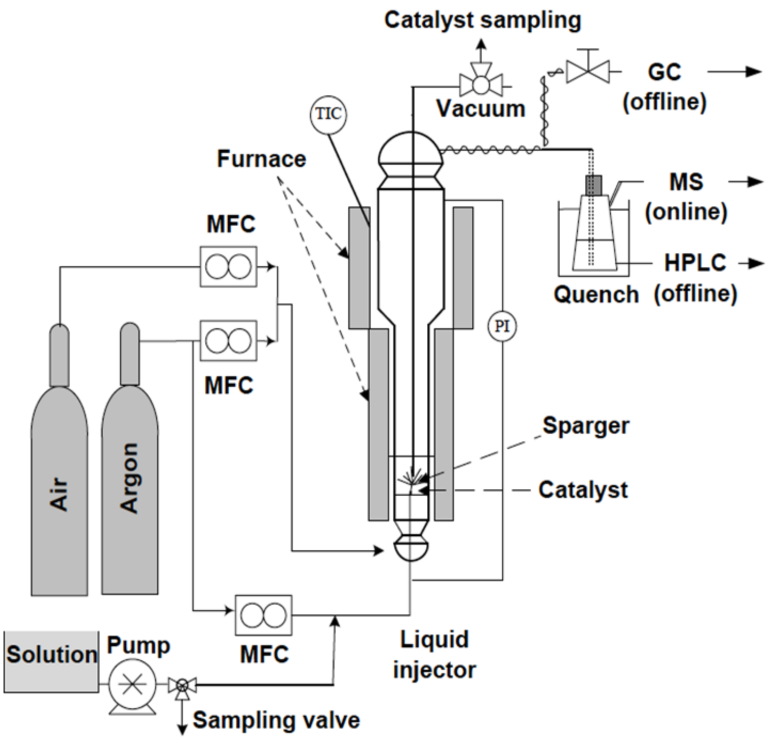

Figure 1: Set-up Schematic

In this study, we have developed a new process in which an aqueous solution of glycerol was injected directly into a fluidized bed of WO_3/TiO_2 catalyst. In order to decrease the rate of catalyst deactivation and reduce formation of hydrogenated by-products, oxygen was co-fed with the liquid and gas feed streams. Since co-feeding of oxygen along with heating has a considerable influence on the yield of acrolein, prior to the catalytic tests, we conducted acrolein blank tests in a quartz reactor. As a result, an optimum required quantity of oxygen concentration was determined for the *in-situ* catalyst regeneration. The conditions under which the glycerol solution atomized, was examined qualitatively.

The gas phase analysis of the products showed a selectivity of 70% towards acrolein while the catalyst was fully active. The reactor exit passed through two quenches to trap the heavy compounds such as acrylic acid, hydroxyacetone, and propionic acid. Other by-products were acetaldehyde, formaldehyde, formic acid, and acetic acid.

PRODUCTION OF CRUDE BIO-OIL AND STABILIZER FOR PHOTOSENSITIVE MATERIALS VIA HYDROTHERMAL LIQUEFACTION OF SPENT COFFEE GROUNDS

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Hydrothermal liquefaction (HTL) of spent coffee grounds (SCG) in hot-compressed water was conducted with an initial pressure of 2 MPa in N_2 atmosphere to produce crude bio-oil. The impact of retention time (5-30 min), reaction temperature (200 - 300℃), and feedstock/water ratio (1:5 and 1:10) on liquid product yields and properties was investigated. The highest yield of bio-oil (37.88%) was obtained at the reaction temperature of 275℃, retention time of 10 min and feedstock/water ratio of 1: 10. The resultant crude bio-oil has much higher heating value (37.7 MJ/kg) than the raw material (20.1 MJ/kg). The N-containing ketone (urazole) in bio-oil can be used as a stabilizer for photosensitive materials.

A REVIEW OF MICROWAVE PYROLYSIS OF BIOMASS AND WASTE FOR ENERGY AND FUELS

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SELECTIVE HYDROGENOLYSIS OF GLYCEROL TO 1, 3-PROPANEDIOL IN A FLUIDIZED BED

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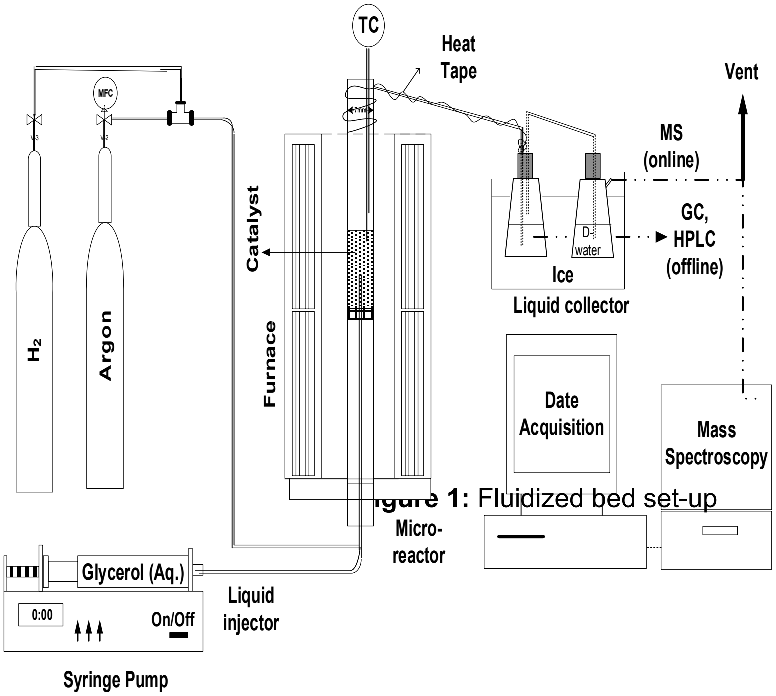
Key Words: Glycerol hydrogenolysis, 1, 3-Propanediol (1,3-PDO), Heterogeneous catalysis, Fluidization gas-solid, and Liquid atomization.

Biodiesel has received considerable attention in the last decade as a renewable, biodegradable, and non-toxic fuel. Its production is expected to grow almost 7-fold from 3.8 MMTPA in 2005 to about 25 MMTPA in 2015. Biodiesel coproduces 10% w/w of glycerol, which must be converted into value added products to reduce the cost of biodiesel compared to petro-based diesel. Significant research focus on the conversion of glycerol to value added products by various catalytic processes such as reforming, oxidation, dehydration, hydrogenolysis, etherification, and esterification[1].

Although the hydrogenolysis of glycerol to 1,2-propanediol is already well developed, the production of the more valuable 1,3-propanediol is still a challenge. 1,3-Propandiol (1,3-PDO) is used for the manufacture of polyester fibers i.e. polytrimethylene terephthalate (PTT)[2]. It also has applications in adhesives, laminates, coatings, moldings, carpets, clothing fibers, and polyesters[3]. 1,3-PDO is produced commercially either from acrolein (Degussa-DuPont route) or by ethylene oxide (Shell route). In the liquid phase hydrogenolysis of glycerol, high reaction pressure is the common drawback. To overcome the drawback, gas phase hydrogenolysis of glycerol offers the potential to open up new routes to produce 1,3-PDO while reducing the number of process steps. This technology relies on atomizing an aqueous solution of glycerol into a fluidized bed operating at temperatures beyond 250 to 300°C. H_2 gas can be purge at ambient pressure for effective conversion and higher selectivity of products. The droplets contact the hot catalyst particles and react on the surface to form the products that are more volatile and will subsequently vaporize and be entrained with the carrier gas. Atomizing the liquid solution through the nozzle as well as selection of active catalysts are the main keys for successful commercialization of this technology.

Preliminary experiments conducted in the micro-reactor system, illustrated in Figure 1, have demonstrated the concept: The collected product is pure as analyzed by GC, GC-MS, and HPLC. The reactor effluent was passed through a quench to collect all non-condensables. Gas-solids heterogeneous catalysis offers the potential to open up the route for producing selective 1,3-PDO, while reducing the number of process steps. The $Pt/WO_3/Al_2O_3$, $Pt/WO_3/ZrO_2$, and $Pt/WO_3/ZSM\text{-}5$ catalysts shown high activity for glycerol hydrogenolysis.



igure 1: Fluidized bed set-up

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UPGRADED PRODUCTION OF A HYDROXYLACTONE ANHYDRO-SUGAR BY CELLULOSE PYROLYSIS AND ITS APPLICATION IN THE SYNTHESIS OF BIOLOGICALLY ACTIVE COMPOUNDS

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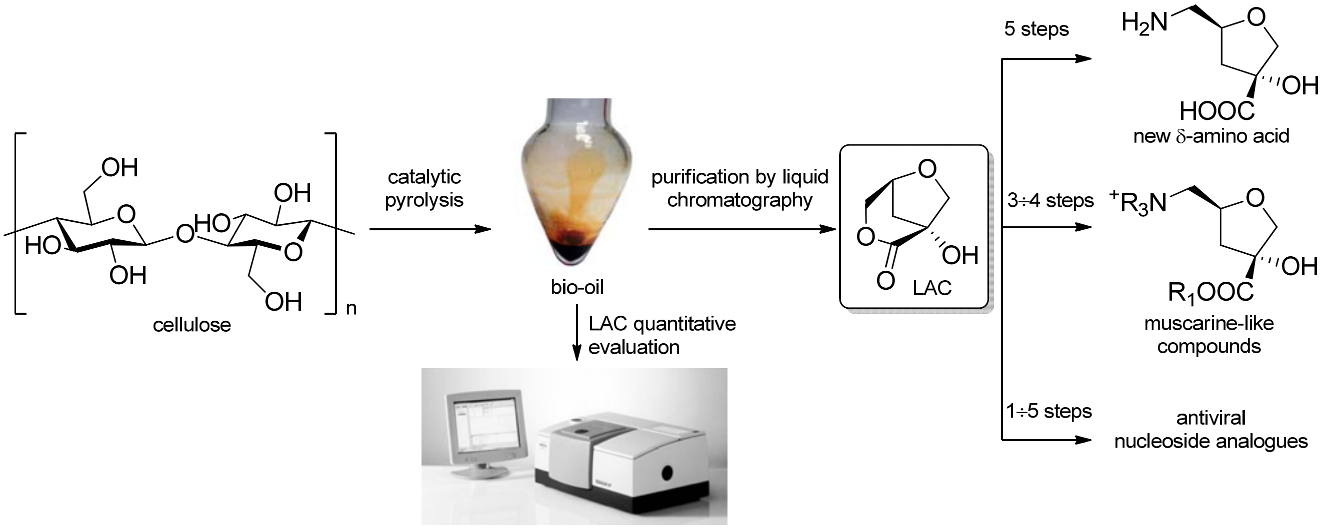
Key Words: Cellulose pyrolysis, amino acids, muscarine analogues, antiviral agents.

The fairly ignored (1*R*,5*S*)-anhydroisosaccharino-δ-lactone (LAC) is a compound formed at significant levels from catalytic pyrolysis of cellulose [1] and lignocellulosic biomass.[2] Recently LAC production in a gram scale by cellulose pyrolysis was upgraded.[3] Isolation and purification procedures were improved and its presence in bio-oils quantitatively evaluated by a fast and efficient FT-IR method, previously validated by ^{1}HNMR analysis. The best results were obtained at 500 °C by mesoporous Sn-MCM-41 catalyst (7.6 % yield from cellulose, 6.6 % after a regeneration cycle) and by the cheap and eco-friendly montmorillonite K10 (4.8 %).

LAC has the potential to be a top building block in biorefinery, being a multifunctional chiral C6 molecule. In this study we demonstrate that LAC is a valuable reagent in the synthesis of enantiomerically pure molecules with potential biological activities. Our first work employing LAC is given by the synthesis of a new tetrahydrofurane δ-amino acid, interesting as an equivalent of glycine-alanine dipeptide for access to new peptidomimetics with conformationally restricted structures.[4]

We also recognized structural similarity of this amino acid with natural L(+)-muscarine. Based on a renewed interest in muscarine-like conmpounds for application to the treatment of Alzheimer’s disease and other cognitive disorders, we have used LAC for obtaining new muscarine analogues. They have been investigated with respect to their binding affinity to human muscarinic receptors, observing a good agreement of these data with results by docking calculations.[5] Another application of LAC is given by the synthesis of a series of potentially antiviral compounds, related to nucleoside drugs.



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PYROLYSIS OF NAPIER GRASS AND PHRAGMITE REEDS PRETREATED WITH ACIDIC PYROLYTIC WATER

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Napier grass, *Pennisetum Purpureum*, and the phragmite reed, *Phragmites Australis*, are high yielding and fast growing perennial plants. The phragmites reed has been classified as Canada's worst invasive plant due to it being almost impossible to eradicate. These plants can be easily grown on marginal land, land that offers poor soil characteristics not suitable for food production, as dedicated energy crops. Inorganic content in grassy feedstocks is typically higher than other woody materials and are known to catalyze unfavorable reactions that affect the pyrolysis yields and bio-oil chemical composition and properties.

Acid washing is a pre-treatment step that can be used to lower the inorganic content of these grassy feedstocks. There are two disadvantages associated with this step, firstly, the chemical cost and secondly, the energy intensive drying stage after washing. These disadvantages have been overcome by using acidic water trapped using a novel fractional condensation system, coupled to a bench scale mechanically fluidized bed reactor (MFR), as a source of acid water for pre-treatment and by mechanical dewatering, using two different proprietary technologies.

The study aims to address the impact of pre-treatment, optimization of pyrolysis conditions and its fraction condensation system on the chemical composition of the bio-oil and char products. Particular attention is focused towards the characterization of the bio-oil sugar content and possible bio-oil conversion opportunities that may arise, such as the conversion of bio-oil to ethanol or butanol.

STUDY OF THE PRESENCE OF ADDED-VALUE CHEMICAL COMPOUNDS IN SEWAGE SLUDGE PYROLYSIS LIQUIDS: EXTRACTION, IDENTIFICATION AND QUANTIFICATION

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Key Words: sewage sludge, pyrolysis, phenols, naphthalene, toluene.

Pyrolysis of anaerobically digested sewage sludge (SS) from urban wastewater treatment plants is being studied as an alternative management way for this waste. Due to the enormous amount of organic compounds present in the SS pyrolysis liquids, a promising application of this product could be the production of high added-value chemical compounds. However, in order to evaluate the possible high added-value chemical compounds that could be obtained from this liquid, it is necessary to develop an analytical method suitable to determine qualitatively and quantitatively its composition.

The analytical method established in this work is based on the fractionation of the different phases that form the SS pyrolysis liquid by means of liquid-liquid extraction with organic and inorganic solvents and by solid phase extraction (SPE). Next, the composition of the separated fractions has been determined qualitatively by GC-MS and quantitatively by GC-FID. Thanks to the use of chromatography standards, the quantification of the compounds identified has been performed in mass percentage, unlike most of the quantifications shown in the scientific works about characterization of SS pyrolysis liquids. Other analytical techniques have been also used: FTIR for the determination of the main functional groups, GPC to study the molecular weight distribution and H-NMR to identify the main nitrogen-containing functional groups.

The fractions that are separated by the extraction method and the families of the compounds identified are the following: a heptane – soluble fraction, which is rich in paraffins, olefins, aromatics, and some aromatic and fatty nitriles, two fractions of dichloromethane – soluble compounds, which contain mainly phenols and fatty acids, and lastly, an acid fraction, in which the basic nitrogen compounds are extracted. This method has been applied for the characterization of a SS pyrolysis liquid obtained in a lab-scale fluidized bed reactor at 530 ºC. According to the quantification of the compounds identified, the yields to the different chemical compound families over SS fed in mass percentage have been determined (see Table 1). The percentage of production of some of these compounds, that could be reached if the 10 mill. of tones of dry SS produced in the EU were pyrolyzed, over the production of these compounds in the European industry have been also calculated (see Table 2).

Table 1 – Yield to the different chemical compounds over SS fed.

Aromatics (mass %)	Steroids (mass %)	Indol (mass %)	Benzyl cyanide (mass %)	Paraffins and olefins (mass %)	Phenols (mass %)	Fatty acids (mass %)
0.34	0.06	0.08	0.07	1.74	0.26	0.19

Table 2 – Possible production of chemical added-value compounds over dry SS generated in the EU (%).

	Benzene	Naphthalene	Toluene	Xylene	Phenols	Paraffins and olefins
Yield over dry SS (mass %)	0.18	0.02	0.13	0.04	0.28	1.86
Production in the EU (kton/year)*	8056	289	2635	2872	1459	115
Possible production over SS generated in the EU (%)	0.22	0.74	0.49	0.15	1.91	0.15

* Production data from the Best Available Techniques in the Large Volume Organic Chemicals Industry.

UPGRADE OF FLASH PYROLYSIS CONDENSATE BY ESTERIFICATION WITH HIGHER ALCOHOLS

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Key Words: flash pyrolysis; pyrolysis liquid upgrading; total acid number; butanol; solid acid catalyst

The utilization of condensates from flash pyrolysis is hindered by unwanted properties like corrosivity, high viscosity and the tendency to polymerization during prolonged storage. These characteristics result from the high content of organic acids and multiple functional groups and C-C double bonds in its constituents. As an alternative to severe hydroprocessing for the mitigation of these challenges, the addition of butanol and subsequent esterification of acids and acetalisation of ketones is investigated.

Ablative flash pyrolysis of different biomasses is performed in a laboratory plant designed for a capacity of 10 kg/h input. The cylindrical biomass with a diameter of 50 mm is pressed by hydraulic piston against an electrically heated, rotating plate. The pyrolysis vapors are cleaned from fine dust by means of a cyclone and condensed in a double-effect cooler followed by an electrostatic precipitator.

Samples of pyrolysis condensates are mixed with butanol and an acidic catalyst is added. This mixture is heated and kept under reflux in a dean-stark-apparatus to continuously boil off the water, which is solved in the organic liquid and additionally produced by the esterification and acetalisation reactions. The process is stopped, when no more water evaporates from the reactor.

As reference homogeneous acids like sulfuric acid and p-toluenesulfonic acid are used and compared to solid acid catalysts like ZnO or zeolithes. Figure 1 gives an overview about the results for the reduction of total acid number for the catalyst screening. The advantage of the heterogeneous, solid catalysts is the possibility to remove the solids after reaction and use them again for another batch in contrast to the homogeneous acids, which remain in the solution and need to be neutralized at the end.

The most promising catalyst candidates from the screening are then used in experiments with varying process parameters like ratio of pyrolysis liquid to butanol, catalyst amount and biomass input to the pyrolysis plant (beech wood as reference and barley straw as example for agricultural residues). All products are analyzed for total acid number, water content, dynamic viscosity and higher heating value.

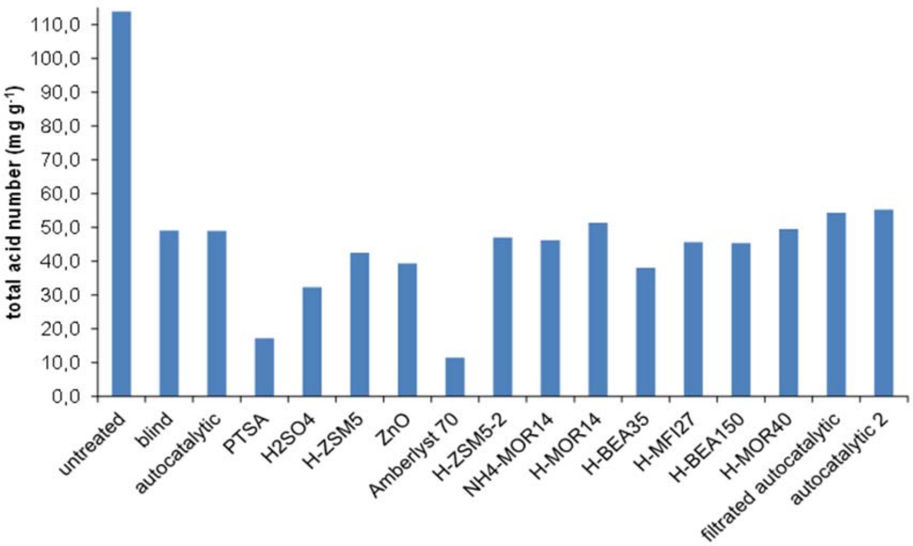

Figure 1 – Total acid number for different catalysts

The total acid number can be reduced by 90 % (from above 110 to below 10 mg/g), the water content by 90 % (from above 25 % to below 2 %), the viscosity by 70 % (from above 18 to 5 cSt) and the higher heating value can be increased by 45 % (from 16.6 to 31 MJ/kg). These improvements should allow the utilization of upgraded pyrolysis liquids in standard boilers and as fuel in CHP plants.

SUGAR PRODUCTION VIA PYROLYSIS

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UPGRADING OF SOLID FAST PYROLYSIS BYPRODUCTS FOR MATERIAL USE WITH HIGH VALUE

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Key Words: char, activated carbon, flash pyrolysis, demineralization

Fast pyrolysis is a thermochemical conversion process for the production of liquid substances from solid organic fuels, be it a blend for energetic use (liquid fuel) or more specific chemical substances for material use. However, complete liquefaction of the biomass cannot be achieved and there is always a solid byproduct, i.e. char. In most industrial and/or pilot plants this char will be burnt within the process in order to supply the heat necessary to keep up the process. Depending on the process design this is not necessarily required and with an energetically optimized system, char could be recovered as byproduct. It can be marketed directly as solid fuel or – after upgrading – for material uses. The amount of char produced is comparatively low for woody biomass since the process is optimized for liquid yield and the potential of such an alternative char use as byproduct is low. However, high ash content of biomass tends to decrease the liquid yield in favor of higher solids and gas yields because secondary pyrolysis reactions are catalyzed and ash will accumulate in the solids. If ash-rich biomass is used for fast pyrolysis, solids will represent a more important byproduct with little more value than its heating value. This is the case for the bioliq® concept which aims at utilizing (wheat) straw as feedstock for fast pyrolysis. While the solid byproduct might be considered a drawback when using biomass residues with high ash content, this contribution aims at elaborating a value addition by producing a solid byproduct with high market value. More specifically, the upgrading to activated carbon is presented to achieve a material use of high value.

The major problem which requires attention is the high ash content of the produced char, naturally. Very few inorganics are present in the liquid pyrolysis product(s) due to the low vapor pressure of most inorganic elements present in biomass. They are almost exclusively recovered with the char, which exhibits much higher ash content than the feedstock in consequence. In the bioliq® concept, wheat straw is one standard feedstock with an ash content of 7-10 wt.% leading to a char with an ash content of 30-40 wt.%. Hence, the experimental procedure of activation started with a demineralization step (in 1N H_2SO_4:HCl 1:1solution) yielding a demineralized char. With this demineralized char, both KOH at 700 °C and steam activation at 750 °C were tested. As expected, steam activation produced an activated carbon with much higher ash content due to the carbon burn off, which results in an enrichment of minerals. In consequence, the BET surface area of the steam activated carbon is comparably low (see Figure 1). Activation with KOH leads to a nearly complete removal of inorganic compounds and a BET surface area comparable to commercially available activated carbons.

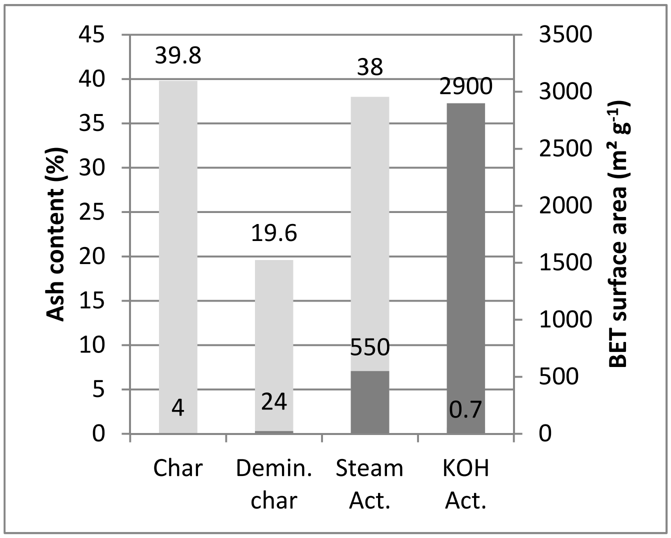

Figure 2 – Ash content and BET surface area of produced materials

Notably, the ash content was only reduced to half by the demineralization step whereas it was reduced to <1 wt.% after activation with KOH (see Figure 1). Further experiments were conducted to investigate the demineralization step and it was found that it can be increased when the char is washed with HCl after soaking. Surprisingly, it was also found that ash removal can be achieved by direct activation with KOH without the demineralization step. Hence, combined demineralization and activation can be achieved in a single step, reducing the complexity significantly.

In conclusion, two major benefits could be achieved. Firstly, it is shown that the byproduct of fast pyrolysis can be used as feedstock to produce an activated carbon representing a value addition to a marketable product. Secondly, a promising pathway is opened to produce activated carbon from biomass residues such as wheat straw instead of fossil resources.

ADVANCED CARBONIZED BIOMASS MATERIALS FOR BIOSENSOR APPLICATIONS

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Key Words: Biomass, Biosensor, Carbon, Electrochemiluminescence, Ruthenium.

In this study results obtained with electrodes for electrochemiluminescence (ECL) detection produced from bamboo and pistachio nut shells are compared. Both materials were carbonized using Argon fluxed chemical vapor deposition system. The carbonization of bamboo sticks was achieved at 850 °C whereas the pistachio nut shells were initially carbonized at 500 °C and then activated with KOH at 900 °C. In order to use them as a working electrode (WE) for ECL detection, the carbonized materials were initially contacted with a copper wire and then encapsulated in to epoxy resin. Tris (2, 2'-bipyridyl) ruthenium (II) ($\mathrm{Ru(bpy)}_3^{2+}$) was used as an ECL label. FESEM analysis (Fig. 1) showed that the carbonized bamboo has more porous and tubular structure than the carbonized pistachio nut shells (CPNS). On its turn surface structure of CPNS are flat and similar to commercially used glassy carbon (GC). The ECL analysis (Fig. 2) showed that the efficiency and stability of Carbonized bamboo was much better than the CPNS. It has also been noticed that due to similarity in the surface structure both CPNS and GC electrode have similar ECL curve. This relationship between such behavior and the surface structure will be discussed in detail.

Both working electrodes are currently lacking satisfactorily reproducibility but their environmental friendliness, low cost of the raw materials and intrinsic bio-compatibility make worth to further investigate the issue for instance by testing various types of functionalization that leads to reproducible cost effective biosensors.

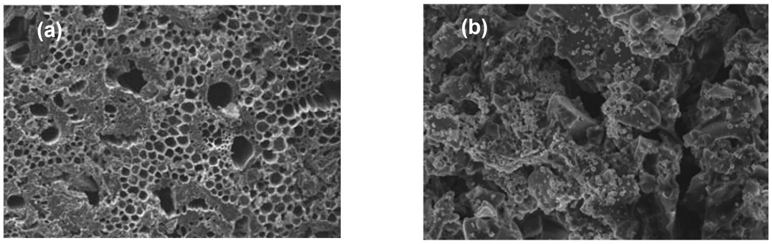

Fig. 1. FESEM image of (a) carbonized Bamboo (b) CPNS

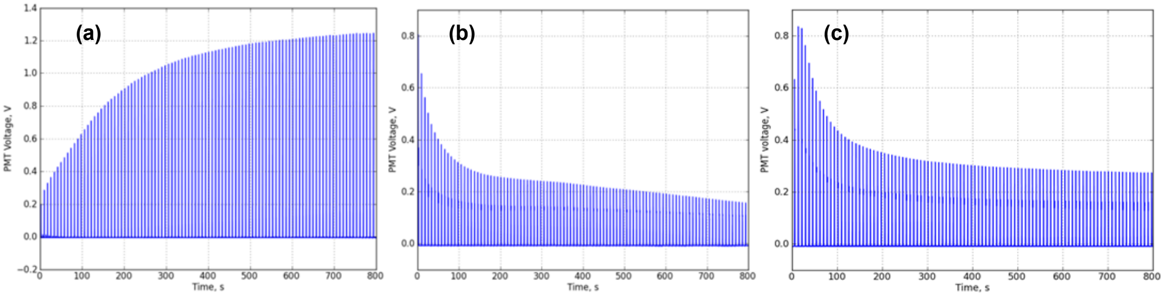

Fig. 2. ECL response with (a) Bamboo WE (b) CPNS WE (c) GC WE

References:

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BIOMASS FAST PYROLYSIS: INFLUENCE OF BIOMASS NATURE ON PRODUCTS YIELD

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Lignocellulosic biomass is a promising renewable resource that presents an alternative to fossil fuels and therefore leads us to achieve desirable environmental outcomes. That is why, in 2010, ADEME financed the GAYA project in France, which is coordinated by GDF-Suez with the goal of setting up a decentralized industrial facility for biomass gasification and methanation.

The objective of this work is to contribute directly to the GAYA project database by studying the pyrolysis behavior of a wide range of biomass under the conditions of an industrial gasifier. More specifically, the aim is to determine the influence of the biomass nature on char yield.

In order to accomplish this purpose, an experimental apparatus was designed to reproduce fluidized bed gasifier heating conditions: the image furnace. This setup was used to study the fast pyrolysis of 54 biomasses at a maximum temperature of 850℃ and specifically determine the yield of char, which is an important parameter for GAYA project’s dual fluidized bed technology. Average yields of char are between 11 and 32%. It was found that two biomass properties have a significant impact on char yield : ash and carbon content. One correlation has been developed on this basis. Furthermore, a complete mass balance with 4 biomasses was performed, wherein the solid, liquid and gaseous pyrolysis products were recovered and the pyrolysis gas was analyzed by micro-GC.

These results allow to take into account biomass heterogenity for process modeling or process operation.
Key words: Renewable energy, pyrolysis, biomass, fluidized bed, biofuels, gasification, image furnace

HYDROGEN PRODUCTION FROM INTERMEDIATE PYROLYSIS BIOCHARS FOR USE IN SOLID OXIDE FUEL CELLS

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Key Words: Solid Oxide Fuel Cells, Biochar, Intermediate Pyrolysis, Steam Gasification, Hydrogen

Biomass derived charcoal or ‘biochar’ is a byproduct of pyrolysis. Biorefineries are expected to use advanced thermochemical technologies to generate heat and power as well as other value added products from biomass, in particular high ash content, non woody biomass. Intermediate pyrolysis has been specifically designed to overcome the limitations associated with the use of fast pyrolysis in handling non woody biomass making it an ideal technology for biorefinery use [1]. Intermediate pyrolysis produces high quality biochars that can be used as fertilizer or gasified to produce a hydrogen rich syngas [2].

To ensure maximum efficiencies are attained, it is essential to use fuel cell technologies. Solid oxide fuel cells (SOFC) in particular are attractive, since they are able to utilise syngas making them perfect for coupling with biomass gasification. SOFCs have up to 50% electrical efficiency and >85% overall efficiency when used in CHP mode. The aim of this study was to investigate the performance of a microtubular SOFC with real syngas derived via the steam gasification of biochar. Previous studies have been conducted using synthetic syngas but there is a scarcity in the literature of using biosyngas in SOFCs.

Gasification experiments were carried out at 850 °C with a steam flow of 277 g min^{-1} kg^{-1} biochar to guarantee high hydrogen contents. Syngas was collected in a gas bag and transferred into a glass reservoir, from where it was pumped into the SOFC. No treatment was applied to the syngas and low humidity content was used to obtain a baseline performance for future references.

Two biochars were used to generate the syngas; rapeseed biochar (RSB) and wood pellet biochar (WPB). Initial investigations revealed that although the RSB syngas had superior hydrogen content, it degraded the SOFC at a much faster rate than the WPB syngas. Further investigations were carried out to examine the effects that WPB syngas has on the microtubular SOFC over an extended period of time. The results showed that over the 7.5 hours of operation, the SOFC performance had degraded by 17.8% at 0.6 V. The high rate of degradation resulted from the harsh conditions that were deliberately used. Energy dispersive X-Ray (EDS) analysis showed sulphur and carbon deposition on the anode, explaining the decrease in performance.

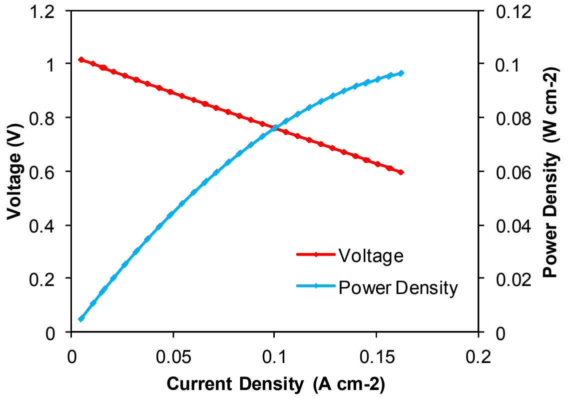

Figure 1. Microtubular performance with WPB syngas

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GENERATION OF HYDROGEN, METHANE AND RECOVERY OF PHOSPHORUS FROM BIOMASS

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Key Words: Hydrogen, Methane, Phosphorus, waste biomass, supercritical water.

Waste biomasses contain usually a high amount of water and a high amount of sulfur, chlorine and salts. Examples of this kind of biomasses are spent grains (the residue of the brewing of beer) grape residue from the wine production and sugar beet. One of the most abound waste biomasses worldwide is sewage sludge, which is more polluted compared to the other biomasses. On the other hand utilization of waste biomass does not affect the food market at all. The production of valuable chemicals from waste biomass requires the application of catalysts. One economic route for cleaning biomass previous to the application of catalysts is a gasification reaction combined with a gas cleaning. Common gasification processes require dry feedstock and thus an energy, cost consuming pretreatment. Our approach is the gasification of waste biomass under the conditions of supercritical water. This process can also be applied as energy and cost effective treatment for the utilization of the residue of other chemical processes in a biorefinery industrial complex. Anaerobic digestion –another option for this purpose- requires residence times up to more than one month and can only utilize half of the residual organic carbon.

Typical reaction conditions for the process of gasification under the conditions of supercritical water are temperatures of 650 °C and pressure from 25 up to 30 MPa. For the treatment of feedstocks as waste biomass or even sewage sludge contaminated with heavy metals, sulfur and chlorine, long time stability of heterogeneous catalysts can become an issue. To avoid this only the catalytical effect of potassium salts combined with the high reaction temperature were investigated in the present study.

Important for a continuous flow operation is effective separation – recovery of the inorganic components of the sewage sludge previous to the high temperature part of the installation. This step increases the environmental value of a biorefinary due to the possibility to recycle elements like phosphorus. The hydrogen of the product gas can be used (in many ways) for various hydrogenation reactions necessary for the operation of a biorefinery.

Highlights:

- High gasification rate up to more than 90 %.
- High hydrogen concentration in the product gas up to 70 %.
- Product gas production at 20 MPa, no dust, no chlorine very low sulfur concentration
- Recovery of phosphorous up to 80 % just by filtration.
- Low consumption of electric energy for compression.
- Demonstration in pilot plant in the 100 kg/h range
- CO_2 separation at low costs

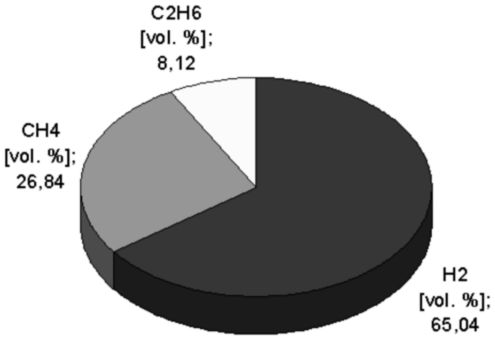

Figure 1 – Combustible components of the product gas. Biomass with 9. wt.% DOM Tmax = 680 °C, p = 28 MPa, mean residence time = 1.3 min, C – gasification yield = 94 %.

BIO-HYDROCARBONS THROUGH CATALYTIC PYROLYSIS OF USED COOKING OILS: TOWARDS SUSTAINABLE JET AND ROAD FUELS

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Session Category: 5. Synthetic fuels, charcoal (derivatives) and other commodity chemicals

Keywords: UCO, vegetable oils, jet fuel, pyrolysis, catalytic conversion, hydro-treatment.

Vegetable Oils (VOs) are still today the most used feedstock for transport biofuel production, namely biodiesel. Triglycerides are transesterified to FAME, which is then blended with conventional fossil diesel. The most recent alternative route to transesterification is VO hydrotreatment; Neste Oil and UOP/ENI are the Companies that today leading this technology, with the NExBTL and ECOFINING processes respectively. These new processes not only produce high quality, diesel-like biofuels, but also bio-kerosene/aviation biofuels, i.e. pure hydrocarbon fuels. By producing drop-in biofuels, these processes overcome the blend-wall, which is typical of biodiesel and first generation biofuels. In the aviation sector, a first non-binding target was set at 2 Mt aviation biofuels by the EU Aviation Flightpath in 2012, but today we are still far from this figure. Today commercial technologies for renewable jet fuel production are mainly based - among others - on either Fischer-Tropsch (FT) synthesis from coal, natural gas and possibly biomass, or hydrotreating of vegetable oil (hydrotreated renewable jet fuel, HRJ, or Hydrotreated Vegetable Oil, HVO). Both routes imply significant costs: in FT-synthesis the main bottleneck is the capital cost, while in hydrotreating the main drawbacks are the availability of sustainable raw material, the feedstock costs, and the large hydrogen demand of the process, which increase the operative costs. Used Cooking Oil (UCO) has high sustainability, according to the RED scheme, and is therefore considered among the possible alternatives to VOs for greening the sector and, under proper circumstances, for reducing the sourcing cost of feedstock. However, the use of UCO as feedstock for biofuels production is not trivial in reactors, as catalysts are sensitive to impurities and contaminations, which are typical of waste oils. Moreover, the chemical composition of UCO is variable regionally as well as seasonally, because the type of base-vegetable oils vary with Country and period of the year.

In the framework of the ITAKA EU FP7 project coordinated by SENASA (ES), (catalytic) thermochemical conversion of UCO has been considered in order to obtain an intermediate biofuel which is suitable for upgrading by hydrotreating. The catalytic conversion of UCO was investigated at RE-CORD in a 1.5-3 l/h pilot pyrolysis unit, available at RE-CORD premises. This unit was upgraded within the ITAKA project, in order to allow for both VO and lignocellulosic biomass feeding. In addition, a revised condensation unit and aerosol collection system was installed.

The work reports the results of catalytic conversion of UCO obtained during an experimental campaign carried out in 2014-2015. Various batches of UCOs were firstly characterized, and then fed to the intermediate continuous pyrolysis reactor. UCO, properly filtered and conditioned, was subjected to thermal and catalytic cracking under controlled conditions. The adopted type of catalyst and the reaction conditions, including several parameters such as temperature, reactor geometry, heating rate and residence time, were evaluated, and selected combinations were tested. The collected pyrolysis oil was characterized in terms of main constituents and hydrocarbons content, and GC-MS and GC-FID analyses were used to qualitatively and quantitatively assess the composition of the fuel.

The main product of the process is a bio-intermediate which greatly differs from the traditional pyrolysis oil obtained from lignocellulosic biomass. This bio-oil has low oxygen content, high calorific value and low viscosity. High mass yield and considerable amount of hydrocarbons were obtained by thermochemical conversion of UCO with relatively inexpensive catalysts. Triglycerides and fatty acids conversion generated alkanes, alkenes, alkadienes, aromatics and carboxylic acids; in presence of a catalyst, the amount of oxygenated compounds was significantly limited, improving both properties and yield of the liquid product. The fractionation of the most interesting compounds in bio-oil could find employment in different sectors of the additives or lubricants market, and the newly identified process route could represent a very interesting solution for sustainable and scalable biofuels production.

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LIGNOCELLULOSIC BUTANOL PRODUCTION FROM CORN-COBS, SWITCHGRASS AND PHRAGMITES

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Key Words: Lignocellulosic, pretreatment, butanol, solvents, clostridia

Three different feedstock’s were evaluated for the fermentative production of butanol, a commodity chemical and also potential biofuel. The three model feedstock were switchgrass, corncobs, and phragmites. Switchgrass (*Panicum virgatum*) is a potential dedicated energy crop. Corn cobs as an important by-product of the sweet corn processing industry and are available in large. Phragmites (*Phragmites australis*) are an invasive (North America) plant species. All three feedstock cannot directly be used for food production. The raw biomass samples were characterized chemically and converted to fermentable sugars via enzymatic hydrolysis after sodium hydroxide pretreatment. Substantial butanol yields could be obtained from all feedstock’s. The effect of pretreatment on enzymatic hydrolysis, as well as the subsequent fermenatbiliy (Figure 1) will be discussed.

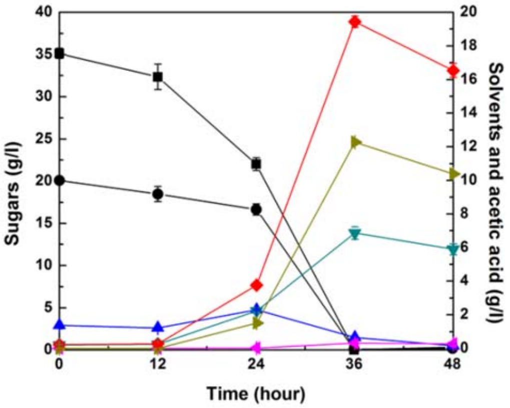

Figure 1: Fermentation of enzymatic hydrolysate of washed NaOH-pretreated corncobs without sediments removal at 37°C and 200 rpm(-■-,Glucose; -●-, Xylose; -◄-, Ethanol; -▼-, Acetone; -►-, Butanol; -◆-, Total solvents; -▲-, Acetic acid).

SEPARATION TECHNOLOGY: MAKING A DIFFERENCE IN BIOREFINERIES

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PRODUCTION OF ACTIVATED CARBONS FROM PYROLYTIC BIOCHAR

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Key Words: activated carbons, oil sands, mercury, ammonia

Activated carbons are the most used adsorbent material. Their applications range from wastewater treatment, air purification, removal of contaminants and many others. According to “Global Activated Carbon Market Forecast & Opportunities 2017”, the demand for activated carbon is expected to increase more than 10% per year for the next 5 years to make it a $3 billion market by 2017. Current processes for the production of activated carbons from renewable resources do not provide valuable co-products. This presentation focuses on the conversion to activated carbon of the bio-char co-product of the pyrolysis process. Pyrolysis also provides valuable bio-oil, which is a source of valuable biochemicals and fuels. This can greatly improve the economics of the pyrolysis process and the development of bio-refineries.

In this study, a number of different agricultural and forestry residues were investigated as precursors for the production of activated carbons. The activated carbons were then tested for the removal of typical pollutants. A lab scale reactor, the jiggled bed reactor, was used for this study. Its unique features such as excellent mixing and heat transfer allowed for the screening of the impact of pyrolysis conditions (ranging from fast to slow pyrolysis) and activation on the final product properties.

Optimal activation and pyrolysis conditions, as well as the most attractive feedstocks, were identified. Two feedstocks were identified as the most attractive: Kraft lignin, a by-product of pulp and paper mills, and olive residue, which is a major environmental concern in the Mediterranean area and, in particular, Crete. Activated carbons from these two feedstocks were tested for removal of contaminants such as naphthenic acids from oil sands process affected water, and ammonia and mercury from wastewater. They performed as well or better than commercial activated carbons, as shown for example in Figure 1 in the case of oil sands process affected water.

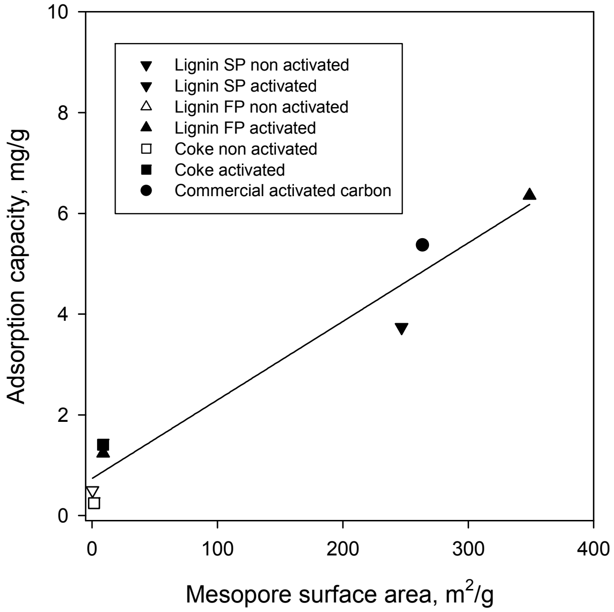

Figure 1- Comparison of the performance of different carbons for the removal of naphthenic acids from oil sands process affected water

MANIPULATING THE PRODUCTION OF SOLVENTS VERSUS 1,3-PROPANEDIOL IN C. PASTEURIANUM FERMENTATIONS USING REDOX BALANCE AND PH STRATEGIES

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Key words: butanol, 1,3-propanediol, Clostridium pasteurianum, glycerol

The current study was performed at the 5L scale in support of the development of a commercial process to convert crude glycerol generated in biodiesel production to the products 1,3-propanediol and the solvents butanol and ethanol by fermentation with *Clostridium pasteurianum*.

We have clearly shown that by controlling the fermentation pH in the range of 4.7 to 5.9, the CO_2 production rate can be manipulated such that the flux of carbon through the pathways producing 1,3-propanediol, butanol and ethanol can be increased or decreased. This has been shown to be a direct response to alternative mechanisms for balancing cellular redox potential.

The biochemical pathways leading to CO_2 and energy production in *C. pasteurianum* convert nicotinamide adenine dinucleotide (NAD^+) to the reduced form ($NADH_2$), thus transferring electrons. Pathways that can regenerate NAD^+ for continued cellular energy production are limited and include solvent production (butanol and ethanol) or 1,3-propanediol. An increase in fermentation pH resulted in an increase in the specific cell growth rate and thus the CO_2 production rate. Consequently the pathway leading to 1,3-propanediol was preferred, as shown by increased 1,3-propanediol production, presumably due to its simplicity which accommodated the higher rate of NAD^+ regeneration. The effect on cellular electron transfer was also confirmed by the redox potential signal during these fermentations. The application of a 'staged' pH program was used to optimize cell growth,1,3-propanediol and solvent production in batch studies.

The knowledge gained in batch studies was the basis for designing a continuous fermentation process utilizing both pH and redox strategies applied to crude glycerol conversion to the desired products, while minimizing crude glycerol pre-treatment requirements.

ON-LINE ANALYSIS OF CATALYTIC BIOMASS PRODUCTS USING A HIGH PRESSURE TANDEM MIRCO-REACTOR GC/MS

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Laboratory scale, Tandem micro-Reactor GC/MS systems are widely used to perform a diverse array of analyses such as fast pyrolysis, hydropyrolysis and catalytic pyrolysis. All three of these methods are used to convert lignocellulosic biomass into biofuel and value added chemicals. Certainly, the efficiency and extent of any transformation is a function of the temperature, the atmosphere and the biochemical composition of the feedstock. However, the effects of pressure on the transformation often play a pivotal role in the process; thus the ability to test at various pressures is of great importance. Studies of high pressure catalytic pyrolysis are conducted in expensive, lab-scale large reactor systems. Because of expense and time considerations, comprehensive temperature and pressure studies of any feedstock-catalyst combination are limited. The introduction of the bench-top, high pressure tandem micro-reactor system overcomes these limitations for biomass researchers. Complex studies can be performed on a feedstock or a catalyst in various atmospheres, temperatures and pressures automatically using the tandem micro-reactor(1).

The tandem reactor consists of two reactors in series. Solids, liquids or gases are introduced into the first reactor. Solids are pyrolyzed, liquids are vaporized. The vapors from the first reactor are swept into the second reactor which contains the catalyst bed. Once through the catalyst, the vapors flow directly to a GC/MS where the compounds are separated and identified. High pressure capability is added to the micro-reactor by incorporating two back pressure regulators into the pneumatics. One sets and controls the pressure in the tandem reactors; the second controls the capillary column flow. The system design will be described. Two different applications were described indicating the effect of reaction gas, pressure and catalytic bed temperature: 1: non catalytic hydropyrolysis of kraft lignin and 2: conversion of ethanol over MgO-SiO2 Catalyst.

(1) **Design Aspects of a Multi-Mode, Tandem Micro-Reactor GC/MS System for Catalyst Testing**, tcbiomass 2013, September 3-5, 2013.

EVOLUTION OF PALM OIL MILLS INTO BIO-REFINERIES: TECHNICAL AND ENVIRONMENTAL ASSESSMENT OF SIX BIO-REFINERY OPTIONS

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Key Words: Palm Oil Mill, Life Cycle Assessment, biorefinery, empty fruit bunches, shell, fiber, eutriphication potential (EP)

Abstract: This study reports the mass and energy balances, the Global Warming Potential (GWP), Eutrophication Potential (EP), and the Net Energy Consumed (NEC) per ton of Fresh Fruit Bunch (FFB) processed for six concepts that could be implemented to convert existing Palm Oil Mills (POMs) into biorefineries. These parameters were also calculated per ton of product obtained using an allocation strategy based on the contribution of each product to the total sales of the biorefinery. These biorefinery concepts were developed as part of an evolution strategy consisting in the hypothetical gradual addition of emerging technologies to POMs. The new biorefinery concepts were: (i) Production of biogas from the anaerobic treatment of the Palm Oil Mill Effluents (POME) and its utilization for electricity generation, (ii) Composting of Empty Fruit Bunches (EFB) and oil palm fiber (fiber) with POME, and electricity generation from biogas, (iii) High pressure steam Combined Heat and Power (CHP) unit for the utilization of 100% of the biomass and biogas combustion for the production of electricity, (iv) Pellets production from dried biomass and biogas production and combustion in a gas engine, (v) Biochar production and combustion of pyrolysis vapors for heat recovery, and biogas combustion for the production of electricity, and finally (vi) Biochar and bio−oil production plus biogas and syngas combustion. The studies were conducted using as starting point (or baseline) a traditional POM technology with a throughput capacity of 30 t Fresh Fruit Bunches (FFB) h^{-1}. The baseline scenario was created using averaged data from some POMs and oil palm plantations in Colombia. The results of the mass and energy balances of the studied biorefinery concepts allow us to conclude that the available biomass residues used in integrated biorefineries schemes could result in the production of up to: 125 kWh t FFB^{-1} electricity, 225 kg t FFB^{-1}compost, 125 kg t FFB^{-1} pellet, 46 kg t FFB^{-1} biochar and 63 kg t FFB^{-1} bio−oil. The GWP based on a Life Cycle Assessment (LCA) of the studied biorefinery concepts concludes that, compared with the studied baseline case, reductions in the range from 12 to 76% could be achieved through products diversification. The addition of an anaerobic digestion unit and the use of the effluents to produce composts contributed to the reduction of the EP of the POM biorefinery in more than 30%. The sustainability of producing crude palm oil (CPO) and kernel improves even more due to the sharing of environmental impacts with additional products generated from the POM biomass. The GWP, EP, and NEC for the CPO could be reduced up to 75%, 31, and 12% respectively. In the case of the kernel the reduction of these environmental impacts that can be achieved was similar (75, 33, and 12 % respectively).

BIOCHAR FROM TCR®-PROCESS – AN OPTION FOR DIGESTATE UTILISATION AND NUTRIENT MANAGEMENT

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One challenge of existing and future anaerobic digestion (AD) plants is an ecologically and economically suitable digestate utilisation. The current option in Germany is the application on arable land. But especially in regions with high density of livestock farms and AD plants that kind of use lead to a recycling competition between manure and digestate. To avoid an over-fertilisation in the surrounding area of AD plants and livestock farms a sustainable digestate management for a specific use of the nutrients is necessary.
The TCR®-process (**T**hermo-**C**atalytic **R**eforming) which combines pyrolysis with an integrated reforming step developed by Fraunhofer UMSICHT provides an alternative option to convert organic residues like digestate into high-value products (oil, gas and char). The carbon-rich biochar is a valuable fertilizer which can be transported and stored easily. Therefore, it can be applicated in agricultural areas where a lack of nutrients is. Moreover, the biochar can be used for nitrogen removal from the produced liquid phase of the digestate in front of the TCR®-process. The application of the treated/nitrogen low liquid phase on agricultural land is less competitive in comparison to untreated digestate. The main advantages of the TCR®-process are the nutrient recovery with the biochar and a reduced negative environmental impact due to low nitrogen amount of the liquid phase. Furthermore, the oil and gas can be co-fired in existing CHP units together with the biogas to increase energy production. Regarding energy crop based AD facilities the substrate demands can be decreased too. Both aspects help to improve the economic situation of AD concepts. Another opportunity would be the material usage of oil in bio-refinery concepts.

BIODIESEL SYNTHESIS FROM DOMESTIC USED COKING OIL IN SOUTHERN EUROPE. EVALUATION OF THE FUEL QUALITY

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MODELING OF POLLUTANT ADSORPTION ON NOVEL MODIFIED BIOMASS AS A MEANS OF SEAWATER DECONTAMINATION

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Key Words: adsorbent, acid hydrolysis, fractionation, lignocellulosic biomass, wheat straw.

Hydrocarbon spills like diesel or crude oil spills cause great damage to the shorelines which usually include sensitive marine ecosystems. Moreover, there are significant negative economic impacts on tourism and fisheries. Chemical dispersion, in situ burning, mechanical containment and adsorption are some of the cleanup methods to combat the oil spills pollution. Adsorbents collect liquid hydrocarbons on the solid phase, thus they can remove oil spills from the sea surface water. The adsorbents can be inorganic minerals, organic synthetics or natural organic products. Waste lignocellulosic biomass is such a natural organic product. The thermochemical treatment of lignocellulosic waste biomass can provide a fraction that can be used as a low-cost adsorbent with increased sorption capacity and biodegradability for cleaning by adsorption the oil spills.

In this work we focus primarily on modeling the process of adsorption of diesel and crude oil on modified biomass fraction. The experimental measurements were performed using (i) representative samples of real seawater, and (ii) simulated/substitute seawater, prepared as recommended by widely used standards, i.e., in accordance with ASTM D 1141-98/Reapproved 2003, to allow the inclusion of results in international relational databases (RDBs), which require reference to a common/established means in order assure comparability of results of different source/origin. This work includes the modeling of adsorption of mixtures of fluids and colloids, containing water, hydrocarbons, salts, dispersants, phytoplankton and predetermined contaminants, such as pigments and soluble heavy metal compounds. Agitation was induced to simulate the sea wave's movement in the case of shoreline flows. The water and oil adsorbency, defined as the ratio of water or oil adsorbed to dry adsorbent weight, according to the ASTM F726-06 method, was performed, following the procedure of this standard method, using crude oil and diesel provided by Hellenic Petroleum SA. The biomass modification process was acid hydrolysis at 100 ^{o}C using sulfuric acid as catalyst in a 20 L glass reactor. Wheat straw was used as raw material for the adsorbent preparation.

The present work is part of a research project co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALIS - University Of Piraeus - Development Of New Material From Waste Biomass For Hydrocarbons Adsorption In Aquatic Environments.

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PRODUCTION OF BIODIESEL BY THE ESTERIFICATION OF OLEIC ACID WHILE USING AMBERLYST 15 AS CATALYST

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Keywords**:** biodiesel, heterogeneous process, esterification

Biodiesel is a potential renewable and carbon neutral energy carrier. With the world's fossil fuel reserves and particularly liquid hydrocarbons being finite, biodiesel is a promising alternative as it can be used as a direct replacement for fossil diesel. One of the main problems with biodiesel production is the formation of soaps with the use of base homogenous catalysts due to the presence of fatty acids in non-pure raw materials. In order to avoid this undesired by product, the use of heterogeneous catalysts has gained more and more relevance due to the fact that it offers easier separation and reusability while avoiding soap formation which allows the use of feedstocks with higher amounts of free fatty acids.

In this work the direct esterification of oleic acid in the presence of the heterogeneous catalyst Amberlyst 15 and ethanol was examined. The selection of alcohol was done based on the fact that ethanol can be obtained from natural sources while methanol is from petroleum based process. The catalyst and reactants were added to a 500 ml glass batch reactor while being stirred by a magnetic stirrer at 200 RPM and heated by circulating water in order to reach the desired reaction temperature. Studies over different reaction temperatures, alcohol to fatty acid molar ratios and catalyst amounts were performed to determine the effect that each variable has on the reaction and its yield.

From the experimental data, it was concluded that the effect of temperature has a substantial effect on the reaction rate and the final conversion. Molar ratio and catalyst amount also significantly affects the conversion of oleic acid but to a lower degree than temperature. This technology is shown to be a good pre-esterification alternative for the purification of waste oils with high concentrations of free fatty acids.

INTERMEDIATE PYROLYSIS AS AN ALTERNATIVE TO FAST PYROLYSIS

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CARBON SURFACE ENGINEERING FOR CONTROL OF EMISSION OF VARIOUS GLOBAL ATMOSPHERIC POLLUTANTS

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University of Saskatchewan

It has recently been reported that the year 2014 globally has been the warmest year ever recorded. The anthropogenic emission of carbon dioxide and various other Greenhouse gases has been the focus of one of the sources of this increase in the global temperature over the decades. Many methods have been reported as being most effective in the control of human sourced greenhouse gases into the global atmospheric environment. One of these methods is the use of activated biochar aerosols as a method of separation of anthropogenic carbon dioxide emission before they reach the global atmospheric environment.

Biochar from various sources has been reported by a number of authors to be an efficient vehicle for controlling anthropogenic emission of gases such as carbon dioxide and elemental mercury into the atmospheric environment. Several authors over the years have outlined the best approach for the capture of CO_2 from an emission stream is with the application of a weak basic functional agent applied to the surface features of biochar material. This creates a surface functional agent that reacts with the CO_2 to remove it from the anthropogenic emission stream. These alkaline surface ‘functional groups’ can be suitable sites for chemical adsorption. Carbon Dioxide capture is then the result of the interaction between the Lewis acid and Lewis base formed. This rate of surface capture then depends upon various other features such as the surface characteristics of the biochar aerosol and the operating conditions of the emission source such as: temperature, pressure and composition of the flue stream. The authors have over the years worked with biochar for the successful removal of elemental mercury atoms from a mixed flux gas stream in a similar manner. The value of the surface roughness of the biochar was seen as one of the key reasons for the success for the removal of this pollutant with an appropriate surface functional agent in place from a mixed flue gas stream. In this presentation the authors will provide an outline of results from several programs at the University of Saskatchewan which have focused upon the application of biochar for the control of greenhouse gas emission and other gases, such as elemental mercury. This presentation will outline the value of biochar for a flue gas stream control of these gases.

BIOREFINERY FOR GREENHOUSE TOMATO PLANT RESIDUES

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A biorefinery is a facility that integrates biomass conversion processes to produce a variety of valuable products from biomass, such as biofuels and biochemicals. The biorefinery concept is analogous to the petroleum refinery, which produces different types of fuels and products from petroleum, to extract as much value as possible from the feedstock. As fossil fuel reserves decrease, both production and environmental costs increase. In contrast, agricultural and forestry residues have low economic value but represent a potential source of energy and high value products, the latter subsidizing the cost of biomass conversion and biofuel production. The use of residues results in beneficial environmental and social impacts. Many high value products are currently produced from plants using complex, expensive and unsafe solvent extraction processes. Pyrolysis is much cheaper, simpler and safer but produces complex liquid mixtures from which it is difficult to recover the desired products. This paper presents a mechanically fluidized reactor (MFR) that combines batch pyrolysis with fractional condensation to produce a liquid with a high concentration of desired product, essentially a two dimensional (2-D) MFR pyrolysis process. With batch pyrolysis, the composition of the product vapors varies as the reactor temperature is raised, and one can select the reactor temperature range that corresponds to vapors with a high concentration of the desired product. Further product separation is performed in a fractional condensation train, which separates vapor components according to their condensation temperature. Another advantage of the MFR is that it produces a pure solid biochar. Greenhouse tomato stems and leaves (*Solanum lycopersicum*) were pyrolyzed in a batch MFR, yielding bio-oil, char and gas at 44, 32 and 24 wt%, respectively. Bio-oil (6 wt% yield) produced between 300-400 ºC showed the highest pesticidal activity against the selected species of insects, bacteria and fungi. Bio-oil (7 wt% yield) produced between 400-565 ºC had the highest concentration and recovery of antioxidant compounds (97 and 87 wt%, respectively). Gases produced through pyrolysis of tomato residues represent a potential fuel source, and activating the biochar product with carbon dioxide can provide a valuable adsorbent, which can be used to filter out pollutants. The biorefinery of tomato residue is a novel example of a sustainable process for converting biomass into a range of bio-based products (e.g., pesticides, antioxidants and activated carbon) and bioenergy (e.g., biofuels).

A REVIEW ON PLASMA TECHNOLOGIES APPLIED TO THERMO-CHEMICAL BIOMASS CONVERSION

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Key Words: Thermal Plasma, Non Thermal Plasma, Plasma Gaseification, Plasma Catalysis, Plasma Reforming, Plasma Pyrolisis

Plasma technology has been developped, patented and applied to the thermo-chemical conversion of the biomass. Most of the plasma technologies focus on plasma gaseification, plasma pyrolysis, plasma catalysis and more specifically plasma reforming and plasma gas cleaning. There is also the possibility of using plasma technology to heat the biomass. All of these plasma technologies have been introduced in order to improve the selectivity, the efficiency as well as the conversion of the biomass compared to traditional conversion reactors.

Plasma technology can be divided in thermal and non thermal plasma. Non thermal plasma technology uses low power systems with high energy levels for the electrons and low energy levels for the ions, which results in two temperatures plasmas. By carefully tuning the electrons energy it is possible to selectively modify specific molecules with an optimum energy coupling without heating a whole gas flow. Applications of such approaches are in the field of plasma catalysis and plasma gas cleaning. Non thermal plasma technologies which are typically used in the industry are arcs and gliding arc discharge, dielectric barrier discharge (DBD), corona discharge, glow discharge, radio-frequency and microwave discharge. The last two technologies don’t need electrodes for the energy coupling.

Thermal plasmas are used in medium size gaseifiers and pyrolisers They are famous for producing the purest syngas. As they can be operated with a lot of flexibility they can accomodate feedstock variations such as biomass water content, biomass type and variations in the biomass feeding rate. Typically the technologies which are concerned are the direct current plasma torches systems or the arc generated plasma. Because of the very high temperature of the plasma, the solids are vitrified and inertized.
Non thermal plasma technologies can be used downstream of the thermal plasma technology to treat the downstream gas as described in the non-thermal plasma section.

Overall plasma technologies applied to the biomass treatment found its way not only in pilot research projects but also in multi-megawatt industrial applications for thermal plasmas and in non thermal systems which are operating around the world..

A NEW TWO-DIMENSIONAL PYROLYSIS PROCESS FOR CONCENTRATING AND SEPARATING HIGH-VALUE LIQUID PRODUCTS FROM PLANT BIOMASS

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Many high-value products are currently produced from plants using complex, expensive and unsafe solvent extraction processes. Pyrolysis is much cheaper, simpler and safer but produces complex liquid mixtures from which it is difficult to recover the desired products. This paper presents a new two-dimensional pyrolysis process that combines batch pyrolysis with fractional condensation to produce a liquid with a high concentration of desired product. With batch pyrolysis, the composition of the product vapors varies as the reactor temperature is raised, and one can select the reactor temperature range that corresponds to vapors with a high concentration of the desired product. Further product separation is performed in a fractional condensation train, which separates vapor components according to their condensation temperature.

The new process is demonstrated for two applications: the separation of nicotine from tobacco (*Nicotiana tabacum*) and nepetalactone from catnip (*Nepeta cataria*). Nicotine has medicinal applications and nepetalactone is a valuable insect repellent. The nicotine concentration in the tobacco leaf used for this project was 1.1 wt% on a dry basis. Figure 1 shows how one can tailor the two-dimensional pyrolysis process to achieve an acceptable compromise between nicotine recovery and concentration. For example, combining a reactor temperature range of 230 to 275 ºC with a first condenser temperature of 190 ºC gave an oil with a nicotine concentration of 50 wt% that contained 77 wt% of the nicotine in the original tobacco leaf.

The application of the two-dimensional pyrolysis process for the extraction of nepetalactone from catnip plant biomass is on-going, but preliminary results are encouraging.

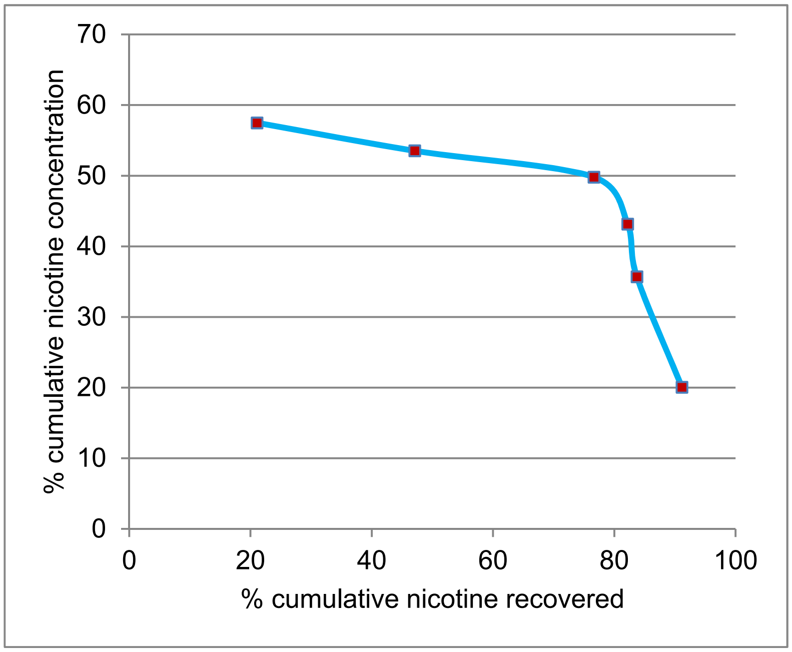

Figure 1. Percent cumulative nicotine concentration and recovery from tobacco leaf biomass by two-dimensional pyrolysis process.

FRACTIONATION OF FLASH PYROLYSIS CONDENSATES BY STAGED CONDENSATION

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Key Words: flash pyrolysis, pyrolysis liquid fractionation, pyrolysis liquid utilization

The utilization of condensates from flash pyrolysis is challenging due to several unwanted properties. The condensates consist of a mixture of many very different compounds, which would have high value in pure occurrence, but each of them are only contained in a low concentration. As additional challenge instantaneous phase separation into an aqueous and a sludgy heavy organic phase takes place, if agricultural residues like barley straw are used as raw material for pyrolysis. A separation of components by means of distillation is not possible as the compounds undergo heavy polymerization reactions when exposed to higher temperature, especially in presence of acids. After removal of water and acetic acid an asphalt-like solid residue remains, which can only be considered as waste without value.

A different approach for separation of components based on boiling temperature is the staged condensation of original pyrolysis vapors with decreasing cooling temperature in the individual steps. Ablative flash pyrolysis of different biomasses is performed in a laboratory plant designed for a capacity of 10 kg/h input. The cylindrical biomass with a diameter of 50 mm is pressed by hydraulic piston against an electrically heated, rotating plate. The pyrolysis vapors are cleaned from fine dust by means of a cyclone and condensed in three stages, each composed of a double-effect cooler followed by an electrostatic precipitator (Figure 1). Figure 2 shows samples of condensates produced by this unit and also the volumetric yield distribution.

Fraction 1 is a very viscous organic liquid, which mainly comprises of oligomeric lignins and sugars with high lower heating value (28 MJ/kg) and low water (2 %) and acid content (1 %). This makes it applicable as sulfur-free bunker fuel and replacement of heavy fuel oil. It can also serve as fuel for gasification plants for the production of either combined heat and power or 2nd generation biofuels.

Fraction 2 has a medium lower heating value (22 MJ/kg), moderate water (8 %) and acid content (6 %) and a high content of methoxylated and alkylated phenols (> 16 %), which make this fraction interesting for the production of phenolic resins.

The last fraction obtained at the lowest cooling temperature mainly consists of water (70 %) and acids (17 %) with a lower heating value of only 6 MJ/kg. The production of pure acetic acid seem economically feasible from this fraction and an utilization in agricultural biogas plants is also possible. This is proved by batch fermentation experiments in the biological laboratories.

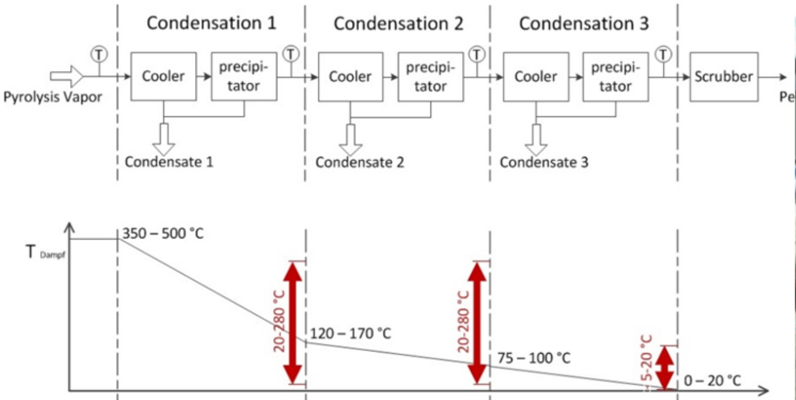

Figure 1 – Schematic of condensation line

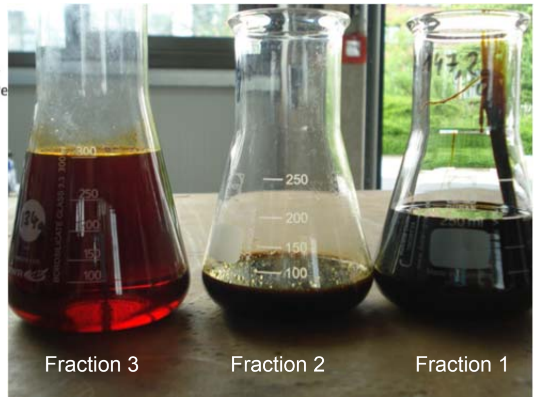

Figure 2 – Product samples

ADVANCED FUELS AND COPRODUCTS FROM TAIL-GAS REACTIVE PYROLYSIS (TGRP) BIO-OIL

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Key Words: pyrolysis, bio-oil, hydrodeoxygenation, biofuels, biomass

To attain an environmentally and financially sustainable fuel economy, the U.S has mandated that by the year 2022, at least 36 billion gallons of all fuels produced in the US must come from biofuels; this is better known as the renewable fuels standards (RFS), as part of the Energy Independence and Security Act of 2005. While corn grain ethanol has proven to be an effective alternative fuel, in 2015 the EISA will also restrict the maximum corn starch-based fuel obtained to 15 billion gallons. Hence, the majority of the RFS must come from other “advanced biofuels” which utilize the entire plant. Thermochemical conversion technologies such as pyrolysis and gasification were then brought under the spotlight; they are the only technologies capable of converting the entire plant into fuels compatible with refinery processes. Such a technology is also necessary to make use of excess refuse from plants, including sugar cane, oil palm, and sorghum to name a few.

In this presentation, we will discuss three ways in which the TGRP process lends itself towards optimal utilization of all bio-oil streams. First, the TGRP process allows for the pyrolysis of feedstocks which were not otherwise possible with traditional pyrolysis. Guayule bagasse normally cannot be pyrolyzed into usable oil due to the very high viscosity resins present. With the TGRP process, low viscosity bio-oils are produced with as low as 8 wt% oxygen on a dry basis. Second, the TGRP oil comprises thermally stable compounds, such that efficient distillation and recovery of dry organic compounds is possible in high yields (~65%), with the distillate bottoms available for conversion into calcined coke. Third, TGRP distillates, by way of their low molecular weight and viscosity, enhance the efficiency of hydrodeoxygenation (HDO) reactions for production of fuels and commodity chemicals. Higher space velocities (LHSV > 0.6) are attainable when TGRP oil distillates undergo continuous HDO in a packed bed reactor. Due to the absence of coke precursors, HDO of distillates produces as high as 70 – 80 wt% yields of hydrocarbons. Case studies using guayule bagasse and algae-based bio-oils will be discussed.

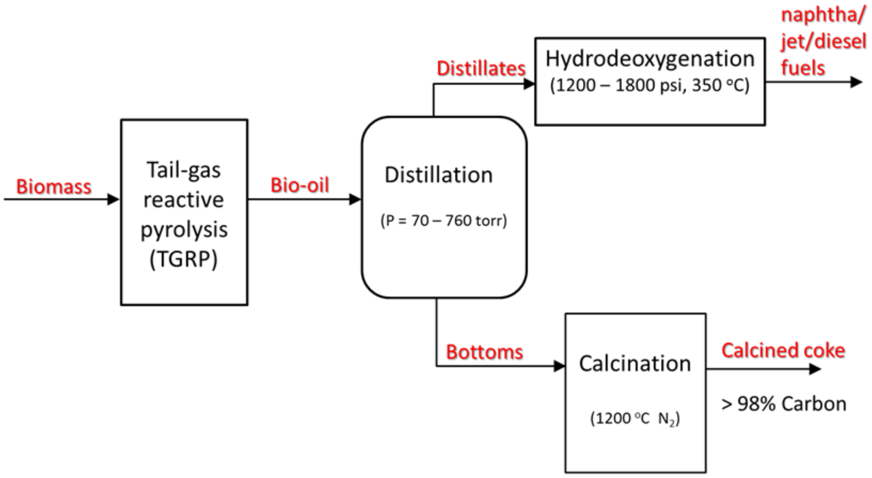

Figure 1 – processes for conversion of TGRP bio-oils into fuels and coproducts.

SYNTHETIC FUELS FROM 3-φ FISCHER-TROPSCH SYNTHESIS USING BIO-DERIVED GAS FEED AND NOVEL NANOMETRIC CATALYSTS

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Key Words: Synthetic Fuel; Fischer-Tropsch; Nanocatalyst, Biorefinery; Biogas; Biosyngas

In this study, synthetic fuel is produced from biomass through Fischer-Tropsch Synthesis (FTS) in a lab-scale setup. Two catalyst families of nanometric cobalt or iron-supported on carbon (Co/C and Fe/C) were synthesised by the plasma spray method and tested for FTS in a slurry continuous stirred tank reactor (S-CSTR). They have been tested as such as well as doped (promoted) with gold (Au) and nickel (Ni) or molybdenum (Mo).

Prior to the tests, and due to the pyrophoric nature of these materials, the catalysts are reduced *in situ* for at least 10 hours at various temperatures (150 – 350°C) in pure H_2 gas, flowing at 250 $ml.min^{-1}$ and 1-2 bar pressure. A feed stream typical of biosyngas [H_2:CO ratio = 2:1] was used, consisting of 60% H_2 and 30% CO, with 10% Ar included for the mass balance closure calculations.

At steady state (after 18 hours on stream, 220°C, 30-bar, GHSV = 3 600 $ml.g_{cat}^{-1}.h^{-1}$), the Co/C catalyst was observed to be more selective towards heavier products such as wax. Devoid of any promoters, the Co/C catalyst achieved over 40% CO conversion, while the Fe/C catalyst showed CO conversion above 20%. Stirring speeds of over 1,800 rpm depressed water formation. Scanning Electron Microscopy (SEM) showed high metal dispersion, while analysis by X-ray Absorption Near-Edge Spectroscopy (XANES), X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD) indicated predominant presence of metallic cobalt species in the fresh and reduced catalysts. However, in the iron-based catalysts, XANES and XRD analysis showed the concurrent presence of metallic and carbides species (possibly Fe_5C_2 or Fe_3C).The XRD pattern of the initial cobalt powder used in sample preparation contained two phases: hexagonal and cubic, but after plasma synthesis, the catalyst appeared to exist in the cubic phase only (Figure 1).

The results with the Au/Ni or Mo-doped (promoted) catalysts will also be available and presented in the conference. Detailed analytical results and interpretation will allow a techno-economic comparison and express an objective opinion about the feasibility of an eventual commercial plant within a Biorefinery.

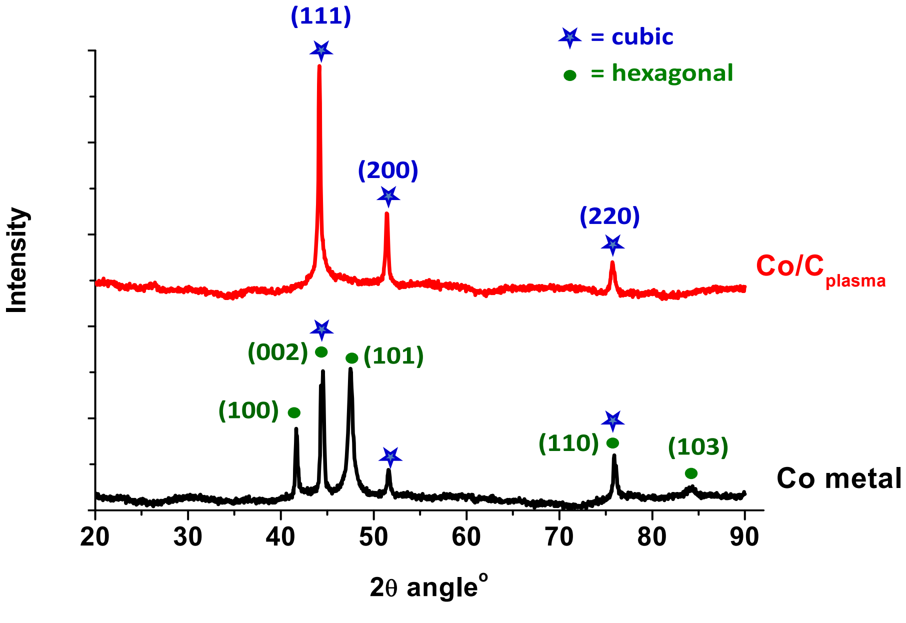

Figure 1 – XRD Analysis of Co-based catalyst

PROCESS CONCEPTS FOR CONVERSION OF SUGAR CANE RESIDUE TO VALUE ADDED PRODUCTS

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Key Words: Techno-economics, 2G Biofuels, Process Simulation, Modelling

The transition from fossil sources to biomass in order to produce electricity, heat, fuels and chemicals has received significant interest during recent years. Nevertheless the exploitation of the residues of such bio-refineries has not yet been established on a large commercial basis. The optimum exploitation route of sugar cane solid residue, bagasse, is investigated in this study in order to strengthen the existing bio-refineries. This study compares in terms of technological (energy/exergy and pinch analysis) and economic (financial and risk assessment) feasibility both thermochemical and biochemical processes **(Figure 1)**.

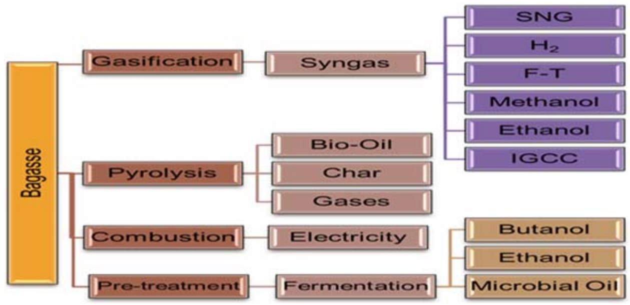


Figure 1 – Bagasse conversion routes

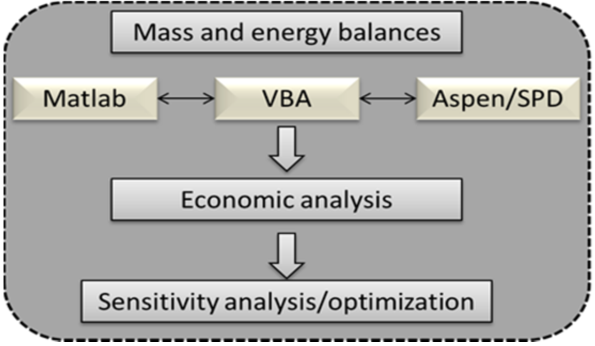


Figure 2 – Methodology

For each pathway a base case scenario has been developed by employing both Aspen Plus or SuperPro Designer simulators and Matlab software for modelling the reactor kinetics of each process **(Figure 2)**. Different routes for each case were designed and tested. The present research makes a consistent and comparative assessment of the overall thermodynamic and economic efficiencies **(Figures 3 and 4)** of the potential biomass-to-value added products conversion options and based on this result, gives a recommendation as to which of the options assessed is most desirable. Mass and energy balance data were extracted from the simulations and the overall yields and financial efficiencies of each process were determined and compared.

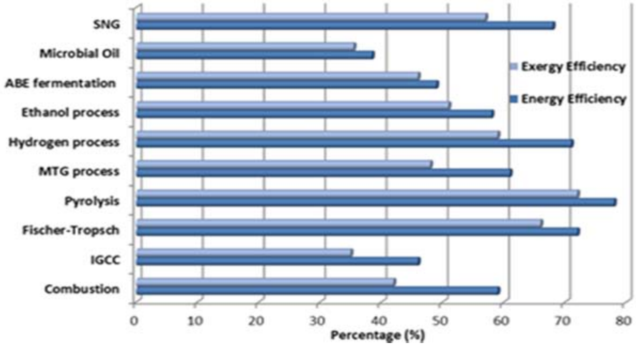


Figure 3 – Thermodynamic efficiencies

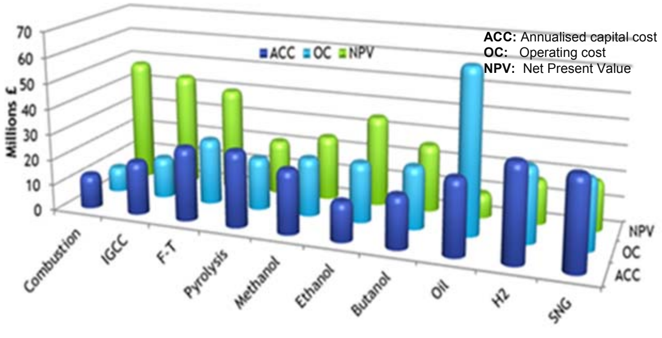
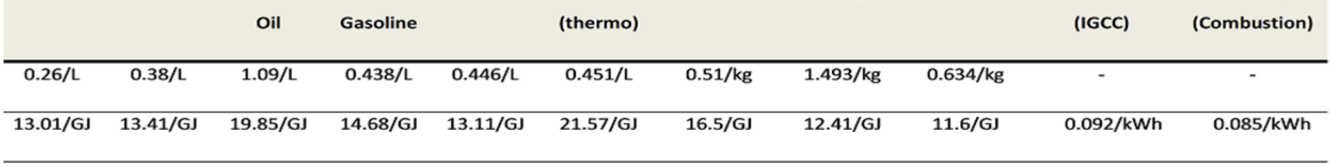


Figure 4 – Financial analysis results

After the selection of one representative from each pathway, fully sensitivity analysis, based on Monte Carlo principles, was conducted in order to define key variables. Finally, optimization was carried out using mixed integer non-linear programming (MINLP) solved with the General Algebraic Modelling System (GAMS), setting as objective function the minimization of production cost **(Table 1)**. All of the processes seem to attain a considerable return. The project plan of bagasse utilization should not exclude electricity production; however the private sector needs to explore other pathways so as to meet the growing demand for liquid fuels.

Table 1 - Biofuel production cost



Ethanol	Butanol	Microbial Oil	MTG Gasoline	F-T fuels	Ethanol (thermo)	Bio-oil	Hydrogen	Methane	Electricity (IGCC)	Electricity (Combustion)
0.26/L	0.38/L	1.09/L	0.438/L	0.446/L	0.451/L	0.51/kg	1.493/kg	0.634/kg	-	-
13.01/GJ	13.41/GJ	19.85/GJ	14.68/GJ	13.11/GJ	21.57/GJ	16.5/GJ	12.41/GJ	11.6/GJ	0.092/kWh	0.085/kWh

ELECTRICAL CHARACTERIZATION OF DIFFERENT CARBON BASED POLYMER COMPOSITES

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Key Words: Multi wall carbon nanotube, Organic residues, Epoxy resin, Complex Permittivity

Electrical properties of polymer composites based on carbon filler are a hot spot in recent years [1,2]. As sp2 hybridised carbon is a good conductor due to the mobility of electrons in its outer valence shells, it can be used as filler material. The consequent possibility to tune electrical properties of composites lead to new applications for them. While carbon naontubes are the most commonly used form of carbon in composites, less expensive and more environment friendly carbon-based fillers derived from recycled materials are attracting more and more interest.

In this work, we will compare the electrical properties (permittivity and electrical conducibility) of polymer filled with CNTs and polymer filled with alternative carbon fillers derived from organic residues. In particular, the solid result of pyrolysis treatment on organic residues will be considered. This material is a carbon based one characterized by a high surface area (up to 1000 m^2/g).Nanocomposites are prepared using various types of multi walled CNTs (MWCNTs) with aspect ratio (AR) ranging from 200 to 1000 and alternative carbon fillers derived from organic residues. A commercial thermosetting resin will be used as polymer matrix and a Field Emission Scanning Electron Microscopy (FESEM) will analyze the degree of dispersion of the filler. Raman spectroscopy will be used to evaluate the carbon materials.The complex permittivity will be measured by using a commercial probe (Agilent 85070D) and a Network Analyser (E8361A) [3,4]. An example of the real part of permittivity and the AC electrical conductivity of a MWCNT (AR=1000) composite is shown in Fig. 1. As it was expected, higher values of both real permittivity and AC conductivity are observed for increasing wt.% of MWCNTs loading.

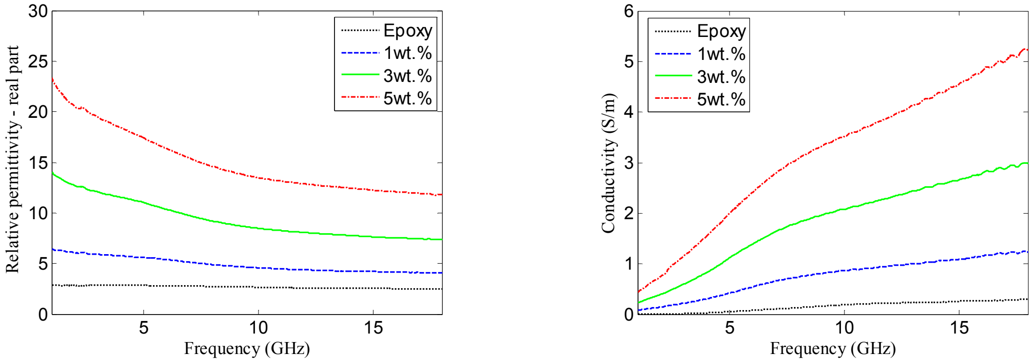

Figure 1 - Electrical properties of polymers composite as a function of filler contents for the case of MWCNT.

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CASTOR BEAN CAKE UPGRADING VIA THERMAL AND CATALYTIC PYROLYSIS

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Introduction

Thermal and catalytic pyrolysis is an efficient process for the transformation of biomass to bio-oil, a liquid energy carrier and a general source of chemicals [1]. In the Jonah fuels project castor bean residues upgrading towards fuels production via thermochemical refinery processes is studied. The castor beans originated from different species of castor bean cultivation and the cakes formed after crushing the beans so as to receive the castor oil. Leftover stalks were also used as feed in the pyrolysis process. The experimental procedures have been described elsewhere [1]. Although there are no significant differences in the elemental analysis of the different feeds, the pyrolysis results were significantly dependent on the type of feedstock used. Mass balances of the thermal pyrolysis products are presented in table 1.

Table 1. Thermal pyrolysis product yields and bio-oil elemental analysis

	Wt.% on dry biomass				Wt.% on dry bio-oil		
	Gas	Coke	Water	Bio-oil	C	H	O
Castor Cake #1	12.39	35.12	18.83	33.65	63.38	10.10	26.52
Castor Cake #2	12.94	34.82	17.99	34.25	64.02	10.24	25.74
Castor Stalks	19.57	25.52	27.81	27.10	57.71	7.75	34.54

In the case of both castor cake samples, both bio-oil and coke production were higher compared to the castor stalks which can be considered a standard biomass feed. Interestingly enough, the castor cakes also produced better quality bio-oils with significantly lower O_2 content compared to the castor stalks. The presence of residual oil in the cake resulted in higher bio-oil yields. This was confirmed by the significantly higher CO_2 yield, compared to CO yield, which is attributed to decarboxylation reactions of the fatty acids of residual castor oils. Catalytic in situ upgrading and bio-oil characterization by GCMS showed that high value products such as aromatic hydrocarbons can be produced. ZSM-5 catalytic upgrading increased bio-oil quality significantly by lowering O_2 content.

Conclusions

Castor bean cakes pyrolysis proved to be a very interesting method for upgrading castor oil residues. The produced bio-oils originating from castor cakes were of better quality compared to bio-oils produced from typical biomass. Catalytic upgrading affected both the product yields and the oil quality significantly, enhancing deoxygenation reactions and aromatic hydrocarbons production.

Acknowledgements

The research leading to these results has received funding from the project JONAH-FUEL, “CASTOR bean (JONAH seed) cultivation in central Macedonia, Greece and industrial exploitation of its derivatives towards BIOFUELs’ production”, agreement no. ISR_3176.

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Posters

Biorefinery I: Chemicals and Materials from Thermo-Chemical Biomass Conversion and Related Processes

September 27-October 2, 2015

Crete, Greece

Engineering Conferences International

Poster Presentations

1. **Fast pyrolysis of differently-treated birch (Betula pendula) sawdust by Py-GC/MSD**
   Maryam Ghalibaf, University of Jyvaskyla, Finland

2. **Bio-char for carbon fibers production**
   Mauro Giorcelli, Politecnico di Torino, Italy

3. **Optical investigation of reaction rates for Hydrothermal Carbonization (HTC) of dry organic matter**
   Andreas Frohner, University of Natural Resources and Life Sciences, Vienna, Austria

4. **Development of the continuous process of solvolytical conversion of lignin to bio-oil – Lignosolv**
   Camilla Løhre, University of Bergen, Norway

5. **Effect of castor bean biochar on plant germination and growth response**
   Zoe Hilioti, INEB/CERTH, Greece

6. **Influence of temperature and residence time in the quality of the charcoal obtained from biomass waste pyrolysis in a continuous screw reactor**
   Jon Solar, UPV/EHU, Spain

7. **SPME-GC-MS determination of mobile compounds in biochar**
   Michele Ghidotti, University of Bologna, Italy

8. **Biomass upgrading and catalyst characterization using a Tandem Catalytic Reactor - GC/MS System**
   Michael Soll, Frontier Laboratories Europe, Germany

9. **Castor bean cake upgrading via thermal and catalytic pyrolysis**
   Kostas Kalogiannis, CPERI/CERTH, Greece

10. **Economic model of a novel process for the fractionation of dried distillers grain with solubles**
    Roman Zakrzewski, University College London, United Kingdom

11. **Water content determination of olive kernels from Chalkidiki and Kalamata olives**
    Aleksander Hykkerud, Norwegian University of Life Sciences, Norway

12. **CO2 capture on bio-based activated carbons**
    Ajay Dalai, University of Saskatchewan, Canada

FAST PYROLYSIS OF DIFFERENTLY-TREATED BIRCH (*Betula pendula)* SAWDUST BY PY-GC/MSD

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Key Words: lignocellulose, pyrolysis-gas chromatography, hardwood, hot-water extraction, biorefinery.

Fast pyrolysis of lignocellulosics has been investigated under a variety of conditions and from several points of view, since by this straightforward technique it is possible to produce liquid biofuels and chemicals [1-2]. On the other hand, biomass pre-treatment technology plays an important role in many biorefinery processes based on lignocellulosics. According to an integrated forest biorefinery (IFBR) concept, one interesting approach, mainly for recovering valuable carbohydrates-derived material, is to apply hot-water extraction ("autohydrolysis") (HWE) to wood chips or sawdust prior to pulping [3]. Besides utilizing the pre-treated wood material for delignification, it might also be a potential feedstock for thermochemical conversion [4-7]. In this study, the fast pyrolysis of untreated (B_{ref}) and hot-water-extracted (170 °C, 38 min) (B_{HWE}) birch (*Betula pendula*) sawdust as well as the soda-anthraquinone(AQ)-cooked (18 % active alkali, AQ 0.1 %, 90 min) pulps of untreated (P_{ref}) and of hot-water-extracted (P_{HWE}) birch feedstocks was investigated by pyrolysis-gas chromatography with mass-selective detection (Py-GC/MSD). The main idea was to detect differences in the thermochemical behavior of these feedstocks with varying chemical composition for evaluating their suitability for pyrolysis. In each case, two pyrolysis temperatures (500 °C and 700 °C) and two residence times (5 s and 20 s) were applied. Major GC-amenable pyrolysis products were classified into several compound groups (mainly furans, phenols, ketones, anhydro sugars, and carboxylic acids including their derivatives) and changes in the relative portions of these monomer-related fragments were determined under varying conditions. The formation of the main products was shown to be characteristically dependent on feedstock and reaction conditions. For example, the peak area% of levoglucosan (with a residence time of 20 s) in pyrolysis products of B_{ref} was 8% (500 °C) and 4.5% (700 °C), whereas the corresponding values for P_{ref} were 23.5 % (500 °C) and 26.2 % (700 °C). In case of B_{HWE} and P_{HWE}, the peak area% obtained were 16.7 % at 500 °C (14.9% at 700 °C) and 21.7% at 500 °C (32% at 700 °C), respectively. Examples of the similar "fingerprint" compounds derived typically from lignin and carbohydrates (cellulose and hemicelluloses) were furfural, 5-(hydroxymethyl)furfural, phenol, 1,2-dihydroxybenzene, 2-methylphenol, 1,2-dihydroxy-3-methylbenzene, guaiacol, syringol, 1-hydroxy-2-propanone, 1,3-cyclopentadione, 2,6-dimethyl-3-(methoxymethyl)-*p*-benzoquinone, and methyl acetate.

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BIO-CHAR FOR CARBON FIBERS PRODUCTION

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As a consequence of the Kyoto protocols on CO2 emission reduction, the transition towards a bio-based economy and sustainable developments offers high perspectives for natural fibres markets. As a consequence polymer-natural fibres composites have been investigated for many applications. Several kinds of natural fibres exist around the world: bamboo in Japan, coconut in equatorial countries [1]. They are supposed to be one of the strongest natural fibres available in nature. Considering continues growing global carbon fibers demand for various applications, we tried to investigate the possibility to convert natural fibres to carbon fibres by pyrolysis. The aim of the study was to use cost effective, easily available, environment friendly material to produce carbon fibers. This may become in perspective substitutes for traditional polymeric precursors of CFs. Carbonised Fibers was studied by FESEM and TGA.

Fig.1a shows the FESEM of carbonised bamboo fibres. It shows micro voids on the surface. Fig.2a shows the coconut carbonised fibres. It shows the microporous channels in structure. TGA was performed at 10 0C/min temp ramp rate in presence of air. Carbonised Bamboo fibres (Fig.1b) show a gradual thermal degradation from 300 to 700 0C with 1.5 wt. % inorganic residue. Carbonised coconut fibres (Fig.2b) show thermal degradation from 400 to 650 0C with 1.5 wt. % inorganic residue. Further study will be performed to use these materials in applications.

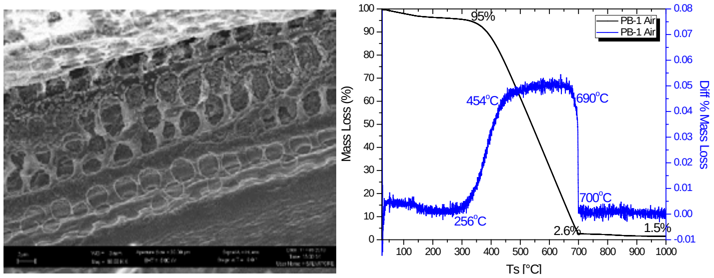

Figure 1 (a) FESEM of carbonised bamboo fibre (b) TGA in air

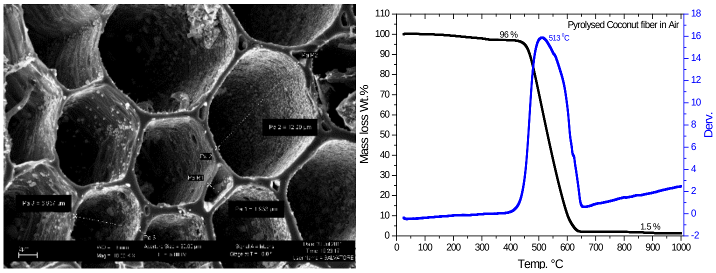

Figure 2 (a) FESEM of carbonised coconut fibre (b) TGA in air

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OPTICAL INVESTIGATION OF REACTION RATES FOR HYDROTHERMAL CARBONIZATION (HTC) OF DRY ORGANIC MATTER

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Key Words: Hydrothermal carbonization, Biochar

Hydrothermal Carbonization (HTC) is a promising chemical process for treatment of biomass. The resulting carbon-rich product, also known as hydrochar, can be used e.g. as bio-fuel for energy generation or as fertilizer. In this work, an experimental campaign has been conducted in an optical cell under realistic HTC process conditions (temperatures between 180 and 200 °C). It is assumed, based on literature as well as on fundamental research, that the grade of carbonization is connected with the colour of the probe. Due to this assumption, it is possible to determine the carbon content online during the process with a colour measurement and following a simple calculation. The carbon content before and after the process needs to be known. Therefore, reaction rate data are obtained for different wood derived feedstocks.

Poster Number 3

DEVELOPMENT OF THE CONTINUOUS PROCESS OF SOLVOLYTICAL CONVERSION OF LIGNIN TO BIO-OIL – LIGNOSOLV

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Work objective and relevance: After fractionation of lignocellulosic biomass to give carbohydrates that can be hydrolysed into sugars and fermented to ethanol, lignin is left as a residual material. Development of thermochemical conversion routes for production of lignin derived bio-oils, such as the Lignin-to-Liquid (LtL) oils [1], needs further research on how the different biomass feedstocks affect the product yield and composition. Organosolv fractionation of lignocellulosic biomass has been considered as a potential pretreatment technique to be combined with the LtL-conversion into a continuous system. Organosolv pretreated lignin [2] has been tested in batch LtL-conversion giving high product yields of a phenolic rich oil. For a more efficient conversion process, the construction of a continuous setup has been initiated, aimed at separating lignin from biomass using Organosolv solubilisation.

Methodology: Systematic experiments on a lignin rich residue originating from enzymatic hydrolysis of Eucalyptus, using different reaction conditions (temperature) and solvolytical reaction ratios (formic acid), were performed. A fraction of the lignin rich material was also exposed to Organosolv solubilisation to investigate potential effects of the raw materials purity. The bio-oil products were quantified after consistent workup procedures and the oil phases were thereafter analysed by mass spectrometry coupled with gas chromatography (GC-MS) to provide a basis for evaluation of suitability of feedstock on product distribution and product composition. Both the oil phase and the solid residue were analysed by elemental analysis to evaluate elemental composition and conversion efficiency.
The continuous setup arising from Organosolv investigation consists of a pressure pump pumping a solvent mixture through a heated column packed with lignocellulosic biomass. After solubilisation, the solubilised lignin is collected, dried off and consequently converted by LtL-solvolysis. The bio-oil products are quantified and analysed using the same workup procedures as the preliminary experiments.

Results: Eucalyptus lignin, previously exposed to enzymatic hydrolysis, showed a prominent decrease in oxygen content after Organosolv cleaning. This resulted in a highly increased oil yield after LtL conversion compared to the lignin-rich Eucalyptus residues directly after enzymatic hydrolysis. Compositional differences in the LtL oils from different lignin raw materials are limited, yet still present. These results will be presented, together with an evaluation of the continuous system comprising Organosolv pretreatment and LtL conversion for the production of fuel or as a basis for production of valuable chemicals.

Conclusion: The pretreatment technique shows a significant influence on quantitative results, and also influences molecular distributions in LtL oils to some degree. Continuous separation processes are an alternative to batch separation.

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EFFECT OF CASTOR BEAN BIOCHAR ON PLANT GERMINATION AND GROWTH RESPONSE

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Key Words: biochar, castor, oilseed crop, germination, plant growth promotion

Castor bean (Ricinus communis) is an oil crop of great economic importance as the seeds are the source of castor oil, a non-ebidle oil with numerous industrial applications. The extraction of castor oil results in the generation of large amounts of the de-oiled castor cake, a solid residue that is usually discarded and contains the highly toxic glycoprotein ricin and therefore requires treatment prior to its valorization [1,2]. Thermochemical conversion technologies, for example pyrolysis, constitute a promising route for biomass valorization. In particular, slow pyrolysis is performed at temperatures up to 700^{o}C and aims to the maximization of the solid residue of added value called biochar [3]. Biochar is a carbon-rich renewable product with distinct physicochemical properties that can enhance soil quality if used as soil amendment. Furthermore, biochar incorporation into soil has the potential to reduce the levels of atmospheric greenhouse gas emissions because of carbon storage into soil.

In this study, biochar was produced from castor oil press cake and stalks both by-products of the castor production, in view of sustainable valorization of a potential large scale cultivation of castor beans in Greece. The two types of biochars produced were fully characterized physicochemically (ash content, elemental analysis, ICP-OES, HHV, SEM, BET). The effect of the biochar as soil amendment was investigated in pots on germination and growth of a castor hybrid bred for mechanized harvesting. The soil was amended with two different types of biochar at three levels of concentration (0, 1 and 5% w/w) and the plants were grown under controlled conditions. Based on the results, differences on seed germination pattern and plant growth responses were found compared to control soil lacking biochar. The results suggest that biochar has the potential to improve castor bean production but the effect of biochar application is highly dependent on biochar type and concentration.

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INFLUENCE OF TEMPERATURE AND RESIDENCE TIME IN THE QUALITY OF THE CHARCOAL OBTAINED FROM BIOMASS WASTE PYROLYSIS IN A CONTINUOUS SCREW REACTOR

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Key Words: biomass waste, pyrolysis, screw reactor, charcoal, reducing agent

During the pyrolysis process (heating in the absence of oxygen), biomass is mostly decomposed into liquid and gaseous products, which can be used as fuels and/or source of chemicals. In addition, a solid product known as charcoal, biocoke or biochar is also generated. Charcoal is mainly composed of carbon and has been reported to have several applications such as fuel, soil-amender or fertilizer, catalyst and adsorbent. Additionally, recent research indicates that if high temperatures (700ºC) are reached through slow pyrolysis, a solid product useful for metallurgical applications can be obtained.

The objective of this work is to study the influence of temperature and residence time in the quality of the biochar obtained in the slow pyrolysis of biomass waste in order to be useful as a reducing agent in metallurgical applications.

The sample pyrolyzed is 2-0.5 mm particle size woody biomass waste sample (*pinus pinaster*) coming from forest maintenance activities carried out in the north of Spain. The experiments are carried out in a continuous laboratory scale plant that consists of two reactors in series. Firstly biomass pyrolysis takes place in a screw reactor where 90 g h^{-1} of biomass is treated at high temperatures. The external heating of the reactor is composed of four heating zones that can be set individually, so that, combined with the speed of the screw, the desired residence time and heating rate can be performed. Then, after a physic separation of the charcoal the pyrolysis vapors are driven to a tubular reactor, where they are treated at 900 ºC in order to enhance gas yield, avoid tar formation and obtain high value gases which can be used for different applications (source of hydrogen, synthesis gas or gas fuel).

Different temperature profiles in the screw reactor achieved programming the four heating zones of the external heating have been tested: a) 573-723-873-1023 K and 573-773-973-1173 K which imply slow gradual heating totwo different final temperatures (750 & 900ºC) heating of the biomass at different final temperatures; b) 1173-1173-1173-1173 K which suppose a faster heating rate combined with a longer exposition to high temperature. Additionally, different residence times have been studied with the temperature profile that had given the best results in terms ofsolid yield and charcoal quality in order to check the effect of the heating rate, exposition time to final temperature and solid-vapor contact. The initial sample, as well as the solid, liquid and gaseous products obtained in the experiments were quantified and thoroughly characterized. Concerning the charcoal the characterization includes its elemental and proximate analysis, high heating value and reactivity tests.

The results show that working at higher temperatures (900 ºC) produces less solid due to a higher carbonization degree of the charcoal, along with a higher gas yield and no tars. Fast pyrolysis gives rise to a quick devolatilization of vapors, with two consequences. On the one hand high temperatures induce further vapors cracking producing lighter molecules that are less reactive with the solid char surface than heavier molecules. On the other hand quicker devolatilization means less solid-vapor contact time. Residence time has some impact on pyrolysis yields, especially on solid yield.

SPME-GC-MS DETERMINATION OF MOBILE COMPOUNDS IN BIOCHAR

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Key Words: pyrolysis, biochar, volatile organic compounds, solid-phase microextraction.

Biochar production from the pyrolysis of residual biomass could be a strategy to turn often unexploited streams of secondary products into a valuable resource. Given its high stability and potential amendment effect, biochar use in agriculture is promising. However, thermochemical process conditions highly influence biochar physical and chemical properties to the extent that low molecular weight compounds could be retained onto its porous complex surface. When not irreversibly adsorbed, these substances could have a certain degree of mobility in water or could be released as vapours (VOCs), potentially generating both beneficial as well as detrimental effect on biota (e.g. plants, microorganisms) [1].

The need of a deep understanding of biochar "volatilome" is important when considering large scale applications to soil and handling of this material and represents an emerging field of research. Qualitative assessment of these compounds was performed on biochar and similar matrices, e.g. on hydrochars by headspace (HS) and gas chromatography-mass spectrometry (GC-MS) [2, 3].

Solid-phase microextraction (SPME) is a solventless valid technique for the determination of low molecular weight compounds in a variety of matrices. However, its application to biochar is new and few reports have dealt with this approach [4]. Due to its on-fiber pre-concentration capabilities, SPME was proved to be a valuable technique for the characterization of trace compounds in biochars; direct immersion SPME coupled with GC-MS was effective in determining lignin phenols from methanol extracts of lignocellulosic biochars.

In this study, a faster HS-SPME-GC-MS method with minimal sample treatment (weighting, heating) was developed and tested on biochar samples obtained from the pyrolysis of different biomass substrates; data were compared with SPME of aqueous extracts to obtain a deep knowledge of mobile trace organic compounds that may occur in biochar. Different classes of molecules were detected after HS-SPME, ranging from non-polar alkyl aromatics, small PAHs, phenols, nitrogen-organic compounds to polar fatty acids, effectively showing that this technique is suitable to determine with minimal sample treatment a wide range of volatile compounds in biochars from various feedstock and the process conditions.

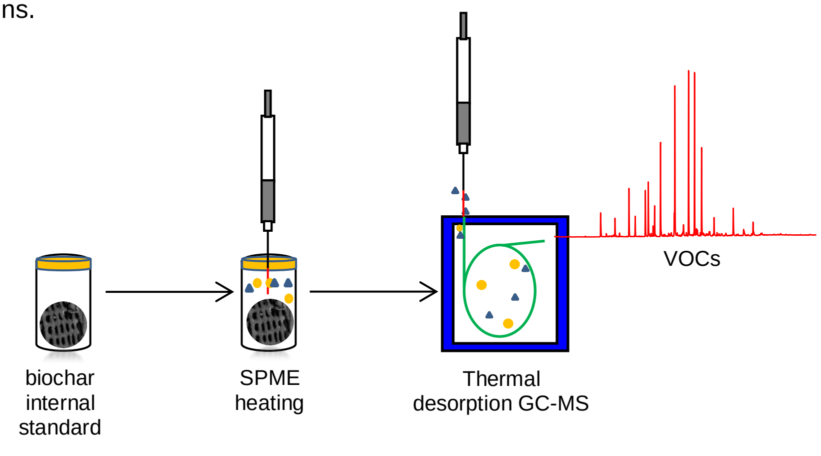

Figure 1: Scheme of HS-SPME-GC-MS method developed for the determination of VOCs in biochar

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Poster Number 7

BIOMASS UPGRADING AND CATALYST CHARACTERIZATION USING A TANDEM CATALYTIC REACTOR - GC/MS SYSTEM

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Fossil fuel exhaustion and the concerns for environmental contamination have increased the demand for alternative energy sources. Biomass is considered a candidate energy source for bio-fuel production because of its renewability, low cost, large availability, low sulphur content, and low greenhouse gas emission.

The promise of converting various biomass feed stocks directly to biofuels or value-added specialty chemicals using catalytic pyrolysis has precipitated a demand for a fast, reliable method to characterize newly developed catalysts. Catalytic pyrolysis is a three-step process: (1) the feedstock is first pyrolyzed (which is often referred to as “fast pyrolysis”), (2) the pyrolyzates flow through a catalyst bed and (3) the ‘products’ are identified and quantitated. The tandem micro-reactor GC/MS system integrates these three processes into a single bench-top instrument.

The tandem catalytic reactor is designed for the rapid evaluation and characterization of catalysts in various atmospheres, at different temperatures and pressures. Three modes of operation allow different experiments to be conducted on the same equipment. The GC/MS can operate in an on-line MS mode for continuous analysis of gases from the catalyst bed. Alternatively, the GC/MS can operate in several integrated high resolution GC/MS modes for step-wise experiments on gases exiting the catalyst bed. There is also a flash vaporization mode is used for the pyrolysis of a solid sample.

The system consists of an upper micro-furnace and lower micro-reactor each with independent temperature and reaction gas controls. The micro-furnace can accept solid or viscous liquid samples in a batch sampling mode with catalysis occurring under different conditions in the micro-reactor. The micro-reactor is designed to allow a quick change of the catalyst bed. Batch or continuous experiments can be performed with this system to evaluate both catalyst performance and to characterize catalysis products. Provisions are also designed into the system to allow catalyst regeneration and evaluation. Each capability outlined above will be illustrated using ethanol, wood flower and a variety of catalysts.

CASTOR BEAN CAKE UPGRADING VIA THERMAL AND CATALYTIC PYROLYSIS

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Introduction

Thermal and catalytic pyrolysis is an efficient process for the transformation of biomass to bio-oil, a liquid energy carrier and a general source of chemicals [1]. In the Jonah fuels project castor bean residues upgrading towards fuels production via thermochemical refinery processes is studied. The castor beans originated from different species of castor bean cultivation and the cakes formed after crushing the beans so as to receive the castor oil. Leftover stalks were also used as feed in the pyrolysis process. The experimental procedures have been described elsewhere [1]. Although there are no significant differences in the elemental analysis of the different feeds, the pyrolysis results were significantly dependent on the type of feedstock used. Mass balances of the thermal pyrolysis products are presented in table 1.

Table 1. Thermal pyrolysis product yields and bio-oil elemental analysis

	Wt.% on dry biomass				Wt.% on dry bio-oil		
	Gas	Coke	Water	Bio-oil	C	H	O
Castor Cake #1	12.39	35.12	18.83	33.65	63.38	10.10	26.52
Castor Cake #2	12.94	34.82	17.99	34.25	64.02	10.24	25.74
Castor Stalks	19.57	25.52	27.81	27.10	57.71	7.75	34.54

In the case of both castor cake samples, both bio-oil and coke production were higher compared to the castor stalks which can be considered a standard biomass feed. Interestingly enough, the castor cakes also produced better quality bio-oils with significantly lower O_2 content compared to the castor stalks. The presence of residual oil in the cake resulted in higher bio-oil yields. This was confirmed by the significantly higher CO_2 yield, compared to CO yield, which is attributed to decarboxylation reactions of the fatty acids of residual castor oils. Catalytic in situ upgrading and bio-oil characterization by GCMS showed that high value products such as aromatic hydrocarbons can be produced. ZSM-5 catalytic upgrading increased bio-oil quality significantly by lowering O_2 content.

Conclusions

Castor bean cakes pyrolysis proved to be a very interesting method for upgrading castor oil residues. The produced bio-oils originating from castor cakes were of better quality compared to bio-oils produced from typical biomass. Catalytic upgrading affected both the product yields and the oil quality significantly, enhancing deoxygenation reactions and aromatic hydrocarbons production.

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ECONOMIC MODEL OF A NOVEL PROCESS FOR THE FRACTIONATION OF DRIED DISTILLERS GRAIN WITH SOLUBLES

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Key Words: DDGS, bio-refining, fractionation, process economics, decisional tool

There is urgency around the world to find alternative sources of energy and to develop a sustainable global economy. *Bio-refining* is a key strategy for tackling this problem by utilising byproducts of *first generation biofuels* such as bioethanol and generating new revenue streams to overcome some of the economic barriers. Dried Distillers Grain with Solubles (DDGS) is a byproduct from bioethanol production plants and distilleries. Due to the development of two large bioethanol plants (Vivergo and Ensus) in the UK the mass of DDGS produced is predicted to increase from the 250 to 960 kt/annum[1,2]. Currently DDGS is used as a relatively low quality animal feed for monogastric animals and if the amount of DDGS produced continues to increase the market is likely to become saturated. Therefore the UK government as well as bioethanol producers are keen to volarise DDGS and find alternative revenue from this byproduct. Collaborative research between multiple UK universities aims at fractionating DDGS into its individual components, sugars, oils and proteins, using steam explosion, supercritical CO2 extraction and alkali extraction, respectively. This group has studied the individual processes at small-scale and evaluated various configurations of the proposed fractionation process. To further optimise the processes for its implementation at industrial scale, a decisional tool and process economic model is required to assess the economic viability of the process. This study is an initial attempt to create such a tool by modelling a newly proposed large-scale process for the fractionation of DDGS to identify whether the process is economically viable and to find scenarios in which it can be.

The model uses small-scale data and DoE equations to generate a mass balance for the fractionation steps. It then combines this with assumptions from decisional tools developed at UCL for the biopharma industry to scale-up and analyse costs of the process. This initial study focuses on modelling the oil and protein extraction steps, as sugar processing is well understood. Industrially relevant case studies are used to highlight the impact of crucial model parameters, such as moisture content, DDGS load mass and composition, on the costs and timing of the process. The developed preliminary tool will be further extended with optimisation capabilities, and its predictive ability will be validated against large-scale experiments.

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WATER CONTENT DETERMINATION OF OLIVE KERNELS FROM CHALKIDIKI AND KALAMATA OLIVES

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Keywords**:** olive kernels, Water content , Kalamata, Halkidiki

With the world's fossil fuel reserves being finite, alternative energy sources must be developed. Biomass is an attractive alternative as it is renewable and potentially carbon neutral as well as being able to be used in equipment designed for fossil fuels. Of the types of biomasses available, waste from industry and food production and consumption is of special interest as utilizing this both creates an energy resource and solves a waste problem.

Olives are a popular and widely grown fruit with over 20 million metric tons being produced in 2013 [1]. Its uses include direct consumption and olive oil production. As a byproduct of industrial processing and food consumption there remain olive kernels and their uses can include burning for thermal energy, animal feed supplements and extraction of remaining oil in the kernel for other uses such as for the production of biodiesel. An important factor in both burning and biodiesel production is water content.

In this work the moisture content of olive kernels from Halkidiki and Kalamata olives were determined by drying them in an oven to evaluate the effect of different operational conditions as well as storage conditions. Several temperatures varying from 25 to 105 C were tested and the results compared. Also the olives kernels where stored in 4 different mediums and conditions such as room temperature, fridge, freezer and in brine before being dried. Even more, the kernels were separated in two different approaches; some of them were not treated while the rest were crushed to homogenized size.

From the results, whole kernels taken directly from olives dried at 105 C were found to contain between 24 to 30 % with stones dried at lower temperatures showing a trend of lower and slower moisture loss with decreasing temperature. Crushed olives dried faster and lost 2-3 % less water than whole kernels, but the temperature dependence trend was the same as for non-crushed stones. The Kalamata kernels lost 2-3 % more water than Halkidiki stones at 105 C, but the temperature dependence was the same for both of them. Stones having been stored at room temperature (22-25 C) for 1 week contained between 6 to 9 % when dried at 105 C.

CO_2 CAPTURE ON BIO-BASED ACTIVATED CARBONS

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Key Words: Activated Carbon, CO_2 Capture, Biomass, Pyrolysis

Climate change has become one of the most important environmental and energy policy issues in the 21st century and the rise in CO_2 emission is considered as the main cause of it. CO_2 adsorption on solid surfaces like activated carbons is one of the methods to develop low-cost and effective adsorbents for carbon dioxide capture applications. The adsorption capacity of activated carbons depends on porosity but it is also influenced by their surface chemistry. In this work, activated carbons are produced from three different type of Canadian waste biomasses including agricultural waste (wheat straw and flax straw), forest residue (sawdust and willow ring) and animal manure (poultry litter). The abundance of biomass precursors in Canada and the increasing demand and market for environmental applications of biochar and activated carbon are the motivation of this research project.

In this study, activated carbons were produced using three different activation methods of steam activation, CO_2 activation and potassium hydroxide (KOH) activation. The performance of produced activated carbons in the temperature range of 25-65 °C and CO_2 concentrations range of 10-30% has been studied for CO_2 adsorption using a fixed bed reactor set-up. The KOH activated carbon with total micropore volume of 0.51 cm^3/g and surface area of 1400 m^2g^{-1} had the highest adsorption capacity of 74 mg/g due to its microporous structure and high surface area. As the KOH activated carbon was the best option for CO_2 capture at atmospheric pressure and low temperature of CO_2, in the next step biochars were produced through the fast and slow pyrolysis processes and then developed into activated carbon through KOH activation process. The adsorption capacity and selectivity of activated carbon were measured using a fixed-bed reactor in a simulated gas mixture of N_2, O_2 and CO_2. The breakthrough adsorption capacity of produced activated carbon was measured under a flue gas condition of 14 mol% of CO_2, 4 mol% of O_2 and 82% of N_2 at 25 °C and atmospheric pressure. Slow pyrolysis based activated carbon had lower surface area and total pore volume but higher adsorption capacity in the presence of N_2. Sawdust based activated carbon synthesized using slow pyrolysis process created the highest ultramicropores volume 0.36 cm^3/g; and the highest adsorption capacity in N_2 (78.1 mg/g) but low selectivity (2.8) over O_2 because of the oxygen functional groups on the surface. The results show that ultra micropores and surface chemistry of adsorbents are far more important than particle size, total pore volume and internal surface area and of the adsorbents. This work also suggests that adsorption capacity and selectivity of activated carbon can be controlled and optimized through choice of starting material and carbonization conditions. The details of activation process, the properties of the adsorbent, including the surface area, pore size distribution, elemental analysis, FTIR, XPS, NEXAFS as well as experimental results will be presented and discussed.

Poster Number 12

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Engineering Conferences International
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Calendar of ECI Conferences

Celebrating 53 years of international, interdisciplinary engineering conferences

2015

Sept 27-Oct 2	**15AA**	**BIOREFINERY I: CHEMICALS AND MATERIALS FROM THERMO-CHEMICAL BIOMASS CONVERSION AND RELATED PROCESSES** (Chania [Crete], Greece) N. Abatzoglou, University of Sherbrooke; S. Kersten, University of Twente; D. Meier, Thünen Institute of Wood Research; NH. Kalogerakis, Technical University of Crete
Oct 4-9	**15AN**	**NANOMECHANICAL TESTING IN MATERIALS RESEARCH AND DEVELOPMENT V** (Albufeira, Portugal) M. Legros, CEMES
Oct 11-13	**15AV**	**SHOTCRETE FOR UNDERGROUND SUPPORT XII** (Singapore) M. Lu, Nanyang Technological University; O. Sigl, Geoconsult Asia Singapore Pte Ltd.; G. Li, Singapore Metro Consulting
Oct 18-21	**15AJ**	**SINGLE-USE TECHNOLOGIES: BRIDGING POLYMER SCIENCE TO BIOTECHNOLOGY APPLICATIONS** (Washington, DC area) E. Mahajan, Genentech, Inc.; G. Lye, University College London
Nov 1-5	**15AD**	**INTEGRATED CONTINUOUS BIOMANUFACTURING II** (Berkeley, California, USA) C. Goudar, Amgen; S. Farid, University College London; K. Lacki, GE Healthcare Life Sciences; C. Hwang, Genzyme-Sanofi
Nov 8-12	**15AC**	**COMPOSITES AT LAKE LOUISE 2015** (Lake Louise, Alberta, Canada) J. Smay, Oklahoma State University

2016

March 6-11	**16AE**	**ELECTRIC FIELD ASSISTED SINTERING AND RELATED PHENOMENA FAR FROM EQUILIBRIUM** (Tomar, Portugal) R. Raj, University of Colorado); T. Tsakalakos, Rutgers University
April 3-8	**16AM**	**DESIGN AND MANUFACTURE OF FUNCTIONAL MICROCAPSULES AND ENGINEERED PARTICLES** (Siracusa (Sicily), Italy) S. Biggs, University of Queensland; D. Weltz, Harvard University; D. York, University of Leeds
April 10-14	**16AY**	**CO$_2$ SUMMIT: TECHNOLOGIES AND OPPORTUNITIES** (Santa Ana Pueblo, NM) H. Krutka, Shenhua Science and Technology Research Institute; F. Zhu, UOP/Honeywell
May 8-13	**16AC**	**CELL CULTURE ENGINEERING XIV** (Palm Springs, CA) R. Kiss, Genentech; J. Chalmers, Ohio State University; S. Harcum, Clemson University
May 22-26	**16AF**	**FLUIDIZATION XV** (Notre-Dame Montebello, Quebec, Canada) J. Chaouki, Ecole Polytechnique De Montreal; F. Berruti, Western University; X. Bi, University of British Columbia; R. Cocco, PSRI, Inc.
May 29-June 3	**16AV**	**INTERNATIONAL WORKSHOP ON THE ENVIRONMENTAL DAMAGE IN STRUCTURAL MATERIALS UNDER STATIC/CYCLIC LOADS AT AMBIENT TEMPERATURES** (Cork, Ireland) A.K. Vasudevan, ONR (retired); R. Latanision, Exponent, Inc.; H. Holroyd, Luxfer Gas Cylinders; N. Moody, Sandia National Laboratories

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June 6-11	**16AL**	**LIFE CYCLE ASSESSMENT AND OTHER ASSESSMENT TOOLS FOR WASTE MANAGEMENT AND RESOURCE OPTIMIZATION** (Cetraro, Italy) U. Arena, Second University of Naples; R. Clift, University of Surrey; P. Lettieri, University College London; T. Astrup, Denmark Technical University
June 12-17	**16AA**	**VACCINE TECHNOLOGY VI** (Albufeira, Portugal) L. Palomares, UNAM; M. Cox, Protein Sciences Corp.; T. Mukhopadhyay, UCL; N. Carcon, GSK
June 19-23	**16AG**	**GREEN PROCESS ENGINEERING** (Mont Tremblant, Canada) F. Berruti, Western University; Cedric Briens, Western University
July 3 -8	**16AJ**	**NANOTECHNOLOGY IN MEDICINE: FROM MOLECULES TO HUMANS** (Hernstein, Austria) L. Eniola-Adefeso, Univ. of Michigan; P. Decuzzi, Italian Institute of Technology
July 10-14	**16AB**	**COLLOIDAL, MACROMOLECULAR AND BIOLOGICAL GELS: FORMULATIONS, PROPERTIES AND APPLICATIONS** (Hernstein, Austria) S. Amin, Malvern Instruments; S. Khan, North Carolina State University
July 17-21	**16AS**	**BEYOND NICKEL-BASE SUPERALLOYS II** (Cambridge, UK) H. Stone, Cambridge University
Summer TBA	**16AH**	**ADVANCES IN MARINE NANOSCIENCE AND NANOTECHNOLOGY** (TBA) A. Bose, University of Rhode Island; G. Bothun, University of Rhode Island
Sept 4-8	**16AI**	**NONSTOICHIOMETRIC COMPOUNDS VI** (Santa Fe, New Mexico) R. O'Hayre, Colorado School of Mines; J. Janek, Justus-Liebig-University; Y. Yamazaiki, Kyushu University; A. McDaniel, Sandia National Laboratories
Sept 11-16	**16AK**	**ADVANCED MEMBRANE TECHNOLOGY VII** (Cork, Ireland) I.Escobar, University of Toledo; J. Hestekin, University of Arkansas
Oct 16-21	**16AO**	**SEPARATIONS TECHNOLOGY X: NEW FRONTIERS IN MEDIA, TECHNIQUES AND TECHNOLOGIES** (TBA) K.K. Sirkar, New Jersey Institute of Technology; S.M. Cramer, Rensselaer Polytechnic Institute; B. Van der Bruggen, KU-Leuven; M. Mazzotti, ETH-Zurich
TBA	**16AQ**	**FAIRNESS IN THE DELIVERY OF HEALTH CARE: AN EXAMINATION OF PRICING, TECHNOLOGY AND PEOPLE ISSUES** (TBA) R. Spier, Univ. of Surrey (Emeritus); B. Buechner, CELLS (Germany), and Indiana University for Bioethics; A. Caplan, New York University; M. Feinberg, Merck Sharp and Dohme; N. Hoppe, CELLS; A. Blasimme, INSERM Toulouse

2017

Jan 15-19	**17AT**	**SCALE-UP AND MANUFACTURING OF CELL-BASED THERAPIES V** (San Diego, CA) W. Miller, Northwestern Univ.; C. Mason, University College London; T. Brieva, Celgene
March 26-31	**17AF**	**SYNTACTIC AND COMPOSITE FOAMS V** (Siracusa, Sicily, Italy)) G. Gladysz, Energy Professionals; K.K. Chawla, Univ. of Alabama; A.R. Boccaccini, Univ. of Erlangen-Nuremberg; T. Ohji, AIST
June 4-9	**17AB**	**BIOFABRICATION FOR ORGANIZED TISSUE MODELS** (Hernstein, Austria) J. Groll, University of Würzburg; J. Malda, University Medical Center Utrecht
June 24-30	**17AL**	**CONFERENCE ON IONIC LIQUIDS (COIL)** (Mont Tremblant, Canada) H. Alper, University of Ottawa; C. Robelin, Ecole Polytechnique de Montreal; J. Clyburne, Saint Mary's University; L. Rehmann, Western University;
Summer	**17AO**	**ADVANCES IN OPTICS FOR BIOTECHNOLOGY, MEDICINE AND SURGERY X** (TBA) P. So, MIT; I. Vellekoop, University ofTwente; K. Bechtel, Triple Ring Technologies; M Choma, Yale University
July TBA	**17AM**	**BIOCHEMICAL AND BIOMOLECULAR ENGINEERING XX** (TBD) W. Chen, University of Delaware; N. Borth, University of Natural Resources and Applied Life Sciences; Stefanos Grammatikos (UCB)
Sept TBA	**17AE**	**ENZYME ENGINEERING XXIV** (Toulouse, France) P. Monsan, Toulouse White Biotechnology; M. Remaud-Simeon, LISBP-INSA, University of Toulouse
Oct TBA	**17AD**	**ELECTROPHORETIC DEPOSITION VI: FUNDAMENTALS AND APPLICATIONS** (South Korea) A.R. Boccaccini, Univ. of Erlangen-Nuremberg; O. van der Biest, KU Leuven; J. Dickerson, Brookhaven National Laboratory; T. Uchikoshi, National Institute for Materials Science
Nov 9-16	**17AC**	**COMPOSITES AT LAKE LOUISE 2017** (Lake Louise, Alberta, Canada) TBA

Engineering Conferences International

Engineering Conferences International (ECI) is a not-for-profit global engineering conferences program that has served the engineering/scientific community since 1962 as successor program to Engineering Foundation Conferences. ECI has received recognition as a 501(c)3 organization by the U.S. Internal Revenue Service and is incorporated in the State of New York as a not-for-profit corporation.

The program has been developed and is overseen by volunteers both on the international Board of Directors and international Conferences Committee. More than 1,400 conferences have taken place to date. The conferences program is administered by a professional staff and the conferences are designed to be self-supporting.

ECI Mission

To serve the engineering/scientific community with international, interdisciplinary, leading edge engineering research conferences

ECI Purposes

The advancement of engineering arts and sciences by providing a forum for the discussion of advances in the field of science and engineering for the good of mankind by identification and administration of international interdisciplinary conferences

To work with engineering, scientific and social science societies and the interested general public to jointly sponsor conferences and to take other actions that will foster complementary programming.

To initiate conferences that will have a significant impact on engineering education, research practice and/or development.

ECI Encouragement of New Conference Topics

The ECI Conferences Committee invites you to suggest topics and leaders for additional conferences and encourages you to submit a proposal for an ECI conference.

Ideally, proposals should be submitted from 18 to 24 months in advance of the conference although the staff can work on a shorter timeline.

The traditional format for an ECI conference is registration Sunday afternoon with technical sessions held each morning and evening through Thursday or Friday noon. Afternoons are used for informal gatherings, poster sessions, field trips, subgroup meetings and relaxation. This format has served well to build important professional networks in many areas.

ECI welcomes proposals for shorter conferences and for conferences which span weekends in order to reduce the number of working days participants are away from their offices.

ECI Works With You

ECI works with conference chairs in two complementary ways. First, an experienced member of the Conferences Committee acts as your technical liaison from the proposal stage through the conference itself. He or she is always available to consult with you on any conference issue.

Second, after your proposal has been approved by the Conferences Committee, the ECI staff will assume responsibility for the administration of the conference.

Your primary responsibilities will be recruiting the organizing committee, developing the technical program and securing third-party funding necessary to support the travel of key speakers.

The responsibilities of ECI's "full service" staff include -- but are not limited to -- the following:

- Recommend, negotiate, contract and make substantial deposits for housing, meals, meeting space, A/V equipment and tours.
- Maintain web sites for the conference and for submission of abstracts.
- Publicize via electronic and print media.
- Administer all finances including grants, contributions and purchase orders. (ECI makes grant funds available as soon as a grant is approved.) There is no need for chairs to set up a conference bank account or file tax returns for their conference.
- Process all applications and registrations.
- Produce bound program/abstracts book.
- Contract for the publication of print or electronic proceedings, if any.
- Provide on-site staff during the conference.

For more information, please contact the ECI Director at Barbara@engconfintl.org