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Paper-ID	93141
Paper title	Biofuels and biorefinery R&D at the Department of Chemistry of Federal University of Paraná
Presentation format	Oral presentation
Date of submission	07.03.2017 23:16 Uhr
Authors	- Luiz Pereira Ramos *(ramosluizp@gmail.com)* (Presenter)

Content

The Federal University of Paraná was founded in 1912 and is the oldest of his kind in Brazil. Located in Curitiba, PR, UFPR has the mission to support, built and disseminate knowledge throughout the society, bringing high quality public education to all citizens and therefore contributing to their sustainable human development. The Department of Chemistry is part of the UFPR structure and hosts several research groups in which more than 50 research professors are involved. The group entitled Research Center in Applied Chemistry (CEPESQ) was founded in 1993 and, ever since, has been particularly devoted to the development of suitable technologies for the valorization and upgrading of wood and agroindustrial residues. Projects developed under its research team include the pretreatment of lignocellulosics for optimal fractionation and enzymatic hydrolysis, production of added-value biomolecules (lipases, proteases, biosurfactants) by solid state fermentation, development of new processes (based on heterogeneous catalysis) and multi-functional additives (cold flow improvers and anti-oxidants) for biodiesel production and use, microalgae biomass production and use for fuels and chemicals for biofuels and production of biodegradable composites and/or plastic films from plant biomass, among others. Our aim is to expand the scope of our research activities through bilateral collaboration with institutions abroad in areas of common interest and, by participating in this satellite event of WCCE, we hope to attract new partners and research opportunities in strategic areas of R&D such as biofuels, biomaterials and green chemistry for the sustainable development of modern society.

Paper-ID	89016
Paper title	Biofuels production by Hydrothermal Liquefaction of Eucalyptus: Influence of reaction conditions and catalyst.
Presentation format	Oral presentation
Date of submission	28.02.2017 20:14 Uhr
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Content

The Hydrothermal Liquefaction (HTL) process is a thermochemical process to transform biomass into biofuels. In HTL, biomass is subjected to temperatures between 250 ℃ and 550 ℃ and high pressure (5-30 MPa) during short residence times in aqueous medium [1]. The HTL is of special interest when the raw material has high moisture content because is a process performed in aqueous medium and biomass do not need to be dried. The products of HTL are: gas, biocrude, water soluble organics and a solid rich in carbon known as hydrochar [2].

This work study the influence of catalyst and reaction conditions over products yield distribution and products energy content of HTL process of Eucalyptus globulus.

The reaction was carried out in a Parr 4575 reactor of 0.5 L of capacity. The temperatures studied were 300 ℃ and 350 ℃ with residence times of 0 and 15 min, biomass: liquid medium weight ratio of 1:1 or 1:6 using water, an aqueous solution of K_2CO_3 1M or $KHCO_3$ 1M as catalyst. The biomass was 15 g of sawdust of Eucalyptus globulus ground and sieved. All the tests were made at a pressure corresponding to the water vapor pressure at reaction temperature plus the pressure of gas produced during reaction and in inert atmosphere (N_2).

The products were separated in order to calculate its yields. The gas volume was measured using air displacement in an inverted test tube, an aliquot was recovered and analyzed by gas chromatography. The hydrochar was recovered by filtration and the biocrude was extracted using acetone and then separated by vacuum evaporation and weighed. The products high heating value was evaluated as well as H/C and O/C ratio. For hydrochar the moisture and ash content was determined.

The results show that energy density of hydrochar and biocrude is higher than raw material. It was possible to decrease the O/C ratio for hydrochar and biocrude relative to woody biomass. The products yield is function of reaction conditions studied. Biocrude production is favored by catalyst use as well as high ratio solution/biomass. Gas production is improved for solution/biomass 1 and high temperatures (350ºC).

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Paper-ID	92611
Paper title	Economic evaluation of biofuels production from lignocellulosic biomass
Presentation format	Oral presentation
Date of submission	03.03.2017 15:54 Uhr
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Content

Introduction

As yet, the production of fossil fuels through refining is characterised by relatively low capital and operating expenditures (CAPEX and OPEX). Both CAPEX and OPEX are usually higher for the production of biofuels, where biomass has to be grown on scarce land and extensive processing is required. High CAPEX, in particular, multiply the risks for potential investors and widen the “valley of death” associated with technological demonstration.

Early economic evaluations, vital to steer R&D, are performed in a data-lean environment. With a conceptual process design available, the OPEX are estimated from an inventory of mass and energy streams. The CAPEX are estimated based on shortcut designs of the main pieces of equipment, through the use of economic correlations. OPEX and CAPEX are then aggregated to estimate the production cost with a ± 30 % precision.

Results and discussion

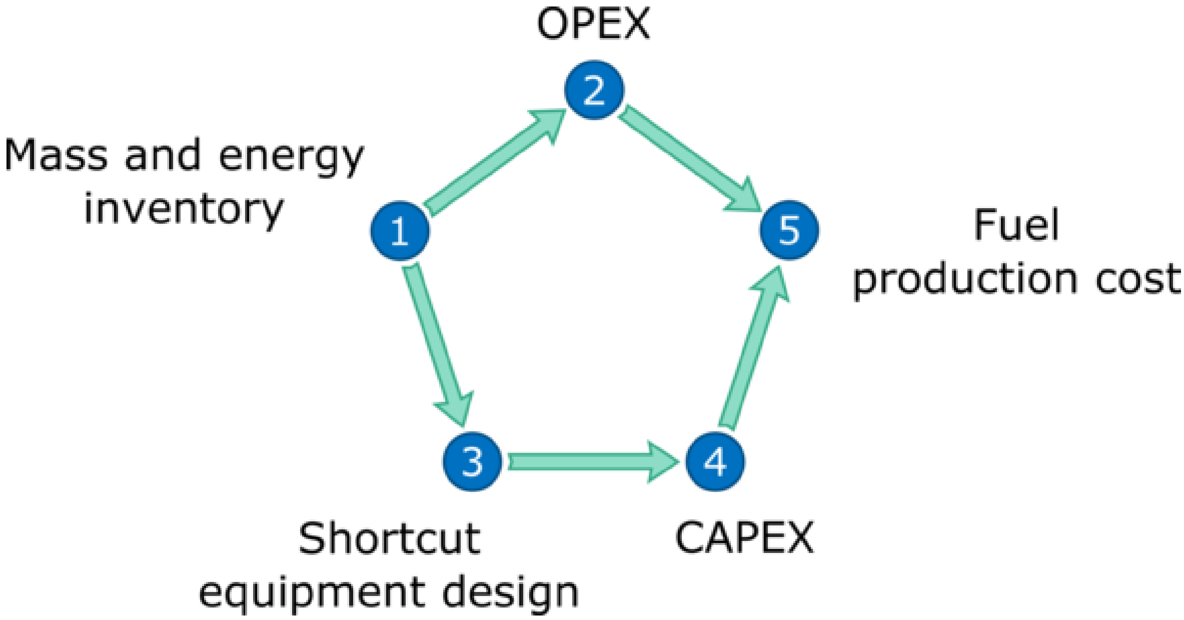
Some important lessons have been learnt by performing economic evaluations in the FASTCARD project, where two value chains are being studied.

The first value chain relies on a gasification of biomass followed by Fischer-Tropsch (FT) synthesis of liquids. This value chain mainly suffers from high CAPEX due to the large volumetric flows being processed. Attempts to reduce the production cost of the biofuel are therefore aimed at reducing the volumetric flows: pressurising the gasification, minimising the accumulation of inert gases, tuning the H_2:CO ratio in the syngas stream and inhibiting the water-gas shift reaction occurring on iron-based FT catalysts by catalyst development.

The second value chain relies on a pyrolysis of biomass. The resulting pyrolysis liquid is being hydrotreated to condition it for co-feeding with vacuum gas oil (VGO) to a fluid catalytic cracking (FCC) unit. Here, OPEX are the main cost contributor, due to the consumption of raw pyrolysis liquid and hydrogen at the hydrotreatment stage. Catalyst development therefore aims at a mild hydrotreatment, stabilising the pyrolysis liquid while avoiding hydrodeoxygenation.

Acknowledgement

The research leading to these results has received funding from the European Union Seventh Framework Programme FP7/2007-2013 under grant agreement n° 604277.



Paper-ID	95741
Paper title	Fuel properties and ageing of bioslurry prepared from crude glycerol/methanol/bio-oil blend and biochar
Presentation format	Oral presentation
Date of submission	02.04.2017 04:11 Uhr
Authors	- wenran gao *(wenran.gao@postgrad.curtin.edu.au)* (Presenter) - Mingming Zhang *(mingming.zhang@curtin.edu.au)* - Hongwei Wu *(H.Wu@exchange.curtin.edu.au)*

Content

Fuel properties and ageing of bioslurry prepared from crude glycerol/methanol/bio-oil blend and biochar

Wenran Gao; Mingming Zhang; Hongwei Wu*

Utilisation of the major by-product crude glycerol is of great importance to the economic and environmental performance of the rapidly-growing biodiesel industry. Mixing crude glycerol with bio-oil and biochar produced from biomass fast pyrolysis to produce bioslurry fuels is a plausible approach for effective utilization of the byproducts (i.e. biochar and glycerol) in stationary applications. Therefore, this study investigates the fuel properties and ageing of a series of bioslurry fuels prepared from formulated crude glycerol/methanol/bio-oil blend (FCGMB) and biochar benchmarking against the glycerol/methanol/bio-oil/biochar (GMBB) bioslurry fuels. Both FCGMB/biochar (FCGMBB) bioslurry and GMBB bioslurry fuels generally exhibit non-Newtonian and thixotropic behaviour, especially those at high biochar to FCGMB blend ratio (4:20). An increase in biochar loading level in those bioslurry fuels also increases the HHV, density, surface tension, viscosity, while decreases water content and TAN. Compared to the GMBB bioslurry fuels at the same biochar loading level, the FCGMBB slurry fuels have much higher water content, while lower viscosity and total acids number (TAN). Ageing leads to decreases in the TAN and viscosity but an increase in water content of both FCGMBB and GMBB slurry fuels due to the esterification, acetalization and/or polycondensation reactions.[1-3] Overall, fuel properties of FCGMBB slurry fuels are equivalent to or even better compared with that of GMBB slurry or FCGMB blend, and the presence of crude glycerol in the FCGMBB slurry fuels slow down the ageing.

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1. W. Gao, M. Zhang, H. Wu, Fuel properties and ageing of bioslurry prepared from glycerol/methanol/bio-oil blend and biochar. Fuel, 2016. 176: p. 72-77.

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Paper-ID	93691
Paper title	Lipid content and fatty acid profile of Choricystis minor var. minor before and after extraction with conventional solvents and/or compressed fluids
Presentation format	Oral presentation
Date of submission	13.03.2017 11:55 Uhr
Authors	- Luiz Pereira Ramos *(ramosluizp@gmail.com)* (Presenter) - Aline Andreza da Cruz Lima *(aline.andreza@ufpr.br)* - Daiane Szczerbowski Vidal *(daianeszcz@yahoo.com)* - Arion Zandoná Filho *(a.zandona@ufpr.br)* - Marcos Lúcio Corazza *(corazza@ufpr.br)*

Content

The lipid content and fatty acid profile of freshly harvested Choricystis minor var. minor was characterized before and after extraction with both conventional solvents and compressed fluids. Among the conventional solvents used for Soxhlet extraction (total extraction time of 12 h), ethanol was the most efficient, yielding around 30 wt.% of microalgae oil in relation to the dry microalgae biomass. However, only one third of this oil could be converted to fatty acid methyl esters (FAME) by hydrolysis followed by esterification. By contrast, extraction with hexane gave an overall yield of 10 wt.% of in which most of the oil could be converted to FAME. Hence, the performance of both extraction solvents revealed that most of the microalga oil contained neutral lipids. Extraction with pressurized solvents was carried out using both supercritical CO_2 (80 and 40°C at 150 and 250 bar) and subcritical (compressed) propane (80 e 40°C at 50 and 100 bar). For experiments carried out for 120 min, propane (100 bar at 80°C) had a better performance than CO_2 (250 bar at 80°C) for extracting the neutral lipids of the microalga, with the best yield being about 10 % lower than the yield derived from Soxhlet extraction with n-hexane. Addition of ethanol as co-solvent in a mass ratio of 1:1 in relation to microalga mass improved the extraction performance of both pressurized fluids (CO_2 and propane) up to the same levels derived from ethanol extraction using a Soxhlet apparatus. More importantly, for both conventional and compressed fluid extraction procedures, the use of ethanol removed the entirety of the microalga oil, demonstrating that no critical mass transfer limitations were observed under the applied experimental conditions. However, the use of compressed fluids reduced both the time required for extraction and the amount of solvent used when compared to the performance of a conventional Soxhlet apparatus. At the best extraction condition using CO_2 and ethanol (150 bar at 80°C), the maximum extraction yield was 31.6 %, reached in 10 min, whereas by replacing CO_2 for propane (80°C e 100 bar), the maximum yield was reached in 16 min and the extraction yield dropped to 27.6%. Nevertheless, in both cases, the extraction times were much shorter than that required for a single solvent cycle in the Sohxlet apparatus, which took around 40 min to occur. Also, the use of ethanol as a co-solvent improved dramatically the extraction efficiency but the resulting microalgae oil contained only one-third of esterifiable materials (fatty acids), therefore representing a good extraction for producing materials other than fatty acid methyl esters. Finally, by chromatographic analysis, the fatty acid methyl esters derived from batches of the microalga oil were shown to be mainly composed of fatty acids that are normally present in vegetable oils, suggesting it as a good source of one-spec biodiesel.

Paper-ID	78086
Paper title	Optimising the sustainability of the reforming of biomass-derived compounds via the by-product carbon nanotubes
Presentation format	Oral presentation
Date of submission	27.02.2017 15:22 Uhr
Authors	- Jun Huang *(jun.huang@sydney.edu.au)* (Presenter)
Content	

Biomass has been regarded as a key renewable feedstock for a step change in energy use, to meet EU energy sustainability targets which require an 80% reduction of greenhouse gas emissions by 2050 compared with 1990 levels. The production of clean fuel hydrogen via the reforming of biomass derived compounds is promising for the commercial application due to the currently available reforming capacity in petrochemical industry. However, one serious challenge for gas phase catalytic reforming is coke generation, which is derived from cracking of nonsaturated, large molecular weight compounds in the crude bio-oil. The production of coke and CO2 (from the regeneration of coked catalyst via calcination) from organic carbons significantly reduce the overall efficiency of the process and promotes greenhouse gas release.

We have developed a promising route to produce clean-fuel hydrogen with high value carbon nanotubes (CNTs) as a byproduct of the process via evaporation/pyrolysis-reforming of biomass derived compounds such as glycerol [1], crude bio-oil [2], toluene [3], and phenol [4]. Since the waste catalyst coke is replaced by high value CNTs, a potential significant increase of additional economic benefit could be contributed to the bio-refining process. Moreover, CO2 emission to the environment from the current practice of coke oxidation during catalyst regeneration would be reduced.

References

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Paper-ID	72721
Paper title	Pretreatment and enzymatic saccharification of castor bean plant pruning for bioethanol production
Presentation format	Poster
Date of submission	23.02.2017 17:26 Uhr
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Content

Bioethanol is a sustainable fuel with a potential to cover the actual global energy demand and to improve the quality of the environment. Second-generation bioethanol (2G) has great potential considering the availability of the raw material, although its economical and technic development is not as advanced as the first generation bioethanol (1G) [1]. Castor Bean plant (*Ricinus communis L.*), a member of the family Euphorbiaceae, is an herbaceous plant from which castor bean oil is obtained, and contains a potent cytotoxin called ricin, making the plant not suitable as food or feed. However, **the hydrolyzable sugars contained in the plant stem and leafs have the potential to be transformed into several important products such as bioethanol** [2]. 2G bioethanol production process basically involves the obtention of an optimum substrate to generate high ethanol yields, the first step consists of a pretreatment of the raw material and can be carried out using different physicochemical methods, followed by a hydrolysis process of the pretreated material, the fermentation of the hydrolysates, and a final step, at which the ethanol is obtained and separated [3]. **The objective of this work was to define the best pretreatment conditions by autohydrolysis and enzymatic saccharification of biomass from castor bean plant pruning.** The pretreatment tests were carried out in a 200 mL Parr® reactor at a mass: volume ratio of 1: 6 (w/v) at different temperatures (140 ° C, 160 ° C, 180 ° C and 200 ° C) for 15 minutes. After the chemical characterization of the pretreated material according to the protocols of the National Renewable Energy Laboratory (NREL), the selected material was subjected to enzymatic hydrolysis using a commercial enzymatic complex Cellic® Ctec3 from Novozymes at different solids loading (10%, 15% and 20%) and enzyme/substrate ratio (10, 15 and 20 FPU / gram of glucan) for 72 h incubation at 50 °C (full factorial design 2^3). **The results of the pretreatment stage showed a higher recovery of glucans (82.98%) and removal of xylans (77.49%), without lignin removal at 200 °C. The enzymatic hydrolysis of material showed a maximum glucose release of 60.39 g/L, corresponding to a 98.81% hydrolysis yield, at a solids load of 20% and an enzyme load of 25 FPU/gram of glucan.**

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Paper-ID	82001
Paper title	Pyrolytic Conversion of Cardboard to a Valuable Chemical: Effect of Acid Pretreatment
Presentation format	Oral presentation
Date of submission	28.02.2017 09:19 Uhr
Authors	- Shinji Kudo *(shinji_kudo@cm.kyushu-u.ac.jp)* (Presenter) - Nozomi Goto *(2ES15025T@s.kyushu-u.ac.jp)* - Koyo Norinaga *(norinaga@cm.kyushu-u.ac.jp)* - Jun-ichiro Hayashi *(junichiro_hayashi@cm.kyushu-u.ac.jp)*

Content

Levoglucosenone (LGO) is a promising biorenewable platform for commodity and fine chemicals. We have recently proposed and demonstrated a method for producing LGO from a microcrystalline cellulose, which was two-step conversion process consisting of pyrolysis and catalytic reforming of the volatiles.[1] The method was designed to realize the conversion only with fast reactions and without the use of solvent. Pyrolysis of cellulose produced the volatiles containing levoglucosan (LGA), which was a main precursor of LGO in the reforming. Because of a high selectivity in the reforming, LGA production at a high yield in the pyrolysis was important for the efficient LGO production. In this study, we employed cardboard, a type of waste paper, as LGO feedstock. Waste papers account for more than half of municipal solid waste. They are currently used for landfilling or combusted to produce a low grade heat while have a considerable potential as a sugar-based biorefinery feedstock because of their main component, cellulose. A problematic property in their direct use is the high ash content, which influences the conventional liquid phase hydrolysis and downstream processes. Pyrolysis leaves majority of the ash in char, and, therefore, the pyrolytic conversion apparently does not suffer from the ash problem. However, the yield of LGA from pyrolysis of cardboard was considerably lower than that of pure cellulose (Fig. (b)). The ash components in the cardboard were mainly $CaCO_3$ and kaolinite. The low LGA yield indicated that the ash metals catalytically influenced the cellulose pyrolysis. In fact, the product contained more low molecular weight compounds than that from pure cellulose. The dilute acid pretreatment removed a portion of ash, calcium in particular, and improved the LGA yield significantly to a level comparable to that from pure cellulose. The result demonstrates that cardboard can be a feedstock of LGO, which is readily available from LGA, according to the scheme in Fig. (a).

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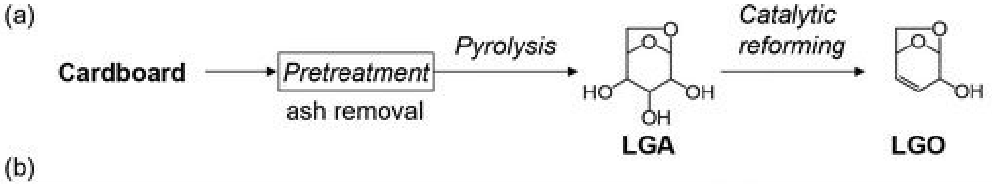

(b)

pretreatment		pyrolysis					
HCl conc.	Ca removal	product (wt%)				yield (%-C, on cardboard basis)	
(mol/L)	rate (%)	char	liquid	CO/CO_2	mass balance	LGA	LGO
3.0	97.3	31.7	56.6	1.0/2.9	92.9	1.6	1.3
1.0	97.2	28.3	63.7	1.2/1.7	94.9	9.1	2.5
0.5	95.9	28.3	60.0	1.1/2.9	92.1	11.5	2.8
0.3	94.3	29.7	57.6	1.1/3.0	91.5	14.2	1.1
0.1	93.1	27.3	63.2	1.7/2.4	94.7	10.9	0.8
0.01	62.3	28.7	59.2	1.6/4.3	93.9	14.0	1.2
0	49.5	32.3	60.2	1.3/1.0	97.8	7.7	1.0
no treatment		30.7	58.1	1.4/6.6	88.9	4.4	0.7
cellulose		18.0	67.8	0.7/2.9	93.9	12.7	2.3

[a] pretreatment conditions: 5 g cardboard in 300 mL HCl aqueous solution, stirring at 25 °C for 24 h. [b] pyrolysis conditions: 0.8 g sample, heating at 2 °C/min to 380 °C under N_2 flow.

Fig. Conversion of cardboard to LGO: (a) process scheme and (b) effect of acid pretreatment on the yield of pyrolysis product.