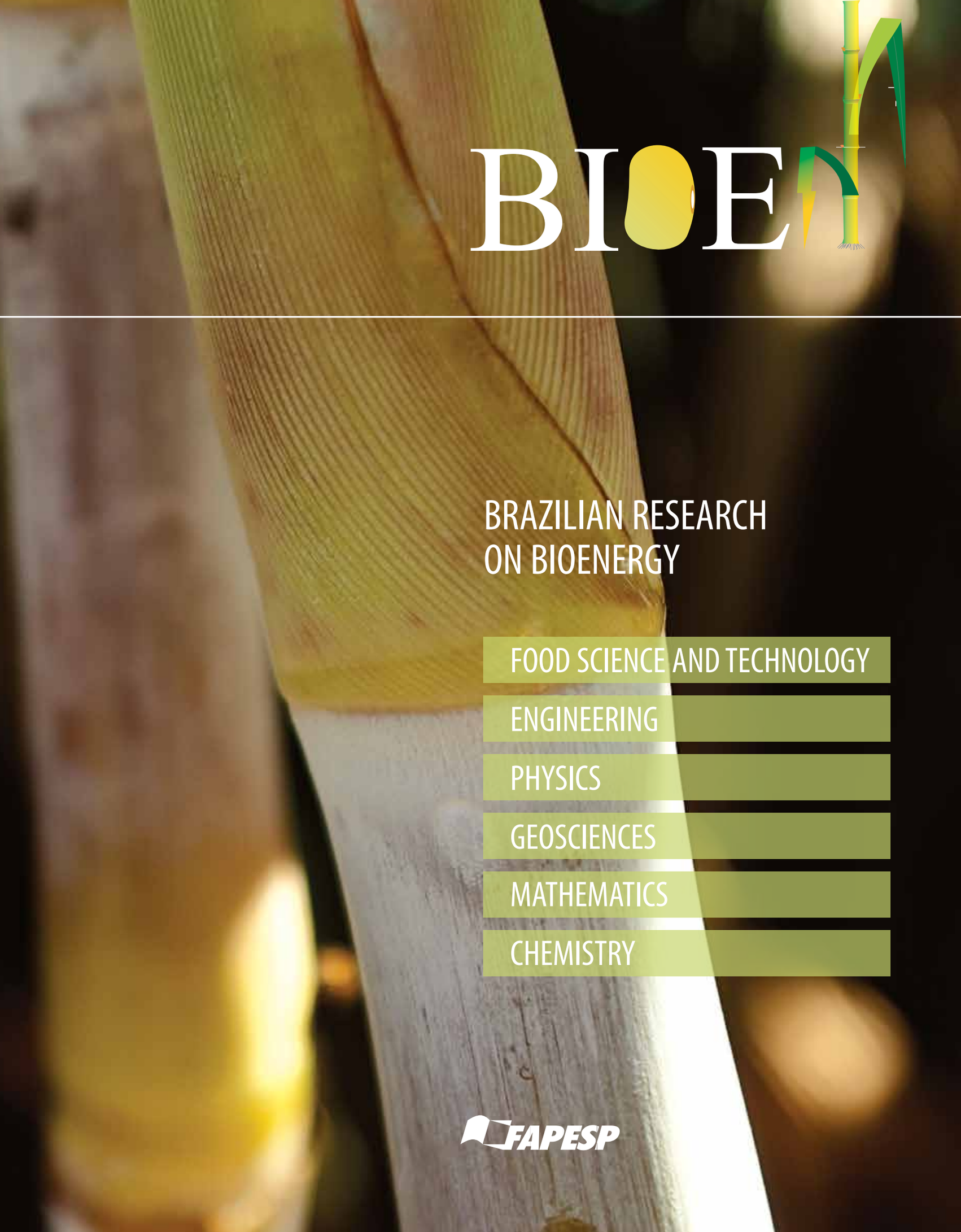

BIOEN

BRAZILIAN RESEARCH ON BIOENERGY

- FOOD SCIENCE AND TECHNOLOGY
- ENGINEERING
- PHYSICS
- GEOSCIENCES
- MATHEMATICS
- CHEMISTRY

FAPESP

BIOENERGY: THE BRAZILIAN EXPERIENCE

Bioenergy is an important clean energy alternative. The Brazilian experience has shown that sugarcane is a highly sustainable crop for bioenergy production

Brazil is outstanding as the world's most intensive user of bioethanol as an alternative to gasoline for powering transport. Total bioethanol production in 2014/15 corresponds to 28.4 billion liters in 366 plants. In 2015/16 around 58 per cent of the 590 million tons of sugarcane will be used for ethanol and 42 per cent for sugar production. The total sugarcane planted area in Brazil is around 10 million hectares (ha). This accounts for only around 6-7 per cent of total area devoted to agriculture and 1.1% of the country's total area.

CLEAN AND CHEAP ENERGY

Brazil and the USA produce more than 80 per cent of world's ethanol. Brazilian bioethanol production costs are the cheapest in the world. In addition to low production costs, ethanol produced from sugarcane in Brazil has another important advantage: in Central-South Brazil, only 1 unit of fossil energy is consumed for each 9-10 units of energy produced by ethanol from sugarcane. The use of ethanol as a biofuel also reduces carbon emissions: when ethanol is used in substitution to gasoline, there is a 76% reduction in GHG emissions with a simultaneous decrease in SO_2 emission. Since 2003, Brazil's use of sugarcane ethanol has avoided the emission of 242 million tons of carbon dioxide.

THE BRAZILIAN MODEL

Sugarcane was introduced in Brazil in 1532 by the Portuguese and it has been cultivated here ever since. The research that started in the first half of the 20th century has gradually improved this crop, with the development of new varieties of sugarcane that enhanced the yields of both culm and sucrose. During the 1970s, the "Brazilian model" of producing sugar and ethanol together brought important technical improvements and enabled an outstanding increase in competitiveness in the international market for sugar and ethanol.

Ethanol has a great potential to become a worldwide replacement or complement for gasoline. In 2014, 88.2% per cent of the 2.9 million cars and light vehicles sold in Brazil were of the flex-fuel type, which run on any proportion of ethanol and gasoline mixture. Considering the existing opportunities related to biofuels, it is expected that R&D will lead to optimization not only of the sucrose content of the plant, which is relevant for sugar production, but also of the overall energy content (biomass yield).

Traditionally, bioethanol is produced from fermentation of the extracted juice and the molasses resulting from the sugar industry. But, in addition to sucrose, there is also a relevant and extractable amount of energy in the glycosidic linkages of cellulose and hemicelluloses, which account for nearly two thirds of the sugarcane plant biomass (bagasse and leaves).

BIOEN FACTS AND FIGURES

US$ 167 million	**research expenditures by FAPESP and partners**
13	**co-funding partners**
7	**private companies co-funding projects**
467	**scholarships –** 89 ongoing and 378 completed
206	**research projects –** 66 ongoing and 140 completed
300+	**researchers involved**
21	**fields of knowledge**
920+	**scientific publications**
17	**patents filed**

THE ENERGY-CANE

With the possibility of cellulosic ethanol production, scientists envisage a new option, the "energy-cane" and not only the "sugarcane", in which the whole biomass is of interest. The development of hydrolysis and/or gasification processes could be applied to the residual bagasse and trash, transforming the lignocellulosic biomass into ethanol or other liquid fuel, using fermentation of the generated sugar (hydrolysis) or the catalytic synthesis of the generated gas (gasification). It is expected that ethanol output might increase from the current 7,000 to about 12,000 liters per hectare-year, i.e., between 60 and 70 per cent.

In 2014, Brazil burned bagasse to produce energy equivalent to 20,823 GWh. This is enough to meet the internal needs of the mills and the surplus energy can be fed into the country's power grid. Investments in co-generation efficiency and power distribution aim at increasing even further the energy supply from bioelectricity. Also, most of the straw still remains in the field after sugarcane harvest and can be, at least partially, transformed in energy. Bioelectricity from sugarcane can contribute to 18% of the country's energy demand. Additionally, sugarcane offers options in development: alternative routes to produce liquid fuels from lignocellulosic materials for road, maritime and aviation transportation could open new possibilities for an industry that is already energy-efficient.

The growing demand for bioenergy brings new scientific challenges in terms of R&D and assessment of the environmental and social impacts related to the expansion of sugarcane cultivation.

FAPESP'S BIOENERGY PROGRAM – BIOEN

To respond to the increasing need for R&D in the area of bioenergy the São Paulo Research Foundation (FAPESP) created a Bioenergy Program (BIOEN). FAPESP is one of Brazil´s leading public funding agencies for scientific research.

The FAPESP Program for Research on Bioenergy, BIOEN, aims to link public and private R&D, using academic research institutions and industrial laboratories to advance and apply knowledge in fields related to ethanol production. BIOEN is organized in five divisions: Biomass, Biofuel Technologies, Biorefineries, Engines, and Impacts and Sustainability.

Over 300 researchers support BIOEN activities with funds in the order of US$ 167 million. BIOEN is increasingly multidisciplinary including projects from 21 areas of knowledge. This highlights the broad scope of questions addressed. The BIOEN Program consolidated the community in an active network of experts leading 206 research projects and 467 scholarships in 21 institutions in the State of São Paulo, in collaboration with other institutions in Brazil and in 29 countries. Since 2008, BIOEN has generated more than 920 scientific publications. Additionally, more than 300 thesis and dissertations with important contributions for the advancement of science and the industry have been concluded. This represents an important step in generating human resources to increase the potential and the number of qualified professionals working in this field.

BIOEN

FAPESP

SÃO PAULO RESEARCH FOUNDATION

RUA PIO XI, 1500, ALTO DA LAPA
CEP: 05468-901 - SÃO PAULO - SP - BRASIL
+55.11. 3838-4000

SUGAR PRODUCTION BY ENZYMATIC HYDROLYSIS OF SUGARCANE BAGASSE

Alfredo Eduardo Maiorano
Industrial Biotechnology Laboratory / Bionanomanufacturing Center / Institute for Technological Research (IPT)
FAPESP Process 2007/51656-2 | Term: Oct 2008 to Jul 2012 | PITE – Business partner: Oxiteno S/A

Figure 1. Steam explosion equipment

The search for renewable materials to replace fossil resources has received considerable attention in recent years. Biomass has been regarded as of great potential to provide energy, chemicals and materials. One important aspect in this field is the industrial use of agroresidues, which would boost production without involving the expansion of the agricultural area. Sugarcane bagasse is a promising lignocellulosic material for such application since it has a high concentration of carbohydrates and is already available at sugar mills in significant quantities. However, the compact structure of the lignocellulosic matrix hinders the hydrolysis of cellulose into fermentable sugars. Thus, a pretreatment step is necessary to improve cellulose accessibility. The aim of this work was the evaluation of the enzymatic hydrolysis of sugar cane bagasse submitted to steam explosion pretreatment to produce sugars. These sugars can be used as substrate for the production of chemicals by biotechnological routes. The effects of steam explosion, alkaline delignification and enzymatic hydrolysis parameters were studied in detail. This research project was carried out jointly by Oxiteno Co and IPT.

In the steam explosion pretreatment, different reaction times were tested for different temperatures and the results were analyzed in relation to: the composition of pretreated bagasse and the corresponding hemicellulosic hydrolysate; the susceptibility of pretreated bagasse to hydrolysis by a cellulolytic complex selected as a model; and the benefits achieved by the delignification process. At the best condition of 220 °C for 9 min, large quantities of pretreated bagasse were produced to study the kinetics of the enzymatic hydrolysis in pilot scale reactor of about 40 L. The effects of the cellulase complex, substrate/cellulase ratio, stirring, degree of delignification and process design were evaluated in relation to both the sugar recovery and the obtained hydrolysis yields.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The objective of pretreatment is to destroy the recalcitrant structure of cellulosic biomass to make the cellulose fibers more accessible to enzymatic hydrolysis. As more drastic the conditions of pretreatment, more significant has been the loss of cellulose and the higher the damages to the fiber structure, causing the folding thereof. The best condition of pretreatment by steam explosion reduced the hemicellulose content of up to 90 % and the yield of glucose obtained in the enzymatic hydrolysis was 76.3 %.

Delignification with NaOH and H_2O_2/NaOH has also been applied in order to improve the enzymatic hydrolysis yield. The results showed that the NaOH concentration has a greater effect than temperature on the lignin solubilization and on enzymatic hydrolysis yield increasing. With bagasse pretreated and delignified was possible to reduce the lignin content of approximately 53% and yield of glucose in the enzymatic hydrolysis was 89.3 %.

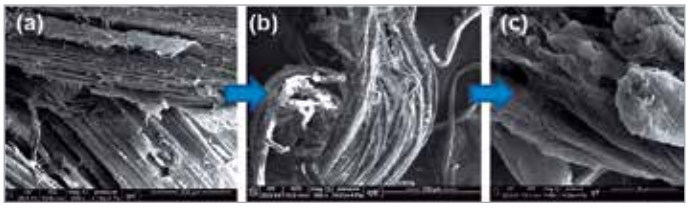

Figure 2. Bagasse Scanning Electron Microscopy (SEM): (a) fresh, (b) pre-treated to 18bar / 9min and (c) pre-treated and delignified with NaOH

Enzymatic hydrolysis of cellulose was performed by commercial cellulolytic enzymes. In the conditions tested the agitation speed had no significant effect on the enzymatic hydrolysis yield. Substrate concentration and enzyme load are important process parameters for the overall economy of the enzymatic hydrolysis. At 10% bagasse concentration resulted high enzymatic hydrolysis yield and high glucose concentrations in the medium. Higher substrate concentrations resulted in lower the rate and the yield of the hydrolysis. Furthermore, a large increase in power is required for stirring the bagasse suspension. Batch enzymatic hydrolysis was modified to fed-batch mode to solve the problems, however no significant effects were observed. Substrate inhibition depends on the substrate/enzyme ratio. This parameter had great influence in the process. Increasing the load of cellulases in the process, increased the yield and rate of the hydrolysis. The best enzyme/substrate ratio was 30 FPU/g, but would significantly increase the cost of the process.

MAIN PUBLICATIONS

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Alfredo Eduardo Maiorano

Instituto de Pesquisas Tecnológicas (IPT)
Laboratório de Biotecnologia Industrial
Núcleo de Bionanomanufatura
Av. Prof. Almeida Prado, 532 – Butantã
CEP 05508-901 – São Paulo, SP – Brasil

+55-11-3767-4315
maiorano@ipt.br

YEAST IMPROVEMENT BY METABOLIC AND EVOLUTIONARY ENGINEERING

Andreas Karoly Gombert
Polytechnic School / University of São Paulo (USP)
FAPESP Process 2007/59776-7 | Term: Aug 2008 to Jan 2011

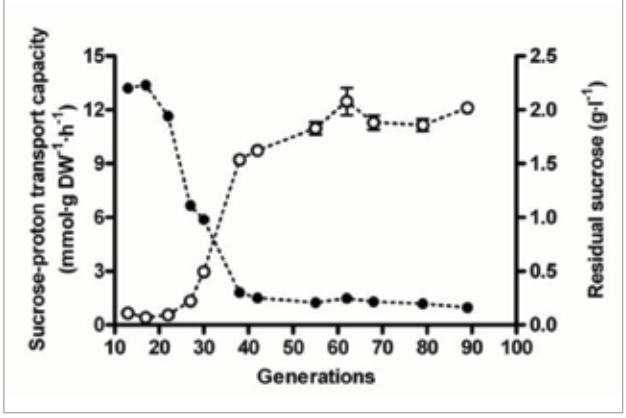

Figure 1. Ethanol yield improvement of Saccharomyces cerevisiae *by evolutionary engineering. Here the improvement of sucrose active transport capacity is depicted. For further details, see the article published in* Metabolic Engineering. *(DOI 10.1016/j.ymben.2011.09.005)*

Using evolutionary and metabolic engineering, either individually or in combination, our global aim is to improve yeast for its use in biorefineries. First-generation bioethanol production in Brazil, in which sucrose from sugarcane is converted into ethanol by *Saccharomyces cerevisiae* with high yields, was chosen as a first case study. We started with a yeast strain which had already been metabolically engineered to hydrolyze sucrose exclusively in the intracellular environment (Prof. Boris Stambuk, Federal University of Santa Catarina, Brazil). Without the capacity of hydrolysing sucrose extracellularly, this strain is obliged to transport this sugar actively into the cells via symport, which causes ATP expenditure to extrude protons from the cells back to the culture medium, in order to avoid acidification of the citoplasm. This energy drain forces the cells to produce more ATP, which, under anaerobiosis, is basically coupled to ethanol formation. As a first aim, we will characterize this strain quantitatively, in order to demonstrate that it converts sucrose into ethanol with a higher yield, when compared to strains with normal invertase activity. Subsequently, this strain will be subjected to evolutionary engineering, in order to increase the ethanol yield on sucrose even further. Future studies will focus on the metabolic and evolutionary engineering of industrial yeast strains, with the aim of improving tolerance towards the most relavant stressors present in the industrial bioethanol production, such as high ethanol concentration, high temperature, high osmolarity, and acid environment. The improvement of second-generation biofuels will also be tackled, by investigating tolerance of yeast towards common inhibitors released during hydrolysis of lignocellulosic materials, such as acetate, furfural, and hydroxymethylfurfural.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

- Yeast invertase was relocated to the cytosol by removal of N-terminal signal peptide
- Improved sucrose uptake kinetics obtained by evolutionary engineering in chemostats
- Strain evolved for intracellular sucrose metabolism shows deregulated MAL genes
- AGT1-encoded proton symporter was involved in sucrose uptake by evolved yeast strain
- The engineered yeast strain shows an 11% increase of the ethanol yield on sucrose

MAIN PUBLICATIONS

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Andreas Karoly Gombert

Escola Politécnica
Universidade de São Paulo (USP)
Departamento de Engenharia Química
Av. Prof. Luciano Gualberto, trav. 3, nº 380
CEP 05508-010 – São Paulo, SP – Brasil

+55-11-3091-2229
gombert@usp.br

DEVELOPMENT OF ANALYTICAL METHODOLOGIES AND ORGANOSOLV DELIGNIFICATION PROCESSES APPLIED TO BAGASSE AND STRAW FROM SUGARCANE

Antonio Aprigio da Silva Curvelo
São Carlos Institute of Chemistry / University of São Paulo (USP)
FAPESP Process 2007/51755-0 | Term: Sep 2009 to Nov 2012 | PITE – Business partner: Oxiteno S/A

Figure 1. Hot water pretreatment and delignification of sugarcane bagasse. (Vallejos ME)

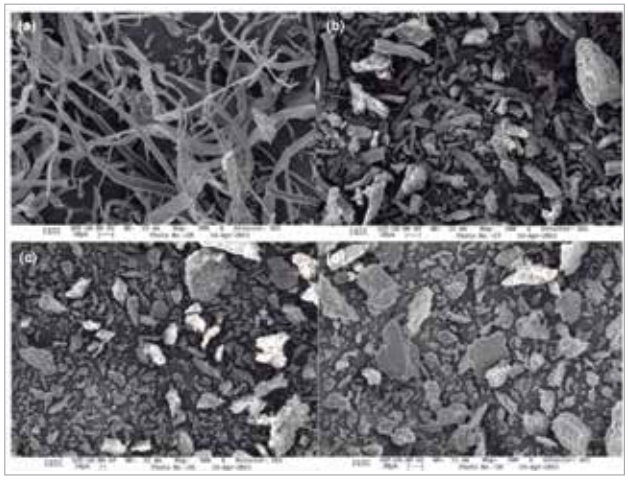

Figure 2. SEM micrographs of (a) bagasse cellulose pulp, (b)Avicel PH101, (c) pulp hydrolyzed at 190 °C for 80 min, (d) pulp hydrolyzed at 210oC for 40 min. (Gurgel LVA et al. 2012. Industrial Crops and Products. **36***: 560-571)*

The proposals in this project were formulated based on scientific output and experience accumulated over 20 years dedicated to the study of characterization and production of cellulose and lignin derivatives from lignocellulosic materials, with special attention to the bagasse obtained from sugar cane processing. The proposed project is focused on the study of lignin's solvency through delignification reactions, the development of analytical methodology for the characterization of the main components of sugarcane bagasse, isolation of natural products present in the skin of the culms and the leaves of sugarcane and the study of cellulose hydrolysis in aqueous acidic media. Lignin's solvency studies include three basic processes: conventional (aqueous solutions), organosolv and organosolv assisted by sub/supercritical carbon dioxide. Considering the pretreatments steps to produce enriched cellulose samples for sugar production, it was included the study of the liquid to solid ratio in the hydrothermal and organosolv delignification. As a result of these procedures, the cellulosic pulps will be employed for the production of glucose by means of acid hydrolysis of cellulose by using mineral acids and carbon dioxide at sub/supercritical state. The technique that uses fluids at sub/supercritical state may allow the hydrolysis of cellulose without the utilization of mineral acids in an attempt to avoid the production of inhibitors for the fermentation processes. The traditional methods for the characterization of lignocellulosic materials were developed and optimized for wood and wood derivatives (pulp and paper). Due to the different characteristics of grasses and agricultural wastes (especially from crushed cane sugar industry) the modifications of existing methods and/or development of new analytical methodologies for the chemical characterization of sugarcane bagasse is of fundamental importance for both academic studies and industrial applications. The waxes present in the skin of the culms and the metabolites present in the leaves constitutes important substrates for the chemical and pharmaceutical industries and will isolated by means of organic solvent and/or supercritical carbon dioxide.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The gravimetric determination of lignin by the acid treatment showed that the optimal acid concentration for the determination of the total lignin is within a defined concentration range (65 - 72%), which was different for each sugarcane bagasse fraction (pith, fiber or straw). The use of the oxidation process for the indirect determination of lignin showed that this method also needed be optimized, to be applied to samples of sugarcane bagasse. The results showed that increasing the amount of oxidizing agent improved the performance of the method, even when excess oxidant may promote oxidation of the polysaccharide present in the samples.

The hot water pretreatment of sugarcane bagasse performed at 170 °C for 60 min, with liquid to solid ratio (LSR) of 3 g/g, produced the maximum concentrations of xylose and xylan (13.76 and 36.18 g/L, respectively), equivalent to 48.29 g/L of xylan. The amount of xylan removed under these conditions was almost 57% of the xylan present in the untreated bagasse. The dissolved xylan is mainly composed of xylo-oligosaccharides (74 wt%). Glucose and glucan contents in the spent liquor were less than 1.1%, which shows that cellulose was not hydrolyzed by the hot water pretreatment. Low liquid–solid ratio (LSR) provided a simple and ambient friendly means to produce high-content xylo-oligosaccharides spend liquor with enormous potential for industrial applications.

The association of high-pressure carbon dioxide in the liquid hot water (LHW) pretreatment of sugarcane bagasse promoted a higher degree of deacetylation in comparison with LHW alone, resulting in an increase of liquor's acidity and allowed higher hemicelluloses extraction. As expected Xylan, Xylose and Furfural concentrations were strongly dependent on the reaction temperature and time. The pretreatments performed yielded operational conditions that can be useful in processes were high concentrations of xylose and/or xylan are required without the drawbacks of a process employing mineral acids and with the benefit of using reduced temperatures in comparison with LHW alone.

The kinetics of sugarcane bagasse cellulose saccharification and the decomposition of glucose under extremely low acid (ELA) conditions (0.07%, 0.14%, and 0.28% H_2SO_4) and at high temperatures were investigated using batch reactors. The ELA conditions were successful applied to the hydrolysis of sugarcane bagasse cellulose in batch reactors and produced glucose yields close to 70%. The residual solids obtained after the chemical saccharification of cellulose were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM). The thermal, XRD and SEM studies demonstrated that the cellulose residues have thermal decomposition behavior, crystallinity index, crystallite size and particle size similar to Avicel PH-101 and can also be considered microcrystalline celluloses.

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Antonio Aprigio da Silva Curvelo

Instituto de Química de São Carlos
Universidade de São Paulo (USP)
Av. Trabalhador São Carlense, 400
CEP 13566-590 – São Carlos, SP – Brasil

+55-16-3373-9938
aprigio@iqsc.usp.br

PHASE EQUILIBRIUM AND PURIFICATION PROCESSES IN THE PRODUCTION OF BIOFUELS AND BIOCOMPOUNDS

Antonio José de Almeida Meirelles
Faculty of Food Engineering / University of Campinas (FEA/UNICAMP)
FAPESP Process 2008/56258-8 | Term: Aug 2009 to Mar 2014 | Thematic Project
co-PI: Pedro de Alcantara Pessoa Filho

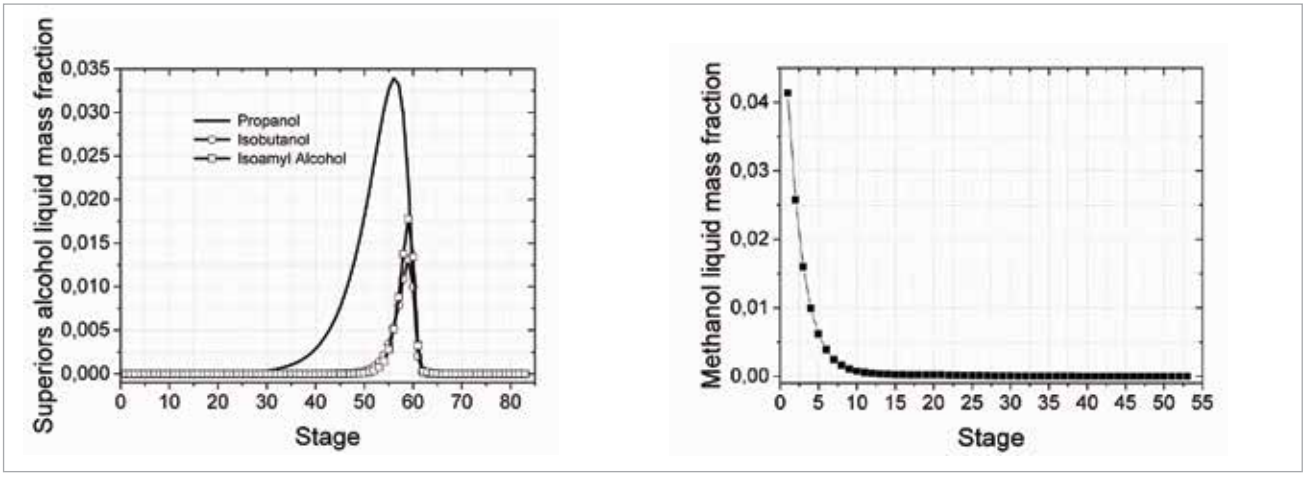

Figure 1. Superior alcohols profile in rectifier column (a) and methanol profile in demethylizer column (b) (Batista, Follegatti-Romero and Meirelles, 2013)

This project aims to optimize purification processes used during biofuels production and to enhance the added value of byproducts generated in those processes. In the case of bioethanol, the distillation process was investigated taking into account minor components relevant for product quality, according to legislation standards for biofuels and for the requirements of a raw material for chemical, pharmaceutical, cosmetics and food industries. Configurations of distillation columns actually used in sugar mills were investigated by experimental measurements in those industrial unities and by process simulation. A comprehensive investigation of the wine phase equilibrium was carried out, taking into account a complete set of minor components. New and innovative configurations of distillation columns were proposed, aiming at better product quality, equipment flexibility, higher ethanol recovery, lower energy consumption, and better byproducts quality. Such configurations were further tested for concentrating bioethanol obtained from wine with high alcohol content and from cellulosic residues. In case of ethylic biodiesel, a comprehensive investigation of the different types of phase equilibrium occurring along the whole production process was carried out. The use of bioethanol, as a solvent for extracting vegetable oils from seeds and grains and for deacidifying crude oils by liquid-liquid extraction, as well as a reactant in biodiesel production can integrate biodiesel and bioethanol productions. In the case of biocompounds, strategies for enhancing the value of byproducts generated during biofuels production were investigated. For instance, the fractionation of high alcohols generated as a sidestream during bioethanol distillation, the use of glycerol in the production of surfactants and emulsifiers, the recovery of nutraceuticals from edible oils, the formulation, fractionation and transformation of fatty mixtures based on solid-liquid equilibrium data.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Bioethanol binary distillation is a frequent research topic found in the literature. However, its distillation taking into account the real complexities of wine composition and industrial column configurations is a subject largely unexplored. The simulation tools available nowadays make possible to reproduce the industrial process with a high degree of confidence, providing a firm basis for optimizing it and suggesting new configurations that can improve the efficiency of bioethanol distillation. The distilling behavior of several minor components, classified into light, middle volatility and heavy compounds, were investigated in the production of spirits, hydrated ethanol and neutral alcohol. Middle volatility components, despite their very low content in the original wine, achieve high concentrations in specific parts of the distillation column, affecting in a significant way the whole process. Strategies for controlling bioethanol contamination with those components, such as superior alcohols and methanol in neutral alcohol production, were also developed (*Figure 1*).

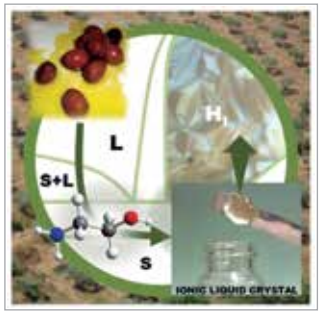

Figure 2. Ionic liquids synthesized from fatty acids (extracted from vegetable oils). These compounds presented interesting liquid-crystalline behavior above melting temperature which is quite important for pharmaceutical applications (Maximo et al., 2013)

Due to several drawbacks, ethylic biodiesel is almost not produced in an industrial scale. If these drawbacks are solved, an approach based on the bioethanol use in several steps of biodiesel production, from the seed to the tank, becomes technically feasible. Traditional and innovative techniques for deacidifying crude vegetable oils were investigated by experimental runs and simulation. The innovative techniques used bioethanol as solvent or extractant. Biodiesel reaction occurs in a two-phase environment, requiring information on the corresponding equilibrium data. Such data were measured and correlated in situations suitable for homogeneous catalysis and biocatalysis.

The production of biofuels generates byproducts whose added value can be increased by fractionation or transformation. Phase equilibrium data provide the basis for optimizing the purification processes; product formulations and biocompound synthesis (*Figure 2*). Physical-chemical properties and equilibrium data were measured and correlated for fatty mixtures containing fatty acids, fatty esters, fatty alcohols, triacylglycerols, nutraceutical and lipidic protic ionic liquid crystal compounds.

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Antonio José de Almeida Meirelles

Faculdade de Engenharia de Alimentos
Universidade Estadual de Campinas (UNICAMP)
Rua Monteiro Lobato, 80
CEP 13083-862 - Campinas, SP - Brasil

+55-19-3521-3888
tomze@unicamp.br

SIMULATION OF 1st GENERATION SUGARCANE BIOREFINERY IN EMSO PLATFORM

Antonio Maria Francisco Luiz José Bonomi
Brazilian Bioethanol Science and Technology Laboratory (CTBE) / National Center for Research in Energy and Materials
FAPESP Process 2011/51902-9 | Term: Jul 2012 to Jun 2016 | Thematic Project
co-PIs: Jose Antonio S. Gonçalves, Marco Giulietti, Maria Regina Wolf Maciel, Rubens Maciel Filho, Silvia Azucena Nebra

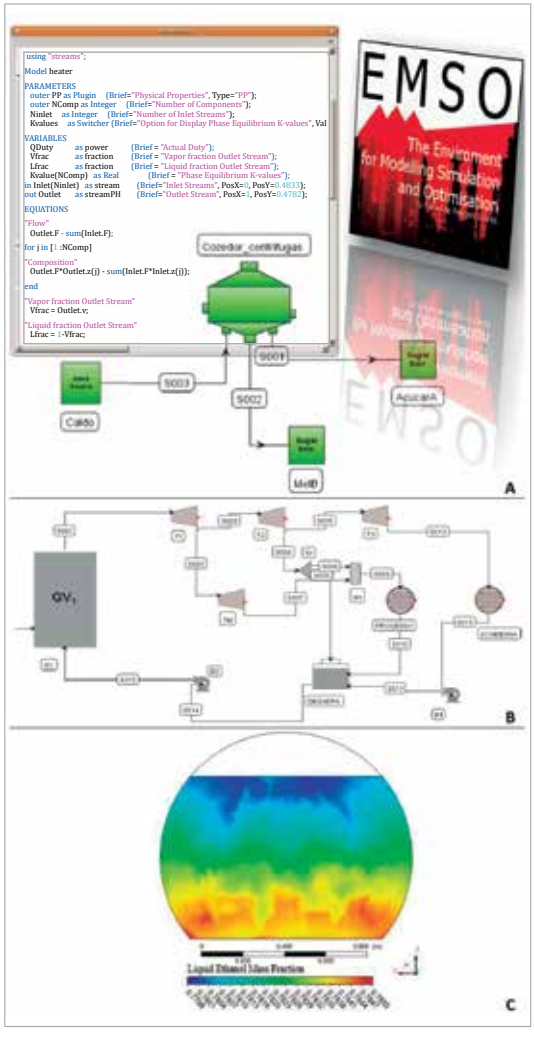

Figure 1. (A) EMSO's user interface and the representation of a unit operation; (B) CHP simulation using models developed by a group of the research team; (C) Mass transfer analysis of a sieve tray, using computational fluid dynamics, performed to provide stage efficiencies to EMSO's distillation models

In the last decade, several R&D institutes, as well as private sector initiatives, have focused on the development of technological solutions aiming to increase the efficiency and sustainability (economic, environmental and social) of the production process of sugar, ethanol and bioelectricity from sugarcane. The use of new technologies and energetic integration of the process may cause a substantial impact on the revenue of the business, as a result of the increase of surplus electricity, reduction in the use of process steam, rational use of subproducts and increase on productivity and efficiency of the unit operations. Moreover, it is clear that understanding and optimizing the 1st Generation plants are essential to enable the production of 2nd Generation ethanol. In this context, this project focuses on the development of a library of mathematical models that represents a "Virtual 1st Generation Sugarcane Plant", providing a framework that allows the comparison and optimization of different technological routes in the production of sugar, ethanol and bioelectricity.

In order to achieve the objectives of this project a simulation platform called EMSO (Environment for Modeling, Simulation, and Optimization) is been used for the development of the Virtual Sugarcane Plant. This software, designed and developed in Brazil, is an equation-oriented dynamic simulator and process optimizer. Besides its solver, the main features of this software are the full access to the developed mathematical models, the ease of insertion of new models or improvements in existing ones. These characteristics make EMSO a suitable environment for the development of a library of models specially focused on sugarcane plants.

The development of the "Virtual 1st Generation Sugarcane Plant" represents a great challenge in terms of gathering and managing large amount of information, so it is required a collaborative and synchronized team-effort and synergic actions of the various groups involved, CNPEM(CTBE), UFSCar(DEQ), UNICAMP(FEQ), UFABC(CECS) e USP (EESC e FZEA), through the management and sharing of the mathematical models generated along the project.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

In order to develop the "Virtual 1st Generation Sugarcane Plant" using the process simulator EMSO, the research groups elaborated several mathematical models of the main processing areas and unit operations of the production process of sugar, ethanol and bioelectricity from sugarcane. Two modeling levels, with simplified and rigorous models, are used to represent the process. The former one, a simplified version, is more adequate to provide analyses and balances for the whole process, and the later one – more complex, when more in-deep area-specific assessments are required. The simplified models of all processing areas are already developed, documented and tested by the research groups. Now, the whole process representation and testing phases, are in progress.

Within the project, the groups have specific responsibilities. One of them is in charge of characterizing samples of sugarcane and bagasse collected from several industrial plants, providing a representative and reliable information to the other groups. In the extraction area, a diffuser's rigorous model is being developed and dynamic models of the crystallization and fermentation areas are already available. The combined heat and power (CHP) and the biodigestion areas already counts with rigorous models of the main equipment and the distillation's rigorous models are being refined and improved to accurately reproduce the expected behavior of this operation. The final whole plant simulation is in progress, but an initial version is being used to perform optimization assessments, energy integration studies and to support the development of the methodology for estimating capital investment cost of 1st Generations plants.

Besides results from the specific researches of each group, some other important deliverables will be available online to the general public on the project's repository, for example, a library of mathematical models, developed specifically to represent and simulate the process operations of 1st Generation Sugarcane Biorefineries, a tool to estimate its capital investment cost and optimization methods, implemented in the EMSO simulator, that can be used to evaluate different technological scenarios.

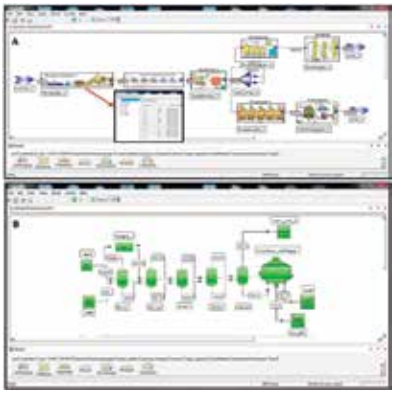

Figure 2. (A) User interface of the capital investment cost estimation tool; (B) EMSO's representation of part of the sugar production process

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Antonio M. F. L. J. Bonomi

Laboratório Nacional de Ciência
e Tecnologia do Bioetanol (CTBE)
Centro Nacional de Pesquisa em Energia e Materiais (CNPEM)
Divisão de Avaliação Integrada de Biorrefinarias (AIB)
Rua Giuseppe Máximo Scalfaro, 10.000 – Bairro Guará
CEP 13083-100 – Campinas, SP – Brasil

+55-19-3512-1010
antonio.bonomi@bioetanol.org.br

CONTRIBUTION TO THE PERFORMANCE IMPROVEMENT OF THE INDUSTRIAL PROCESS FOR OBTAINING ETHANOL FROM SUGARCANE BY USING MICROWAVE AND ULTRASONIC ENERGIES

Antonio Marsaioli Junior
Food Technology Institute (ITAL)
FAPESP Process 2008/58047-4 | Term: May 2009 to Apr 2012

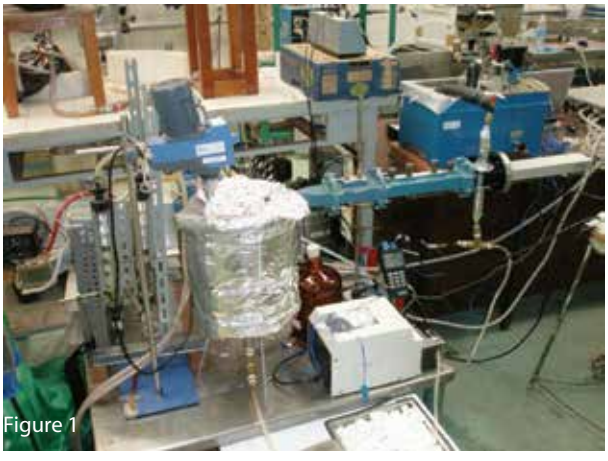
Figure 1

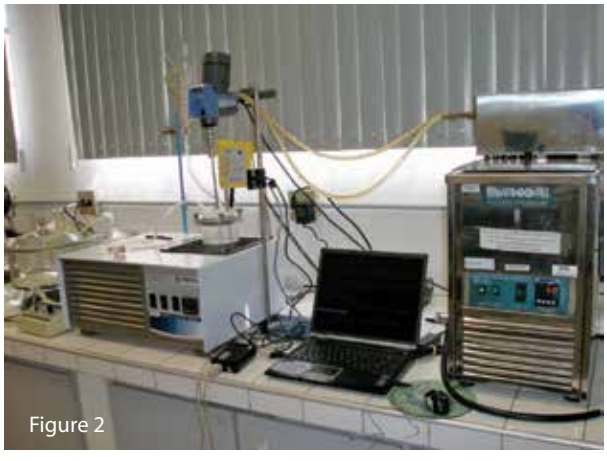
Figure 2

Figure 1. Assembly for continuously pasteurizing sugarcane must by using a microwave applicator. Figure 2. Assembly for studying the effect of applying US on the fermentation of pasteurized sugarcane must

The present study consists of searching techniques to improve the productive capacity of the ethanol industry, by developing new technologies based on the application of microwaves (MW) and ultrasound (US), envisaging a better performance during the fermentative process. One of the first objectives is to pasteurize the sugarcane must before fermentation. The must is composed by the mixture of the sugarcane juice and the syrup coming from milling the cane and from the sugar manufacturing, respectively, carrying a heavy microbiological load of bacteria and wild yeasts. The presence of bacteria into the fermentation vats is associated to the decreasing of process performance, because part of the substrate is spent to make other products like acetic and lactic acids, thus decaying the quality of the ethanol. Besides, bacteria may induce the occurrence of ferment flocculation, bringing a series of drawbacks to the process, such as yield reduction, expenditures with additives and bactericides, decrease of productivity, among others. On the other hand, wild yeasts are mostly flocculants by their nature, exhibiting low ethanol productivity and high multiplication rate.

The industrial ferments utilized in most of the Brazilian sugar mills, selected in conformity to their excellent fermentation potential at the beginning of the harvest season, are rapidly substituted by the wild yeasts, changing the process performance. Pasteurizing by MW is an efficient and rapid method, easily adaptable to the present ethanol plants, where the majority of equipment operations are based on batch processes. In order to aggregate efficiency to the fermentation process after MW pre-pasteurization, it is suggested applying low power US energy: a few research works have already shown that its ministration under controlled conditions can accelerate the metabolism of *Saccharomyces cerevisiae*, among other capabilities, although this kind of energy for stimulating fermentation has not found any industrial scale application yet. Combining the two technologies could bring significant contribution to increase the ethanol production. Besides developing new technologies for the sugar-alcohol industrial sector, employing MW and US would take advantage of clean energies by co-generation from the surplus energetic sources of the sugarcane mills.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

1. Dielectric properties. Electromagnetic energy and dielectric materials interacts by the conversion of MW into thermal energy, by means of several mechanisms of molecular and atomic scale. In order to determine the dielectric parameters of the sugarcane must, variable with temperature and frequency of the electrical field, a special cell was designed and developed so as to lodge the probe of the dielectric properties measuring system, allowing for the fluid to circulate continuously through it, inserted into a suitable circuit. Thus it was possible to determine dielectric properties within the range of MW frequencies (300 kHz to 6 GHz), as functions of temperature.

2. Lethality parameters. The lethality parameters, known as D and z values, specify times and temperatures needed to destroy the deteriorating target microorganisms, making possible to determine equivalent values of pasteurization at any other temperature. One continuous MW heating system of 2.45 GHz x 1,900 W (*Figure 1*) was assembled for the pasteurization and determination of the thermal death time studies. It terminates by a specially designed coiled-shape holding tube, immersed into a precisely adjusted constant temperature bath, having five orifices plugged with silicone septa, for withdrawing the sample aliquots. The MW system adjustment is such as to establish a standing wave with the electric field increased to a maximum value in the tubular applicator. The bath holding temperature is set according to the desired pasteurization temperature obtained from adjusting the MW power, whereas five treatment times of the samples are automatically obtained for each flow rate. After expiring the processing period, a counting of cells is done by using a microscope for confirming the reduction of the initial count.

3. Ultrasound Application. A bench scale fermentation system was prepared and filled with a pasteurized model solution inoculated with a selected strain of Saccharomyces cerevisiae in order to study the effects of applying low intensity ultrasound energy to the ethanol productivity of the yeast (*Figure 2*). The system consists of a glass cylindrical vessel of about 1.5 liters useful volume immersed into a constant temperature bath, equipped with an agitator, as well as access points for samples withdrawal, for purging CO_2 from fermentation and recovering escaped ethanol vapors by condensation, for feeding the solution at the process start up, and for inserting a probe connected to a lab size low-power US generator. As samples are withdrawn, they are sent for RMN and HPLC analyses in order to determine the relative rate of evolution of glucose, sucrose, fructose and ethanol from the fermentation reactions, as functions of applied specific US power and time cycle mode of such application.

4. Expected Results. This study proposes to improving the fermentation process of sugarcane must for obtaining ethanol by means of: 1. Time and waste reduction in the process; 2. Processing of a better quality product, characterized by less contaminants of ethanol (lactic and acetic acids, among others); 3. Decreasing of acid treatment for ferment deflocculation; 4. Reducing the employment of bactericide agents; 5. Clean energy utilization, possible of being obtained by co-generation through taking advantage of the bagasse from sugarcane.

It is expected through this study to get significant improvements in obtaining products and processes for the bio-combustibles fabrication, specifically ethanol, keeping the Brazilian leadership in the production of bio-ethanol.

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Antonio Marsaioli Junior

Laboratório de Microondas Aplicadas (LMA/GEPC)
Instituto de Tecnologia de Alimentos (ITAL)
Av. Brasil, 2880 – Jardim Chapadão
CEP 13070-178 – Campinas, SP – Brasil

+55-19-3743-1831
tonymars@uol.com.br

ANAEROBIC DIGESTION OF WASTEWATER TOWARDS BUTANOL AND ETHANOL PRODUCTION

Ariovaldo José da Silva
School of Agricultural Engineering / University of Campinas (UNICAMP)
FAPESP Process 2012/09785-8 | Term: Sep 2012 to Feb 2015

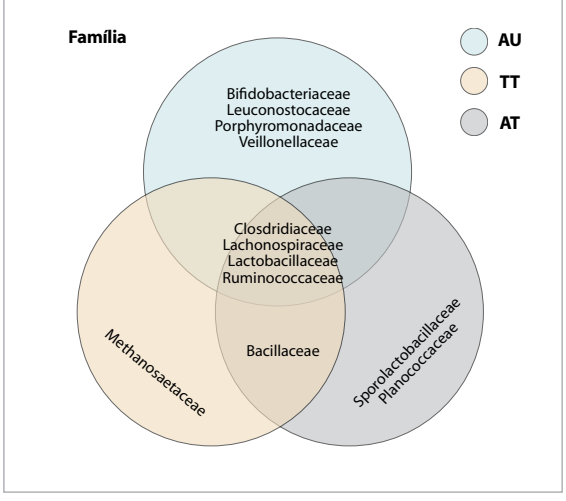

Figure 1. Venn's Diagram of families classified among the bacterial communities present in the reactors were the inoculum was treated with AT, TT and AU

The recovery of energy from wastewaters can be a feasible alternative for butanol and ethanol production via ABE fermentation, a biological biphasic process conducted by *Clostridium* genus bacteria. The ethanol or butanol production in the anaerobic digestion of wastewater depends of the wastes characteristics and operational conditions. In this context two projects were done at laboratory scale aiming to define and evaluate the operational parameters that could lead the metabolism in anaerobic digestion to ethanol or butanol pathway and verify the possible generation of these alcohols from vinasse.

Performance of fixed bed anaerobic reactors coupled in series for ethanol and butanol production from wastewater

This work was conducted in two fixed bed anaerobic reactors (FBR) inoculated with fermentative biomass obtained by natural auto-fermentation of sucrose-based synthetic wastewater. The reactors were operated in acidogenic and solventogenic conditions using hydraulic retention time (HRT) of 2, 4 and 12 hours and organic matter concentration expressed in COD of 500 mg L^{-1}, at 1000 mg L^{-1}, 4000 mg L^{-1} and 12000 mg L^{-1}. Furthermore, experiments were conducted at variable temperature of 25 ºC and 30 ºC and controlled temperature of 35 ºC.

Effect of vinasse in the biological production of alcohols and volatile organic acids by microbial consortium

In this work, the potential of vinasse as source of feedstock and nutrient for alcohols and volatile organic acids (AVT) production was evaluated by batch fermentation using a microbial consortium from anaerobic reactor treating cattle production wastewater. The sludge was exposed to thermic (TT) and acid-thermic (AT) treatment in order to select bacteria of *Clostridium* genus. The inoculum treated was incubated in two distinct medium one containing only sucrose as organic substrate and another containing sucrose plus vinasse in three different percentages, 33%, 50% and 66%.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Performance of fixed bed anaerobic reactors coupled in series for ethanol and butanol production from wastewater

The mean values of influent and effluent pH were 8.0±0.9 e 4.6±0.2, respectively. The stability of pH in the reactors for control of solventogenesis was obtained by adding sodium bicarbonate in the influent and permitting the driving of anaerobic digestion process of synthetic wastewater to ABE fermentation. The variations of the HRT and the organic loading rates (OLR) in the feed and operational conditions resulted in increase of AVT concentrations, mainly acetic and butyric acid. The maximum concentration of this acid at variable temperature, HRT of 4 h and OLR of 24 g COD $m^{-3}d^{-1}$ were 0.61 g L^{-1} and 0.52 g L^{-1}, respectively. The maximum concentration of ethanol detected was 0.92 g L^{-1} when the temperature was controlled at 35 °C, HRT of 4 h and OLR of 24 g COD $m^{-3}d^{-1}$.

Effect of vinasse in biological production of alcohols and volatile organic acids by microbial consortium

The highest productivity of butyric (44.2± 2.3 mg L h^{-1}), and acetic (9.3 ± 0.2 mg L h^{-1}) acids occurred in the reactors were the inoculum was treated by AT and with vinasse. We observed highest productivity of ethanol (8.4 ± 0.1 mg L h^{-1}) when the inoculums was treated by TT in presence of vinasse. The yield of ethanol production and AVT in relation to total carbohydrates ($g.g^{-1}$) was the highest in the reactor that received 66% of vinasse, with values of 0.26; 0.69; 0.28; 0.14g g^{-1}, respectively.

The microbiological characterization done by pyrosequencing technic revealed the occurrence in large quantity of bacteria of *Clostridium* genus, mainly in the consortium were autoclaved sludge was used at 120 °C during 10 min, at 1 kgf/cm^2 (AU) of pressure. At this conditions, the *C. pasteurianum*, a butanol specie producer bacteria of *Lactobacillus* genus was found in consorcium treated with TT and AT.

The addition of vinasse improved significantly the production of butyric acid, being an excellent source of nutrients for butyric fermentation. Butyric acid is the main precursor for butanol production, because high concentrations of butyric acid were produced as the main product of the fermentation process.

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Ariovaldo José da Silva

Faculdade de Engenharia Agrícola
Universidade Estadual de Campinas (Unicamp)
Avenida Cândido Rondon, 501 – Barão Geraldo
CEP 13083-875 – Campinas/SP – Brasil

+55-19-3521-1025
ariovaldo.silva@feagri.unicamp.br

PRETREATMENT OF SUGARCANE BAGASSE TO ACID OR ENZYMATIC HYDROLYSIS APPLYING THE ADVANCED OXIDATION PROCESS BY IONIZING RADIATION TO ETHANOL BIOFUEL PRODUCTION

Celina Lopes Duarte
Nuclear and Energy Research Institute (IPEN)
FAPESP Process 2008/56066-1 | Term: Feb 2009 to Jan 2011

Figure 1. Sugarcane bagasse irradiation in batch system at the Electron Beam Accelerator from Radiation Dynamics Inc., USA, with 1.5 MeV, and 37 kW

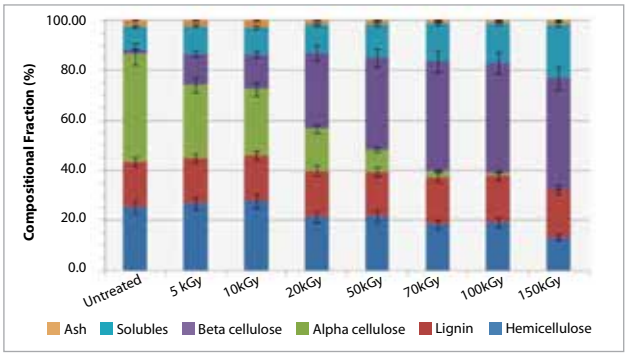

Figure 2. Compositional fraction of sugarcane bagasse untreated and irradiated in different absorbed doses

The main objective of the project is to study the cleavage of lignocellulosic material from sugarcane bagasse using ionizing radiation from an industrial electron beam accelerator, in order to make easier the cellulose hydrolysis and the fermentation of their sugars to ethanol biofuel production. The major drawback of pretreatments technologies is the formation of byproducts as carboxylic acids, furfural, and hydroxymethylfurfural formed by the dehydration reaction of xylose. Because of this fact, it is very important to keep a compromise between the severity and yield of the hydrolysis in order to get a maximum of glucose and celobiose liberation with the minimum byproducts formation.

Chemical modification of cellulose reactions by the free hydroxyl groups is one method for the production of value-added products, resulting in the production of cellulose derivatives. The reactive species generated by the interaction of ionizing radiation with water (oxidant OH radical, reductants e-aq, and H radical) reveal to be a very efficient method for the organic compounds oxidation in simple molecules and can modiify the structure of biomass making cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars. The main challenge of electron beam treatment is to obtain the desirable effects applying doses as low as necessary to get some break in the polysaccharides, and at the same time to avoid the loosing of sugars due to uncontrolled degradation of cellulose and hemicelluloses.

This project evaluated the effect of irradiation on the structure and composition of sugarcane bagasse, and on the combination with enzymatic hydrolysis, and hydrothermal treatment. The combination of technologies is meant to decrease the severity of the process avoiding sugar degradation and the formation of toxic byproducts.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

1. Radiation effect on structure and composition of sugarcane bagasse

The radiation processing promotes an increase in the soluble portion that is related to hemicellulose and cellulose cleavage. The cellulose with high molecular weight (alpha) presented a total reduction with absorbed dose of 50 kGy. The changes observed in the cellulose suggest some effects on the lignin structure (*Fig. 1*). The main sugars identified in the soluble fraction are glucose and arabinose, and it is also detected the water-soluble cello-oligosaccharides of glucanases and xylanases. The obtained results show that radiation interacts initially on the surface of hemicelluloses liberating the arabinose, and then act on the xylose polymers. The main byproduct liberated is acetic acid originated from the deacetilation of hemicelluloses; the removal of this acetyl group enhances the accessibility of the enzyme to the cellulose and can increase the enzymatic hydrolysis. This sequence of radiation interaction probably happens due to the location of xylose in the backbone of arabinoxylan, while arabinose is located in the branches of the macromolecules where the glycosidic bonds are easier to hydrolyze.

2. Radiation effect on enzymatic hydrolysis of cellulose

The enzymatic hydrolysis were done in the Sugarcane Technology Center, using a commercial Trichoderma reesei cellulase preparation (Celluclast 1.5 L), kindly supplied by Novozymes (Bagsvaerd, Denmark), with 5 FPU/g of cellulase and Beta-glycosidase 0.5% (p/p). The enzymatic conversion yield of cellulose to glucose increased from 8% to 14%, and from 6% to 18% in the Sample 1 and 2, respectively with 20 kGy of absorbed dose and 48 h of incubation. In an additional experiment applying absorbed doses up to 500 kGy, the conversion yield of cellulose to glucose did not increase for doses higher than 50 kGy. One reason for these results is the degradation of glucose by radiation and the inhibitory products formation.

3. Radiation combined with hydrothermal treatment

The hydrothermal hydrolysis of sugarcane bagasse at 180°C after irradiation with 50 kGy show a total reduction in oligosaccharides, liberating mainly xylose. However, the presence of formic acid and furfural, after 40 minutes of thermal treatment, mean that xylose and glucose are decomposed just after their liberation from hemicelluloses and cellulose. With the addition of diluted acid, the same amount of xylose is liberated as before, reducing the time from 40-10 minutes and the absorbed dose 50-10 kGy. In *Fig. 3* is showed the increase in solubility that is proportional to the radiation dose and hydrolysis time; otherwise, radiation processing is more important when the samples were treated with thermal rather than acid hydrolysis.

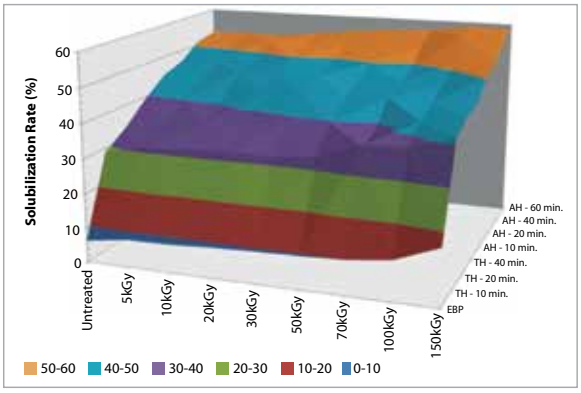

Figure 3. Sugarcane Bagasse Solubilization after Electron Beam Processing (EBP) followed by Thermal (TH) and Acid Treatment (AH)

4. Radiation combined with hydrothermal treatment and enzymatic hydrolysis

The conversion of hemicelluloses reached 42% after thermal treatment by 40 minutes for sugarcane bagasse irradiated with 50 kGy. After the addition of diluted sulfuric acid (0.1% v/v), almost the totality of hemicellulose is converted in xylose and byproducts, mainly furfural. The enzymatic conversion yield of cellulose reached 72% in samples irradiated with 50 kGy and 60 min. of thermal treatment. When dilute sulfuric acid was added, it was observed an increase in the cellulose conversion, however the time was reduced, and the higher value (74%) was reached in 40 minutes of diluted acid treatment and 24 h of enzymatic hydrolysis.

The structural and chemical modifications produced by ionizing radiation in the sugarcane bagasse are very important matter to be included in the second generation energy production and it depends on the combination of pretreatment technologies to transform these modifications into bioethanol production growth. The industrial application of electron beam accelerator on the second generation process is a challenging task and very feasible since the equipment could take part in the first generation installation.

Celina Lopes Duarte

Centro de Tecnologia das Radiações
Instituto de Pesquisas Energéticas e Nucleares (Ipen)
R. Prof. Lineu Prestes, 2242 – Cidade Universitária
CEP 05508-000 – São Paulo, SP – Brasil

+55-11-3133-9820
clduarte@ipen.br

SIMPLIFICATION OF THE BIOMASS TO ETHANOL CONVERSION PROCESS BY INTEGRATION WITH THE PRODUCTION OF ENZYMES *IN-HOUSE*

Cristiane Sanchez Farinas
Embrapa Instrumentation
FAPESP Process 2014/19000-3 | Term: Feb 2015 to Jan 2017

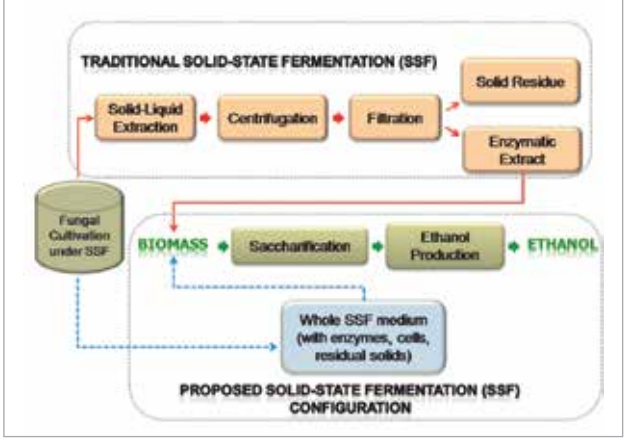

Figure 1. Schematic illustration of a simplified biomass-to-ethanol conversion process. On-site enzyme production is included by using the enzymes from the whole medium of fungal cultivation under SSF in the configuration of the saccharification and fermentation process to obtain ethanol. Conceptually, this process could be carried out in a single reactor system, avoiding the need for additional separation steps (Pirota et al., 2014).

The development of novel and efficient processes for the production of enzymes is a key step to ensure the economic viability of the enzymatic route for the production of biofuels and other bioproducts from plant biomass. To address this technological challenge, researchers from the Agroenergy Laboratory of Embrapa Instrumentation in collaboration with the Federal University of São Carlos conducted a preliminary study to assess the feasibility of an innovative strategy for the simplification of the biomass conversion process using enzymes produced *in-house*. These studies demonstrated the feasibility of using the whole solid-state fermentation (SSF) medium containing enzymes, fungal cells, and residual solid substrate for the saccharification of a lignocellulosic biomass and ethanol production. By using the whole SSF medium, the steps of extraction and filtration can be excluded from the overall process, providing advantages in terms of cost reduction and also avoiding the generation of waste streams. Since the results obtained by the group have shown potential results, this project aims to develop new strategies for the improvement and validation of this novel bioprocess. As a result of this project, it is expected to gather information in order to effectively contribute to generate the necessary technological advances to enable the use of plant biomass as a renewable energy source.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

A novel simplified configuration has been proposed for the conversion of biomass to ethanol, using whole-medium enzymatic cocktails (WM) and enzymatic extracts (EE) from different filamentous fungi (*Trichoderma reesei*, *Aspergillus niger*, and *Aspergillus oryzae*), cultivated under solid-state fermentation (SSF), for the hydrolysis of steam-exploded sugarcane bagasse (SESB). The hydrolyzed material derived from the saccharification of SESB using the combinations *A. niger* WM + *T. reesei* EE, *A. oryzae* WM + *A. niger* EE, and *A. niger* EE + *T. reesei* WM resulted in the best biomass conversion yields (66, 65, and 64% of the theoretical reducing sugar yields, respectively). The best ethanol production (84% of the theoretical yield) was obtained using the material hydrolyzed by a combination of *A. oryzae* WM + *A. niger* EE. The enzymatic conversion of SESB using on-site produced enzymes from the whole SSF cultivation medium, followed by an ethanol production step, could be a potential configuration for the biomass to ethanol conversion process. This novel simplified configuration would enable the use of a single reactor system, avoiding the need for additional separation steps. Further evaluation of the operating parameters and the addition of surfactants in the enzymatic hydrolysis step with the whole SSF medium, as well as the realization of fungal co-cultivations under SSF followed by the hydrolysis step with the whole SSF medium is currently been conducted.

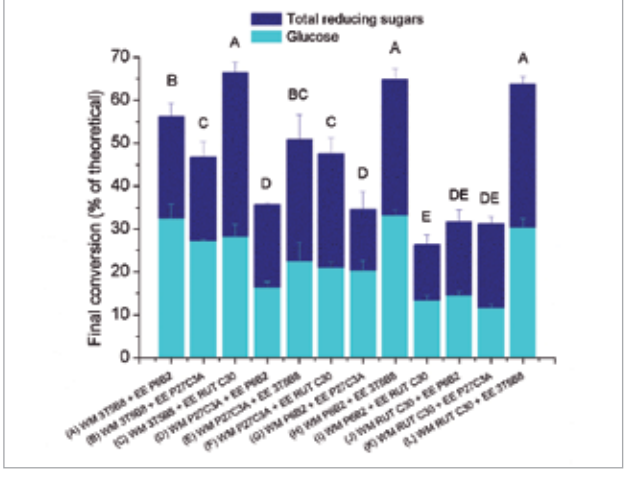

Figure 2. Total conversion of steam-exploded sugarcane bagasse (SESB) after 72 h of hydrolysis using enzymes from the different combinations of whole medium and enzymatic extract. Means with different letters are significantly different (Tukey's test, $p<0.05$) (Pirota et al., 2014).

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Cristiane Sanchez Farinas

Embrapa Instrumentação
Rua XV de Novembro, 1452
CEP 13560-970 - São Carlos, SP - Brasil

+55-16-2107-2908
cristiane.farinas@embrapa.br

CHLORELLA SP MICROALGAE SUSPENSIONS RHEOLOGICAL BEHAVIOUR ANALYZES IN DIFFERENT CULTURE TIMES

Daniela Helena Pelegrine Guimarães
Lorena School of Engineering / University of São Paulo (EEL/USP)
FAPESP Process 2014/03244-0 | Term: Aug 2014 to Jul 2016

Figure 1. Bubble columns reactors (Environment Laboratory/ DEQ / EEL / USP)

Renewable fuels production got great incentive recently, with fuel prices increase and more environmental issues concerns. Among raw materials available for biofuels, microalgae emerge as a sustainable alternative due high productivity and needlessness in land and water quality. Taking into account the growing interest in microalgae use as biodiesel raw this research aims to analyze rheological behaviour of microalgae suspensions (*Chlorella sp*) in different culture times, in order to estimate the energy demands of each step, aimed optimizing the a continuous-feed tubular bioreactor construction. At the same time, *Chlorella sp* oil and biofuel physical-chemical properties and rheological behavior will be analyzed. The oil will be characterized regarding saponification, acidity and iodine contents, and fatty acids average composition. Dantas (2006) and Silva Filho (2010) methodology will be followed for biodiesel produce, which will be characterized regarding specific heat, cetane number, fatty acids average composition and triglycerides absence. Rheological analyses will be conducted with rotational concentric cylinders rheometer. To carry out this work, it will be necessary improve Environment Laboratory (Chemical Engineering Department, in Lorena Engineering School - DEQUI/EEL/USP) infrastructure through LVDV2T Brookfield rheometer and HDA620 Herz06 manual distiller acquisition. These acquisitions intended to provide rheology research consolidation, an area lacking research theme, which certainly would contribute in department potential strengthening. Besides, distiller acquisition will contribute to other biodiesel research projects in EEL because, for this fuel, cetane index is one of the most quality indicators and this property is calculated, among other parameters, from 50% of the product temperature distillation.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

In all temperature and CO_2 concentrations the cultures showed non-Newtonian behavior, for all different culture times.

	Bingham				Casson			Power Law	
	η	τ_0	X_2	K_C	K_{0C}	x^2	n	K	X^2
1	2,82 (0,13)	0 (0)	0,98	4,33 (0,19)	0,97 (0,07)	0,99	1,61 (0,01)	0,075 (0,01)	0,99
2	3,08 (0,11)	0 (0)	0,98	4,92 (0,24)	1,27 (0,12)	0,99	1,68 (0,02)	0,056 (0,01)	0,99
3	2,89 (0,19)	0 (0)	0,99	4,61 (0,25)	1,18 (0,05)	0,99	1,68 (0,03)	0,053 (0,01)	0,99
4	2,94 (0,14)	0 (0)	0,98	4,59 (0,33)	1,10 (0,18)	0,99	1,62 (0,04)	0,07 (0,01)	0,99
5	2,94 (0,12)	0 (0)	0,97	4,60 (0,25)	1,02 (0,06)	0,99	1,62 (0,03)	0,08 (0,001)	0,99
6	3,04 (0,12)	0 (0)	0,98	4,84 (0,25)	1,25 (0,14)	0,99	1,67 (0,04)	0,06 (0,01)	0,99
7	2,92 (0,10)	0 (0)	0,99	4,53 (0,21)	1,07 (0,03)	0,99	1,63 (0,03)	0,07 (0,01)	0,99
8	3,00 (0,22)	0 (0)	0,98	4,72 (0,45)	1,26 (0,21)	0,99	1,69 (0,03)	0,06 (0,01)	0,99

Table 1: Chlorella sp suspension of Rheological Parameters

Casson, Power Law and Bingham models adjusted well to the data of shear stress as a function of shear rate. It was observed no effect of culture times and little effect of temperature and CO_2 concentration on the apparent viscosity. Besides, *Chlorella sp* suspension proved a material with dilatant characteristics, such as, in all cases, the behavior index resulted values greater than one.

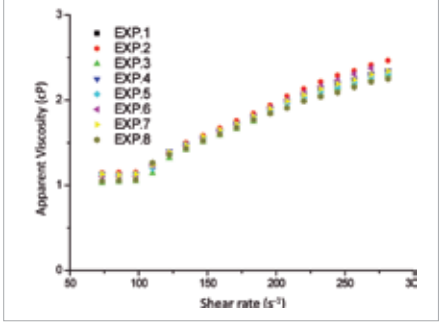

Figure 2. Apparent viscosity at different process conditions

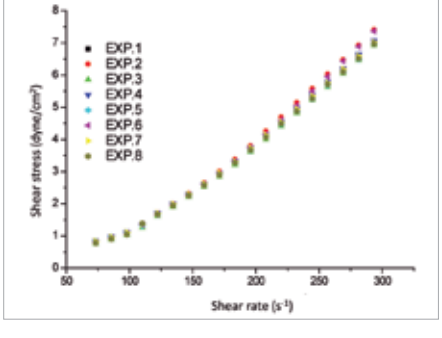

Figure 3. Rheograms in different process conditions

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Daniela Helena Pelegrine Guimarães

Escola de Engenharia de Lorena (EEL/USP)
Universidade: Universidade de São Paulo (USP)
Estrada Municipal do Campinho, s/n
CEP 12602-081 – Lorena, SP – Brasil

+55-12-3159-5327
dhguima@usp.br

CATALYSTS FOR GLYCEROL HYDROGENOLYSIS: PRODUCTION OF GLYCOLS FROM BIOMASS DERIVATIVES

Daniela Zanchet
Brazilian Synchrotron Light Laboratory (LNLS)
FAPESP Process 2007/51754-4 | Term: Oct 2008 to Mar 2011 | PITE – Business partner: Oxiteno S/A

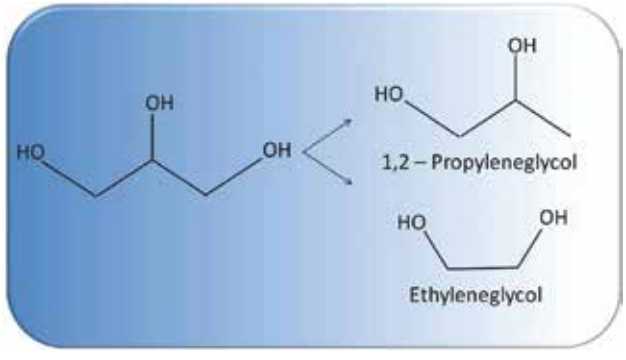

Figure 1. Hydrogenolysis of glycerol producing 1,2-PG and EG

The conversion of biomass and other renewable sources to higher-valued chemicals is one of the strategic goals of the 21th century. It is also a requirement concerning the challenges to be overcome related to environment and energy. Glycerol, a major byproduct of biodiesel production, is one of the main examples of low-cost, large-volume market product that can be used as a starting material for chemical transformation. The "glycerochemistry", which search for routes to process glycerol into more valuable commodity chemical, has become an intense area of research. An industrially relevant route involves the hydrogenolysis of glycerol to 1,2-propylene glycol (1,2-PG) and ethylene glycol (EG) (*Figure 1*). Both chemicals are widely used for manufacturing important products, from fibers to antifreeze and pharmaceuticals. In the hydrogenolysis reaction, hydrogen gas reacts with glycerol in the presence of a catalyst in several coupled steps, producing intermediates that are finally converted to EG or 1,2-PG. It is a complex reaction that is usually carried out under high pressure of hydrogen (500-1050 psi), high temperature (180-2500C) and for long reaction times (4-20 h), and alternatives routes and optimized catalysts are still desirable for large scale applications. As part of the partnership between Brazilian Synchrotron Light Laboratory (LNLS) and OXITENO S/A, the presented project co-funded by FAPESP aims the development of selective catalysts for hydrogenolysis of glycerol to glycols and the comprehension of the physicochemical characteristic that determine their performance. One of the main parameters guiding this work is the optimization of the selectivity to EG or 1,2-PG in a batch reactor, taking into account requirements for scaling up process. Studies on model systems and reactions supported by advanced characterization of catalysts using synchrotron techniques and electron microscopies will help to speed up the understanding of the system.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The control of glycol selectivity to 1,2-PG or EG requires the deep understanding of the reaction mechanism behind the glycerol hydrogenolysis. Although several works can been found on maximizing the selectivity for 1,2-PG [1] only in the last couple of years a good compromise between conversion and selectivity to EG has being achieved [2] . The main drawback is the uncontrolled C-C bond cleavage that may lead to a high percentage of gas products. For 1,2-PG production, Cu-based catalysts have presented good results while for EG production, Ru/C, transition-metal carbides and Ni-Raney are the most promising alternatives.

In the first year of the project the main effort was focused on the installation of the infrastructure required for catalytic tests. The assembled catalytic unit is composed by a batch reactor (Parr Instruments) of 300 ml, maximum operation pressure of P=1900 psi, temperature T=3500C and stir rate R= 1800 rpm, fed by H_2 from a P-controlled tank. The parameters of the reactor (P, T, rpm) as well as the pressure of the H_2 tank can be controlled remotely. For reaction products analysis we installed a gas-chromatograph (GC) equipped with FID and TCD detectors. The whole system was project following the set-up installed at OXITENO to promote a routine exchange of information and experience. *Figure 2a* shows the catalytic unit installed at LNLS.

Different catalysts have already been obtained and tested, such as Ru/C, Ni/C, Ni-W_2C and Ni-Raney. A general trend is the tendency for 1,2-PG formation among the liquid products after several hours of reaction. Selectivity to EG has been maximized only at short times and low conversions. *Figure 2b* shows preliminary results for Ni-Raney catalysts. This is in agreement with the main challenge to high production of EG that is to control the excessive cleavage of C-C leading to gas products. Next steps involve the detail analysis of the gas phase products, optimization of reaction conditions using concentrate glycerol solution (closer to industrial need), exploration of model reactions and improvement of Ni-W_2C catalyst synthesis.

a)

b)

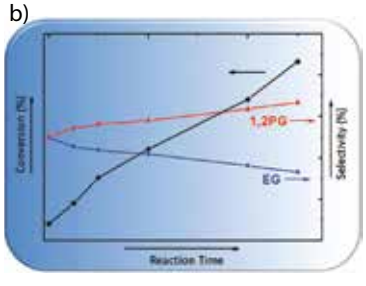

Figure 2. (a) Catalytic unit at LNLS and (b) preliminary results obtained with Ni-Raney catalysts

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Related to bioenergy, not derived from this project.

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Daniela Zanchet

Associação Brasileira de Tecnologia de Luz Síncrotron
Departamento Científico
Rua Giuseppe Máximo Scolfaro, 10.000
Caixa Postal 6192
CEP 13084-971 – Campinas, SP – Brasil

+ 55-19-3512-1049
zanchet@lnls.br

ELECTROCATALYSIS IV: FUNDAMENTAL AND APPLIED ASPECTS OF ELECTROCATALYTIC PROCESSES, BIO-ELECTROCATALYSIS AND KINETIC INSTABILITIES

Edson Antonio Ticianelli
São Carlos Institute of Chemistry / University of São Paulo (USP)
FAPESP Process 2009/07629-6 | Term: Oct 2009 to Sep 2013 | Thematic Project
Co-PIs: Ernesto Rafael Gonzalez, Fabio H. Barros de Lima, Germano Tremiliosi Filho, Hamilton B. Varela de Albuquerque

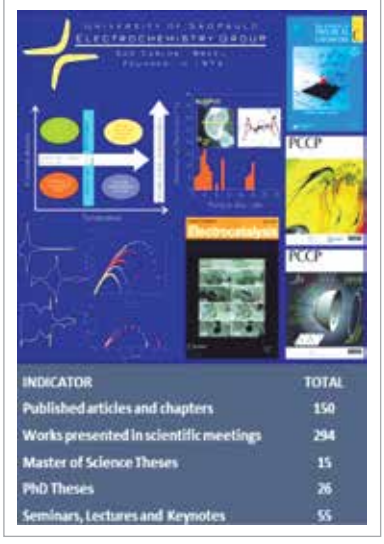

Figure 1. Highlights of the scientific production between 2010 and 2013. The cover pages appeared in the following periodics are included: J. Phys. Chem. C *114, 2010, issue 43;* Phys. Chem. Chem. Phys. *13, 2011, issue 2; Idem 14, 2012, issue 23; and* Electrocatalysis *4, 2013, issue 2*

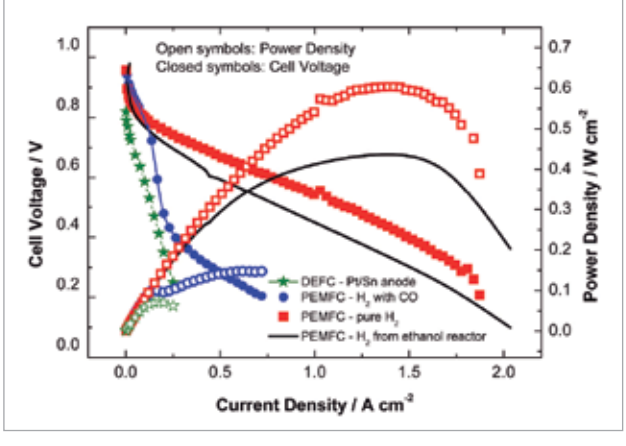

Figure 2. Stabilized polarization and power density curves of PEMFCs with anodes operated under H_2 coming from an ethanol dehydrogenation reactor compared to pure H_2, H_2 with 100 ppm CO, and a pure ethanol. Cathode: pure Oxygen. T = 70 °C. More details in: Sato et al. 2015. J. Power Sources. ***294****: 269-573*

The goal of the project consists of the study of electrocatalytic processes taking place in energy conversion and storage systems, particularly the ones involving reactions in fuel cells, including bioactive electrodes. Attention will be paid to the study of the oxygen reduction reaction and of the oxidation of alcohol molecules and hydrogen deliberately contaminated with traces of carbon monoxide. The investigation will also include the study of kinetic instabilities usually observed, for instance, during the electro-oxidation of small organic molecules such as formic acid, methanol, and ethylene glycol. It will be studied some fundamental aspects of the electrocatalysis as well as the kinetic instabilities of such reactions on massive pure metals (both single crystals and polycrystalline) and metallic alloys, and carbon dispersed electrocatalysts. In this case, it will be employed nanoparticles of pure noble metals, alloys, core-shell structures formed by a transition metal covered by monolayers of noble metals, and metallic oxides. Finally, the development of biomaterials for low temperature bio fuel cells will be also considered, with emphasis on the immobilization of enzymes such as cloroperoxidase, peroxidase, lacase, tirosinase e glicose oxidase. Further development might also include operational systems of gas diffusion electrodes, on which the study of electrocatalysed reactions of fundamental and practical interest will be carried out.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

New insights have been achieved regarding the understanding of fundamental aspects of the reactions and processes, as well as on the improvements of the catalytic performances. In this way, studies on the electrocatalysis of the oxygen reduction reaction were conducted either in acid and alkaline electrolytes, employing a number of nanostructured carbon-supported Pt-based (PtM/C) electrocatalysts, where M were Ni, Co, Fe, etc., with special structures such as hollows and core-shells, and different catalyst supports such as non-noble metal carbides and oxides. In addition, the electrocatalysis of alcohol oxidations such as methanol, ethanol, glycerol, were investigated aiming at applications on acid and alkaline fuel cell systems. Electrocatalyst materials were nanocrystalline and polycrystalline bulk metals (Pt, Pd, and Au). Several types of carbon-dispersed nanoparticles (PtRu/C, PtRh/C, PtSnOx/C, PtWOx/C, etc) were also considered. In these systems, different types of oscillatory kinetics have been commonly investigated for obtaining kinetic parameters under far-from-equilibrium reaction regimes. In the bioelectrocatalysis area, works to study the electron transfer reactions mediated by triphenylen-derived compound and the pseudomonas aeruginosa bacteria for the electrocatalysis of the glycerol oxidation were carried out. Finally, the electrocatalysis of the cathodic and anodic reactions on proton exchange membrane fuel cells (PEMFC) were investigated focusing practical and fundamental aspects of the oxygen reduction reaction and hydrogen oxidation reaction in the presence of contaminants such as CO and sulfur.

Figure 1 shows, in an illustrative way, some of the main results obtained in the project, including four cover pages that appeared in specialized journals. The academic production achieved inserted in *Fig. 1* clearly show that the project was completed very successfully. The quality of the scientific production is attested by the large number of articles published in journals of high scientific impact such as Chemical Sciences, Chemical Communications, Applied Catalysis B, Journal of Physical Chemistry, Journal of Power Sources, Electrochemistry Communications, Electrochimica Acta, PLoS One, among others. Typical results obtained on PEMFCs are illustrated in *Figure 2*.

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Edson Antonio Ticianelli

Instituto de Química de São Carlos
Universidade de São Paulo
Av Trabalhador Sãocarlense, 400, Pq Arnold Schimidt
CEP 13560-590 – São Carlos, SP – Brasil

+55-16-3373-9945
edsont@iqsc.usp.br

BIOGAS PRODUCTION BY ANAEROBIC DEGRADATION OF SUGAR CANE VINASSE: INVESTIGATION OF THE HYDRAULIC AND ORGANIC RATES APPLIED TO UASB REACTOR FOR PROCESS OPTIMIZATION

Eduardo Cleto Pires
São Carlos School of Engineering / University of São Paulo (USP)
FAPESP Process 2013/17591-1 | Term: May 2014 to Apr 2016

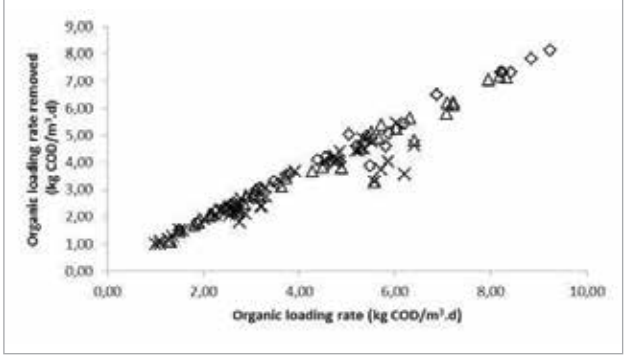

Figure 1. Organic loading rate removed in R1 (X), R2 (Δ) and R3 (◊) as a function of organic loading rate applies to the reactors

In an alcohol distillery, 40% of the chemical energy contained in the cane sugar is recovered as alcohol while 31% remains in the bagasse (26%) and vinasse (5%). Sugar cane mills uses bagasse extensively to meet the demand for energy in the production process; however, the content of energy remaining in the vinasse, although significant in the energy balance, is still mostly unexploited as such. Usually, the primary use of vinasse is for fertigation in its raw state.

The anaerobic digestion of organic matter is a suitable option to exploit the vinasse energy potential without loss of the fertilization potential. This process generates biogas, a fuel with a high-energy content, composed primarily of methane, similar to natural gas and as such having the same uses.

Researchers have conducted studies aiming to degrade vinasse and generate biogas, using anaerobic reactors at various scales. However, reactor design imperfections and the natural difficulties of maintaining high rate anaerobic digestion for extended periods for such a difficult to degrade waste have prevented the widespread use of this technology to process vinasse. There are many steps to overcome before a high rate anaerobic compact and efficient reactor will reach the maximum potential of organic matter removal and biogas production. Furthermore, as large quantities of alkali are needed to maintain the proper pH for anaerobic digestion of vinasse, its balance optimization is an important research topic.

To overcome at least part of the difficulties, this project aims to investigate the hydraulic and organic loads applied to a pilot scale anaerobic reactor, to obtain rational criteria for reactor design and ensure optimum anaerobic degradation of vinasse, biogas production and minimization of alkali use.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Three pilot-scale upflow anaerobic sludge blanket (UASB) reactors were operated. Reactor 1 (R1) operated without recirculation, while reactors 2 (R2) and 3 (R3) operated with recirculation rates of 1:3 and 1:5, respectively. The hydraulic organic loading rate (OLR) gradually increased in steps in order to adapt the anaerobic sludge to the vinasse. The OLR applied to R1, R2 and R3 ranged from 1.0 to 6.4; 1.0 to 8.3 and 1.0 to 9.3 $kgCOD.m^{-3}.d^{-1}$, respectively.

The COD removal efficiencies over the applied OLR were (83±13)% for R1, (88±7)% for R2 and (90±7)% for R3. The results indicate that there is an almost perfect correlation between applied and removed OLR (r^2 higher than 0.95), as shown in *Figure* 1. The higher efficiencies shown by reactors R2 and R3 are attributed to the effect of recirculation, as this is the only operational parameter that differs from reactor to reactor in this experiment.

The biogas production from anaerobic degradation is directly proportional to the removed organic load. The highest productivity (2.25 $LCH_4\ L^{-1}d^{-1}$) was obtained from reactor R3 under 8.25 $kgCODm^{-3}d^{-1}$, generating 344 gCH_4d^{-1}. The methane potential for power generation is 1.686 kWh/$kgCH_4$, considering as 35% the overall energy conversion efficiency of gas generator sets (Van Haandel, 2005). Based on this result, the production of 1 m^3 of ethanol, that would result in 13 m^3 of vinasse as waste (40 gCODL), will yield 190 kWh of electric energy (*Figure 2*).

The distillery that supplied vinasse for this research produced 140,000 m^3 of alcohol during the 2014/2015 harvesting season. Using UASB reactors with the same methane productivity obtained in this research this plant could supply electric energy for 48,000 homes (157kwh / month), equivalent to approximately 216,000 inhabitants, in this period.

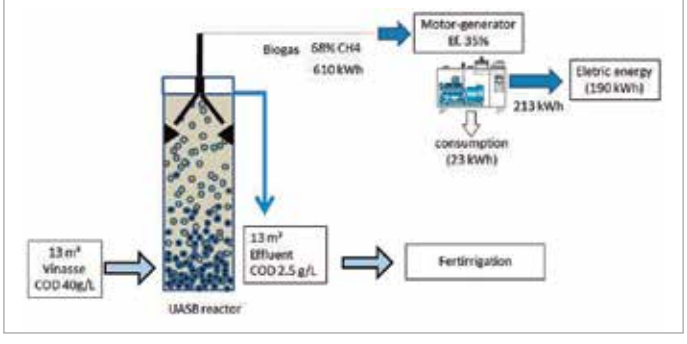

Figure 2. Flowsheet of electric energy generated by 13 m^3 of vinasse

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Eduardo Cleto Pires

Escola de Engenharia de São Carlos, Departamento de Hidráulica e Saneamento
Universidade de São Paulo
Av. Trabalhador Sãocarlense, 400
CEP 13566-590 – São Carlos, SP – Brasil

+55-16-3373-9571/9539
ecpires@sc.usp.br

ENVIRONMENTAL AND SOCIOECONOMIC IMPACTS ASSOCIATED WITH THE PRODUCTION AND CONSUMPTION OF SUGARCANE ETHANOL IN SOUTH CENTRAL BRAZIL

Evlyn Márcia Leão de Moraes Novo
National Institute for Space Research (INPE) / Ministry of Science, Technology and Innovation (MCTI)
FAPESP Process 2008/56252-0 | Term: Nov 2010 to Oct 2014 | Thematic Project
co-PI: Bernardo Friedrich Theodor Rudorff

This research project covered a wide range of topics related to environmental and socioeconomic impacts of the sugarcane ethanol production and consumption in the South Central region of Brazil. With the use of remote sensing imagery and geographic information systems the project mapped the sugarcane crop expansion observed in the South-Central region since crop year 2003 as well as the dramatic reduction of straw burning practice during harvest in São Paulo state since 2006. Furthermore, the land use and land cover change (LULCC) observed since the year 2000, due to sugarcane expansion in South-Central Brazil, was evaluated based on time-series of remote sensing images (*see Figure 1*). The observed sugarcane crop expansion dynamic has supported the generation of scenarios related to plausible spatial patterns for sugarcane crop expansion in the short- and medium-terms in South-Central Brazil. These scenarios were used to drive biosphere-atmosphere interaction models, designed to assess physical-chemical changes in the atmosphere related to LULCC and to trace gases and aerosol atmospheric emissions in response to sugarcane expansion. The quantitative outcomes of these models in terms of atmospheric chemistry provided spatial-temporal distribution of green-house gases, toxic primary or secondary gases, and aerosols, which could be used to access the impacts on human health. Runoff from agricultural fields is one of the main routes of nonpoint source pollution whose main components are sediments, organic residues, pesticides, nutrients, and bacteria which can induce eutrophication in surface waters. In this topic a temporal-spatial evaluation of inland aquatic system's eutrophication was carried out by integrating *in situ* and remote sensing time series to detect change in water optical properties linked to algal blooms. In addition to this, econometric and economic models were conceived to analyze the resulting changes of production and consumption of sugarcane ethanol in the urban network and infrastructure, in the natural environment assets, in the social well-being, in the jobs market and related scientific-technological scenario, in the agri-business economics, in agricultural financing policies, in the commodities market and food security (at national level), and in the trade balance. The knowledge gained with this work provided information to increase the understanding of the complex relationships among the sugarcane production and consumption and its related environmental and socioeconomic impacts, allowing thus a strategic contribution to public policies and actions aiming at maximizing the benefits of the sugarcane ethanol and minimizing at the same time its undesirable side effects and externalities.

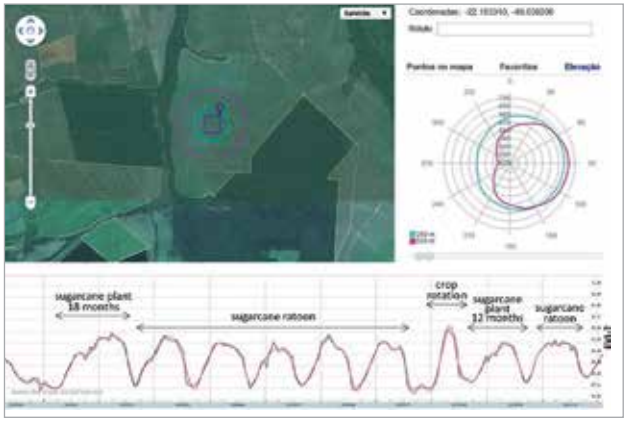

Figure 1. The bottom part of the figure represents a time-series of vegetation index values (EVI2) derived from remote sensing images (MODIS) showing a 10-year series of the crop growth cycle dynamic for a sugarcane field pixel depicted in the balloon of the virtual globe of Google Maps (www.dsr.inpe.br/laf/series)

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The annual sugarcane crop mapping has been performed for the South Central region of Brazil since 2003 within the context of the Canasat project (www.dsr.inpe.br/laf/canasat/). *Figure 2* illustrates the available sugarcane area for harvest in São Paulo State from 2004 to 2011 indicating the area of sugarcane expansion. *Figure 3* illustrates the dynamic of land conversion since 2000 for the sugarcane area expanded from 2006 to 2009 in South-Central Brazil. This information was used to subsidize studies concerning the environmental and socioeconomic impacts associated to the current and predicted extensive production of ethanol in South-Central Brazil. With the use of the Dinamica-EGO modeling platform, scenarios for sugarcane expansion in the short- and medium-terms were generated. These scenarios supported several aims in the project generating annual LULCC scenarios (2008 to 2020) with the indication of sugarcane areas prone to be harvested without the straw burning practice. Maps showing the spatial distributions of algal blooms along several moments were obtained based on *in situ* measurements of an automatic data collecting system of environmental variables (SIMA), and on remote sensing and GIS techniques for a selected reservoir. A series of spatial information about the phytoplankton distribution in selected reservoirs subjected to algal blooms were obtained. An assessment of the impacts associated with sugarcane production and derived biofuel use in São Paulo State was generated based on the use of a state-of-the-art limited-area atmospheric model coupled on-line with a chemistry transport model: CCATT-BRAMS (Chemistry-Coupled-Aerosol-Tracer Transport model to the Brazilian developments on the Regional Atmospheric Modeling System). CCATT-BRAMS fed with the LULCC scenarios and estimated emissions inventories allowed an evaluation of the associated changes on the planetary boundary layer properties, hydrological cycle and air quality. With the social-economical study it was possible to assess the parameters that were used to establish public and private measures in relation to the sector.

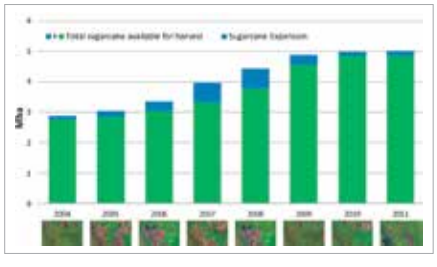

Figure 2. Sugarcane area available for harvest in São Paulo from 2004 to 2011 (sugarcane expansion in blue)

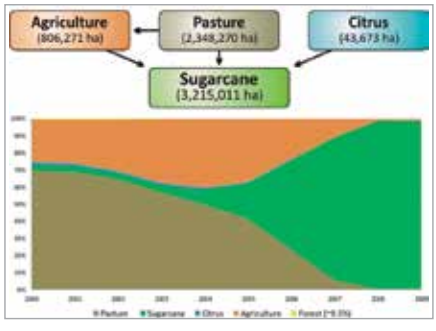

Figure 3. The dynamic of land conversion since 2000 for the sugarcane area expanded during crop years 2006 to 2009, in South Central Brazil

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Evlyn Márcia Leão de Moraes Novo

Instituto Nacional de Pesquisas Espaciais (Inpe)
Ministério de Ciência e Tecnologia (MCT)

Av. dos Astronautas, 1758
CEP 12227-010 – São José dos Campos, SP – Brasil

+55-12-3208-6490
evlyn@ltid.inpe.br

THERMOPHILIC ANAEROBIC TREATMENT OF VINASSE IN A TWO STAGE SYSTEM: SULFETOGENIC BIOREREACTOR FOLLOWED BY METHANOGENIC BIOREACTOR

Flavia Talarico Saia
Institute for Health and Society / Federal University of São Paulo (Unifesp)
FAPESP Process 2012/17002-3 | Term: Dec 2012 to May 2015 | FAPESP-BE-Basic

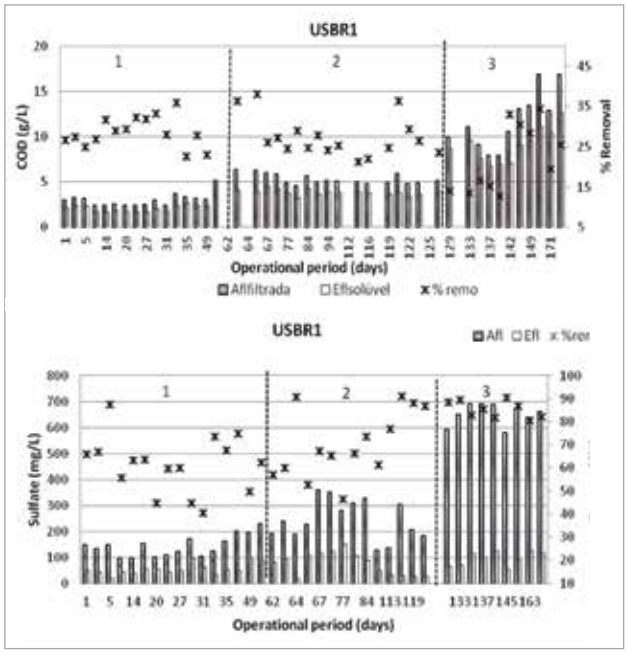

Figure 1. Concentration and removal of COD (a) and Sulfate (b) during the operational time of USBR 1

Alternative energy sources are becoming more and more important, and hydrogen (H_2) and methane (CH_4) production from biomass and residues are options for renewable energy. Currently, research is focused on optimization of H_2 and CH_4 production from vinasse, the liquid residue left in the distillation of ethanol from sugarcane derivates. Due to its high biochemical oxygen demand (17,000 to 50,000 mg/l), vinasse has the potential to be converted into renewable energy. However, gaps related to the process, e.g. removal of sulfate, configuration, operation and stability of reactors and limited knowledge of the involved microbiota need to be overcome in order to evaluate the potential application of anaerobic technology for the treatment of vinasse and bioenergy production. In this research, structured fixed bed reactors were operated at 55 ºC fed with vinasse in order to and improve organic matter and sulfate removal as well as methane production.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

In order to evaluate the effect of organic loading rate (OLR) and stability of sulfetogenesis and methanogenesis, two lab-scale up-flow structured bed reactors (USBR) were operated under thermophilic condition (55 ºC) for 173 days at three different loading rates conditions: phase 1 from day 1 to day 60; phase 2 from 60 day to 128 day and phase 3 from day 128 to day 173. USBR1 was inoculated with auto-fermented vinasse and USBR2 was inoculated with anaerobic sludge from UASB reactor treating vinasse and sewage. Polyurethane foams were used as support bed in both bioreactors. USBR1 was continuously fed with diluted sugarcane vinasse, in order to obtain the desired values of COD and OLR. USBR2 was continuously fed with the effluent of USBR1. Hydraulic retention time of USB1 was 2h and of USBR2 was 48h. COD and OLR´s applied for USBR1 were: phase 1 COD of 2.0-3.6 g/L (OLR 24-43Kg COD/m^3*day); phase 2: 5-6.3 COD g/L (OLR 60-75.6 Kg COD/m^3*day); phase 3: 9-16.9 COD g/L (OLR 108-202 Kg COD/m^3*day).For USBR2, the values of COD and ORLR´s were: COD: 1.6-2.6 g/L (OLR 0.8-1.3 Kg COD/m^3*day); phase 2: COD of 3.2-4.5 g/L (OLR 1.6-2.25 Kg COD/m^3*day); phase 3: COD 7.6-12.6 g/L (OLR 3.8-6.3 Kg COD/m^3*day).

Values of pH of influent of USBR1 ranged from to 6.0 to 6.5, and effluent pH were stable during all operational period with values ranged from 6.5 to 7.0 The pH of effluent with values superior when compared with affluent show the formation of alkalinity, characteristic of sulfate respiration. These results are important for application of anaerobic technology since it is not necessary to add alkalinizing to send the effluent to methanogenic reactor. Organic matter removal was stable during all operational period, with values of COD removal ranged from 22 to 36% (*Figure 1a*). Removal of sulfate increased with ORL applied with values ranged from 40 to 90% (*Figure 1b*). These results show that sulfate removal was improved by availability of organic electron donors, such as valeric, butyric, acetic, fumaric and malic. Valeric was present in vinasse and metabolized in USBR1. Organic acids butyric, acetic, fumaric and malic were produced and consumed by microbial community of USBR1. This is the first report that shows the stability of a sulfetogenic bioreactor operated with vinasse and with low hydraulic retention time (2h), and so the potential to apply compact anaerobic reactors.

pH of USBR2 was stable during all operational period with values ranged from 7.0 to 8.0. The predominant organic acids acetic and butyric, from USBR1, were metabolized by microbial community of USBR2 with removal of residual of organic matter (COD) with values ranged from 60 to 75% (*Figure 2a*) and sulfate removal ranged from 40 to 100% (*Figure 2b*). Methane was produced and increased with the increase of OLR applied, with values ranged from 0.5 umol to 3.8 umol.

MAIN PUBLICATIONS

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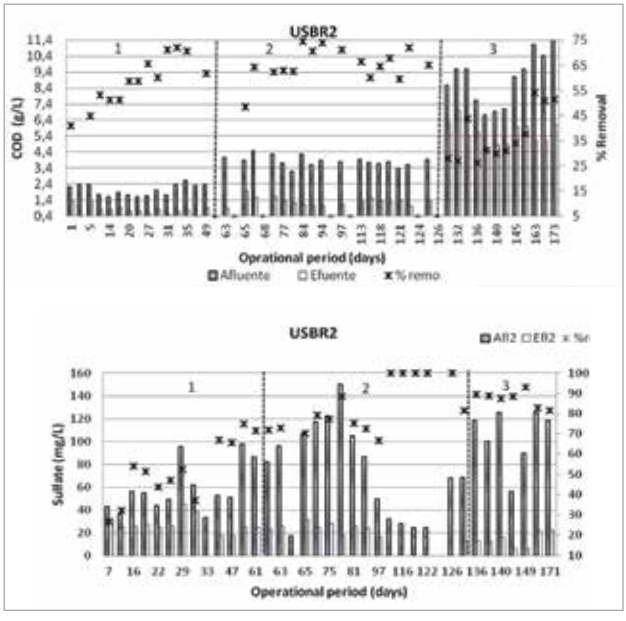

Figure 2. Concentration and removal of COD (a) and Sulfate (b) during the operational time of USBR 2

Perspectives: Structure of microbial community of USBR1 and USBR2 of each operational phase is being analyzed by DGGE. Phylogenetic identification of both bioreactors at the end of operational period is in progress.

Flavia Talarico Saia

Universidade Federal de São Paulo
Campus Baixada Santista
Departamento de Ciências do Mar
Av. Almirante Saldanha da Gama, 89, Ponta da Praia
CEP 11030-400 – Santos, SP – Brasil

+55-13-3878-3966
ftsaia@yahoo.com.br

THE ENVIRONMENTAL IMPACT OF BIOFUEL PRODUCTION FUNCTIONAL BIO-INDICATORS FOR SUSTAINABLE AND OPTIMAL BIOFUEL PRODUCTION

Flavia Talarico Saia
Institute for Health and Society / Federal University of São Paulo (Unifesp)
FAPESP Process 2012/51496-3 | Term: Feb 2014 to Jan 2016 | FAPESP BE-Basic

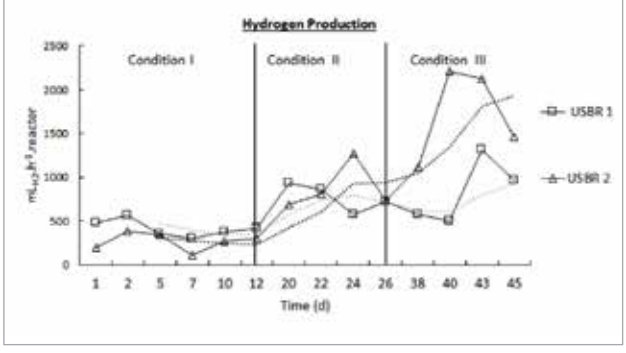

Figure 1. Hydrogen Production during the operational time for USBR 1 and USBR2

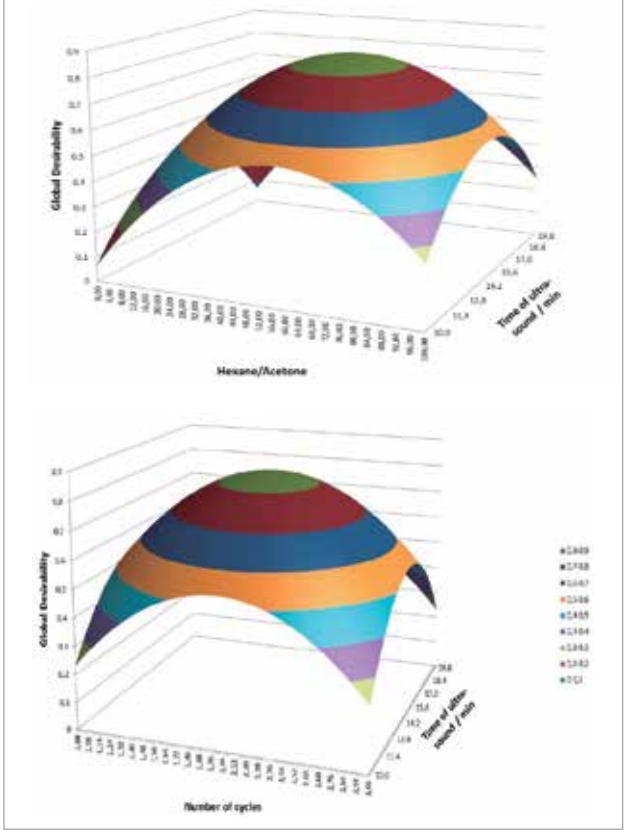

Figure 2. Graphics surface of solvents x time of ultra-sound (a) and number of cycles x time of ultra-sound (b)

Alternative energy sources are becoming more and more important, and hydrogen and methane production from biomass and residues are options for renewable energy. Currently, research is focused on optimization of hydrogen and methane production from vinasse, the liquid left in the distillation of ethanol from sugar-cane derivates. Molasse is also generated during the process of sugar and ethanol production and due its high organic content, it is also has the potential for hydrogen and methane production. Gaps related to the process, e.g. configuration, operation and stability of reactors and limited knowledge of the involved microbiota need to be overcome in order to evaluate the potential application of anaerobic technology for the treatment of vinasse and molasse and bioenergy production. In addition, the used pesticides can either remain in the environment, causing environmental problems, or transform into harmless compounds.
The work proposed in this project will address the use of anaerobic technology on hydrogen and methane production from molasse. In addition, molecular tools such as qPCR assays will be developed to monitor the key players. Biodegradation tests will be performed, to identify the biodegradation potential for the used pesticides in the environment. Finally, the biodiversity in soil systems at sugar-cane production sites that have received pesticides will be studied. Both geochip and qPCR assays will be used to monitor indicator species in the contaminated soil. This is in line with the strategy that will be used for the relation between biodiversity and eutrophication in a BE-Basic project.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Bionergy from sugarcane molasse

In order to evaluate the effect of organic loading rate (OLR), material support and source of inocula on hydrogen production, two lab-scale up-flow structured bed reactors (USBR) were operated under thermophilic condition (55ºC) for 45 days at three different loading rates conditions: condition I from day 1 to day 12; condition II from 12 day to 26 day and condition III from day 26 to day 45. USBR1 was inoculated with auto-fermented vinasse and low density polyethylene cubes were used as support bed. USBR2 was inoculated with anaerobic sludge from UASB reactor treating poultry slaughterhouse wastewater and polyurethane foams were used as support bed. The bioreactors were continuously fed with sugarcane molasses.

Values of pH of influent ranged from to 5.5 to 6.5, and effluent pH values were stable during all operational period for both reactors with values from 4.0 to 4.5. The low pH values of effluents show that acidogenesis occurred. In fact acids were formed and oxidation of organic matter was incomplete with average values of COD removal of 24% (USBR1) and 30% (USBR2) for total COD and 35% (USBR1) and 37% (USBR2) for soluble COD. Hydrogen production was related with the organic loading rates, material support and sorurce of inocula. According to the *Figure 1*, hydrogen production rate increased with organic loading rate but started to decrease at the end of operational period with ORL of 120 gCOD $g*L^{-1}*d^{-1}$. Hydrogen production was higher in USBR2 than in USBR1 starting from condition II. In USBR2 the production of acids was also higher with predominance of acetic and butyric acids, precursors of hydrogen production.

Perspectives: USBR2 has been in operation over 200 days to evaluate the stability of hydrogen production for long period of time. Methanogenic bioreactor was coupled to acidogenic bioreactor and the system has been in operation with crescent OLR to evaluate the bioenergy production (hydrogen and methane) by the combined system.

Analytical method for pesticide determination in soil

Chemiometric tool Box-Behnken was used as experimental design to develop a gas chromatographic method for determination of fipronil and metabolites in soil. Three variables were evaluated: (1) solvent ratio, (2) number of cycles and (3) time of ultra-sound . The variables were analyzed in pairs and according to global "desirability" (D global) (*Figure 2*) the best methodology of extraction of analytes from soil is use the solvents hexane:acetone in ratio of 1:1 (v/v), two cycles of ultra-sound for 15 min each.

Perspective: This methodology was validated and it has been used to monitor biotransformation of fipronil and metabolites in soil with historical of sugarcane plantation.

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Flavia Talarico Saia

Universidade Federal de São Paulo
Campus Baixada Santista
Departamento de Ciências do Mar
Av. Almirante Saldanha da Gama, 89, Ponta da Praia
CEP 11030-400 – Santos, SP – Brasil

+55-13-3878-3966
ftsaia@yahoo.com.br

PLASMA TECHNOLOGY FOR ENERGY PRODUCTION: CONVERSION OF COAL TO SYNTHESIS GAS, CO_2 REFORM AND TAR TREATMENT

Gilberto Petraconi Filho
Technological Institute of Aeronautics (ITA)
FAPESP Process 2010/51298-1 | Term: May 2012 to Apr 2016 | PITE – Business partner: Vale S/A

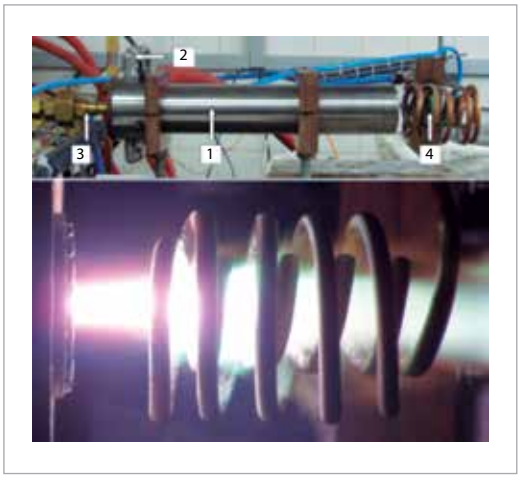

Figure 1. DC transferred arc steam plasma torch of ITA, Brazil for power P = 30-300 kW, thermal efficiency h = 95-97%. 1. Plasma torch, 2. Gas inlet, 3. Cathode, 4. Anode

The aims of this project are the development of plasma technologies for coal and biomass gasification and the reform of compounds generated by this process, especially tars (condensable hydrocarbons : furans, phenols, etc.), non-condensable hydrocarbons (as methane, ethane and dioxins) and carbon dioxide (CO_2), in order to enhance the generation of synthesis gas (CO and H_2). The planned activities have been focused on the coal and sugarcane bagasse gasification processes by using air and steam plasma torches. To fulfill of gasification process a number of efficient thermal plasma torches were last years developed, including of DC transferred electric arc torch (EAT) with water steam or air as plasma gas and power of 50-300 kW, which is currently adopted at ITA for experiments with coal feedstock (*Figure 1*). For engineering design of plasma gasifiers with EAT (*Figure 2*) is necessary to determine the chemical composition and transport properties of high temperature medium in these under gasification, with a taking into account the specific characteristics and composition of feedstocks. This work presents the thermochemical assessment for the comparison of plasma gasification process with low grade coal and biomass feedstock at use of different oxidants.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The thermochemical assessment of plasma gasification efficiency for the case of Brazilian industrial scale coal and coal-based water slurries with using of steam and air as gasifying agents was carried out. The data calculated show that for reforming this coal feedstock (with quite high ash content of 28 %) to syngas with yield of near 100% the energy consumption level of 10-12 MJ/(kg of syngas) is sufficient on the thermodynamic results at the using of regimes with ratio of mass flow rates of feedstock to gasifying agent $G_C / G_{ST} = 4.0$ for coal. The calculated level of calorific value of syngas, that is possible to produce from this kind of low–grade feedstock at the optimal thermochemical conditions of plasma gasification is quite high for special fuel using of syngas in the industrial combustion and power generation systems and is as 9.6-10.0 MJ/ nm^3. Thermochemical assessment for the case of biomass waste composed of sugarcane bagasse was carried out for different variants of use of individual gasifying agents, which can be used for practical realization in operating regimes of thermal plasma reactors for syngas production with heating value up to 25-30 MJ/kg. The data obtained for the case of simplified analysis for the equilibrium thermodynamic conditions shows that the most efficient case among the analyzed individual and mixed gasifying oxidative agents is use of steam oxidant. For this case the optimal regime predicted from realized series of calculations corresponds to value of the steam to biomass ratio SBR = 0.4 at such temperature level as 1000 K (at 0.1 MPa) and for these conditions maximal value of energy efficiency (cold gas efficiency) is 0.91 and value of exergy efficiency is 0.84. This level is even 4-5 % higher than the one, which was found for the case of use of air gasifying agent with optimal ratio of ER operating parameter. The results show that the case of gasification of these two kinds of feedstock using air as gasifying agent is more efficient on such output parameter as energy efficiency, which is higher (up to 0.65 for the bagasse and up to 0.79 for the coal) at the optimal level of temperature (1250 K) and the ratio of mass flow rates of the feedstock to air.

Figure 2. Plasma gasifier of ITA

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Gilberto Petraconi Filho

Instituto Tecnológico de Aeronáutica – ITA
Praça Mal. Eduardo Gomes, 50
CEP 12228-900
São José dos Campos, SP – Brasil

+55-12-3947-5914
petra@ita.br
http://www.ita.br

THE DEVELOPMENT OF MULTI-FUNCTIONAL CATALYSTS TO REPLACE PT FOR FUEL OXIDATION REACTIONS IN LOW TEMPERATURE FUEL CELLS TOWARD ENVIRONMENTALLY FRIENDLY ENERGY PRODUCTION

Hebe de las Mercedes Villullas
Araraquara Institute of Chemistry / São Paulo State University (UNESP)
FAPESP Process 2013/50206-4 | Term: Oct 2013 to Dec 2016

The environmentally friendly generation of energy has brought new scientific and technological challenges. Among the various alternative systems for energy production, fuel cells are particularly attractive because they allow clean and efficient conversion of chemical energy into electricity. Currently, the most active catalyst for the oxidation of fuels such as hydrogen, methanol and ethanol in fuel cells are Pt and Pt-based materials, which are too expensive for affordable clean energy production. The development of catalysts based on cheaper materials for fuel oxidation reactions in fuel cells is needed. The proposal aims to develop novel multi-functional catalysts to replace Pt for fuel oxidation reactions in fuel cells through collaborative efforts by electrochemists from Brazil, USA and China. Specifically, combining electrochemical measurements, in-situ spectroscopy characterizations, density functional theory simulations and fuel cell testing, the joint team will focus on studying reaction mechanisms of hydrogen, methanol and ethanol oxidation reactions (HORs, MORs and EORs) on various catalysts in both acid and alkaline media. Through understanding how surface and electronic structures of various catalysts affect the reaction kinetics of HORs, MORs and EORs in acid verse alkaline media, new multi-functional catalysts based on low cost materials (such as Pd, Ni and other earth abundant elements) with comparable HORs, MORs and EORs activity to Pt-based catalysts will be designed and characterized. For example, alloying Pd with transition metals will induce structural changes that alter the electronic characteristics of Pd surface active sites and the availability of oxygenated species on the catalyst surface needed to oxidize alcohol and its fragments. The effects of electronic properties on reactivity will also be investigated by varying metal-support interactions. The successful execution of the proposed project will provide viable new non-precious metal catalysts for fuel oxidation in fuel cells and a means to produce energy in an environmentally friendly fashion.

Hebe de las Mercedes Villullas

Instituto de Química
Universidade Estadual Paulista (UNESP)
Rua Francisco Degni, 55
CEP 14800-900 – Araraquara, SP – Brasil

+55-16-3301-9653
mercedes@iq.unesp.br

ETHANOL APPLICATION AS FUEL: PLASMA IGNITION FOR VEHICLE ENGINES

Jayr de Amorim Filho
Brazilian Bioethanol Science and Technology Laboratory (CTBE)
FAPESP Process 2008/58195-3 | Term: Apr 2009 to Dec 2011

Figure 1. Spark plug electric discharge

Petroleum oil is an important source of energy and a raw material that has been widely exploited by mankind. There is a concern about its storage in nature, since it is a non-renewable source and will be exhausted in near future. The indiscriminate use of oil products produces serious consequences for environment, like carbon compound emissions. Therefore, it is necessary to develop strategies to minimize emissions of air pollutants. The replacement of fossil automotive fuels by alternative and renewable fuels is increasing in order to reduce emission of toxic gases in the atmosphere. In this sense, the ethanol fuel, in Brazil, was implemented through National Alcohol Program (Pro-Alcool). More recently, the National Laboratory of Science and Technology of Bioethanol (CTBE) was also created in order to ensure Brazil leadership on sustainable production of sugarcane and bioethanol through development and innovation. The ethanol is undoubtedly cleaner than gasoline due to less toxic emission substances, such as benzene and butadiene. Furthermore, by having a simpler composition, bioethanol releases lower levels of complex substances into the atmosphere during its combustion.

Ignition engines by spark discharges (or internal combustion engines) initiate their combustion mechanisms leaded through electrical discharges. For a fuel-air mixture ignites into an engine combustion chamber, an electric discharge which occur between the electrodes of spark plug, provides enough energy to the mixture to be completely burned, thus obtaining the maximum engine power.

This project focuses on the investigation of processes occurring during the ignition of plasma and its consequences in post-discharge for an internal combustion engine, especially considering the spark plug discharge (*Figure 1*), aimed at finding the proper parameters to be applied in cars that operate on "poor mixtures" reducing pollutants released into the atmosphere. The research aims is to point out methods and materials to be used in order to provide an analysis of the processes occurring in plasma and combustion.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

After the implementation of a synchronic circuit, we are able to generate controllable electrical discharges . These discharges were characterized in terms of electrical properties from a high resolution oscilloscope. Voltages and currents were measured according to the applied pulses. The voltage values were found to be around 6 kV for 40ns. However, the current values were found to be around 100 mA for 2.3ms (*Figure 2*). Through these data, it is possible to conclude that even without electric field, there still exist the production of ions and reactive species.

In collaboration with the Geophysics Space Division Group of National Institute for Space Research (INPE), the emission light during the breakdown process of the discharges was recorded from
a high-speed camera usually used to shoot lightning. From these data, the discharge light intensity was inferred as a function of time. Comparing the light curve with the normalized electric current graph (*Figure 3*), it is possible to check that the discharge duration is about 2.3ms.

By using techniques of emission spectroscopy, several discharge parameters, such as temperature, electron density and electron temperature will be obtained during the combustion.

The aim of our work is then to optimize these discharges in order to improve the burning of the bioethanol fuel inside a high-pressure combustion chamber and therefore to use a "poor mixture" to achieve good engine performance.

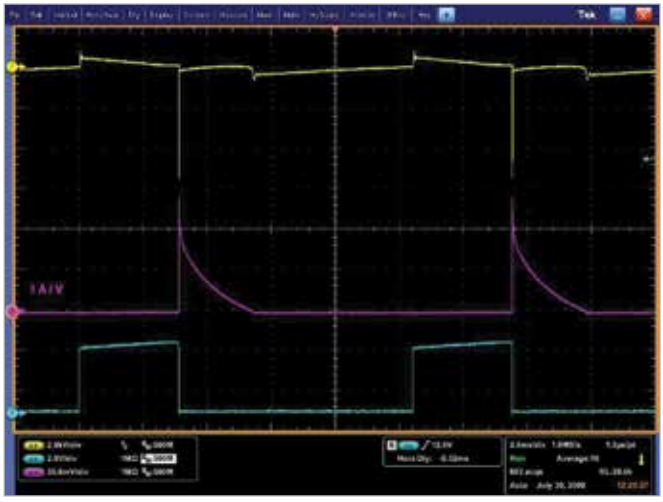

Figure 2. Curves of voltage (yellow) and current (purple) for the entrance pulse (blue) with 10ms and 30 % of duty cycle

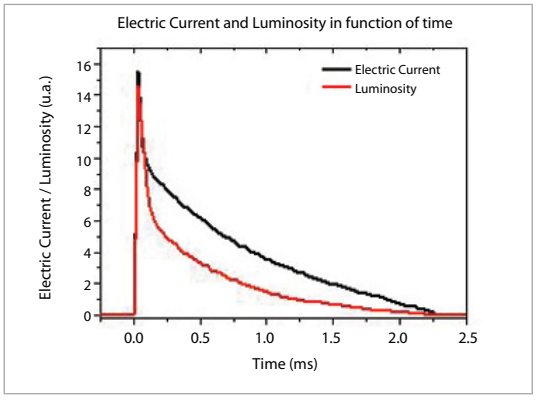

Figure 3. Curves of electric current and luminosity as a function of time

Jayr de Amorim Filho

Laboratório Nacional de Ciência e Tecnologia
do Bioetanol (CTBE)
Rua Giuseppe Máximo Scolfaro, 10.000
Caixa Postal 6170 – Guará
13083-970 – Campinas, SP

+55-19-3518-3137
jayr.amorim@bioetanol.org.br

USE OF CFD IN THE OPTIMIZATION OF STAGE EFFICIENCY OF DISTILLATION COLUMNS FOR ETHANOL PRODUCTION

José Antônio Silveira Gonçalves
Center for Exact Sciences and Technology / Federal University of São Carlos (UFSCar)
FAPESP Process 2008/56212-8 | Term: Apr 2011 to Mar 2014 | PITE – Business Partner: Dedini S/A Industria de Base

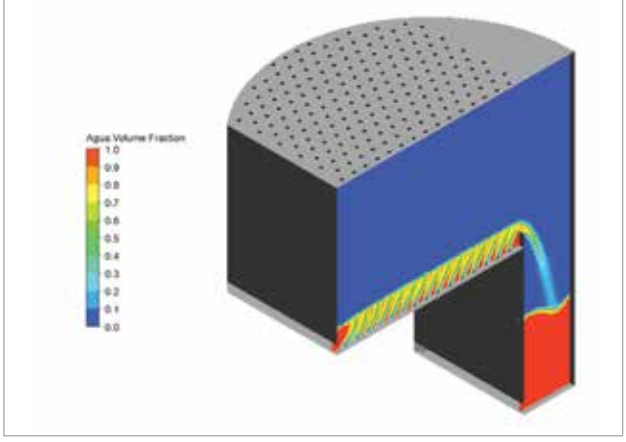

Figure 1. Water volume fraction on a plane 0.017 m from the symmetry plane. The chosen plane passes through the first row of orifices

A Distillation column plate is designed to promote mass and heat transfer between the liquid and the vapor phases. The efficiency with which this transfer is made depends on several factors, such as the chemical species diffusivities, concentrations, flow rates and flow regime. Parameters which are defined at the design, as, for instance, plate dimensions, bubbling area, bubbling characteristics, can affect significantly the stage efficiency. The higher the efficiency, the smaller will be the cost of the column.

The search for plate design with higher efficiencies was done, until recently, by experimentation and trial and error processes. These are expensive methods. Recently with the advances in computer technologies, the plate performance can be simulated even before it is constructed, immensely simplifying the search for more efficient solutions.

The overall purpose of this research project is to design a distillation column plate for use in ethanol production that presents a higher efficiency than those typically employed nowadays in Brazil. To reach this goal, the research is divided into two parts: 1) exam of several possible alternative designs through computational fluid dynamics (CFD) simulations; 2) construction of the most promising designs for experimental data acquisition.

This research is being conducted by a team of researchers from the Federal University of São Carlos and the Institute for Technological Research of The State of São Paulo. The research started in April/2011 and will be concluded in April/2014.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The research started only a few months ago. The achievements so far are:

- A thorough bibliographical review has been completed;
- The simulation of the hydrodynamics for a water/air system in an industrial scale (column diameter equal to 1.22 m) has been completed (Figure 1). Experimental results by Solari and Bell (1986) on this system are available, and were used to validate successfully our simulation.

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José Antônio Silveira Gonçalves

Centro de Ciências Exatas e Tecnologia
Universidade Federal de São Carlos (UFSCar)
Rodovia Washington Luis, Km 235
Caixa Postal 676
CEP 13565-905 – São Carlos, SP – Brasil

+55-16-3351-8045
jasgon@ufscar.br

MATHEMATICAL MODELING OF OPTIMAL BIOLOGICAL PEST CONTROL STRATEGIES FOR EFICIENT AND SUSTAINABLE SUGARCANE PRODUCTION

Marat Rafikov
Center for Engineering, Modelling and Applied Social Sciences / Federal University of the ABC (UFABC)
FAPESP Process 2008/57942-0 | Term: May 2009 to Apr 2011

Ethanol is a good choice as a fuel and additive because it is produced from renewable resources; promises cleaner combustion leading to a cleaner environment; produces relatively low levels of greenhouse gas emissions over its lifecycle; can be seamlessly integrated into the existing transportation system; provides a new outlet for agricultural products; reduces the global dependence on depleting reserves of crude oil; and has a potential to have a large-scale impact. The increase in world demand for ethanol will bring an increase of the sugarcane planted in Brazil. One of challenges of the improvements in the farming and harvesting of cane is the biological pest control. In spite of the biological control of *Diatraea saccharalis* by *Cotesia flavipes* is considered successful in Brazil , there are some areas where *Cotesia flavipes* has not the good control. The using of the parasitoid *Trichogramma galloi* is considered an interesting option in this case. In other hand, the dynamics of pest – parasitoid populations become complex, making the prediction of outbreaks difficult. Understanding the processes of these interactions can lead to a mathematical modeling playing a decisive role in controlling pest populations and contributing to the stability of natural systems.

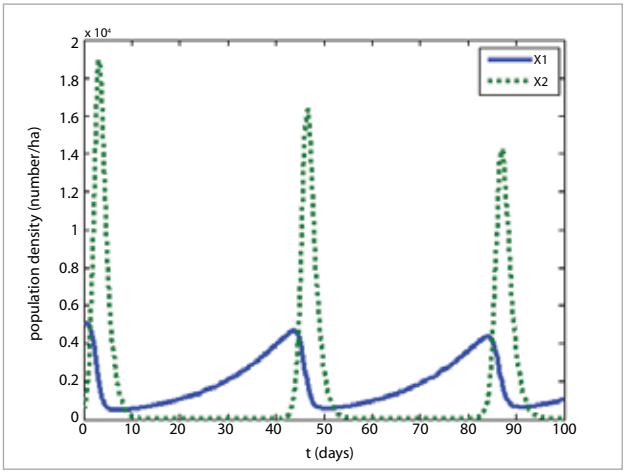

Figure 1. Evolution of sugarcane borer and parasitoid populations without control according to the mathematical model (Rafikov, Angeleli, 2009)

The main aim of this project is to apply methods from optimal control theory and from the theory of dynamic systems to the mathematical modeling of biological pest control strategies.

The specific aims of this project are: modify existing and/or develop new mathematical models adequate to represent interactions between the sugarcane pests and its enemy populations; identify coefficient and parameters of proposed mathematical models and determine the equilibrium level of sugarcane ecosystems from mathematical models; formulate and solve the biological pest control in sugarcane as optimal control problem that determine algorithms of the optimal strategy, minimizing cost functional; elaborate the computational tools based on above mentioned algorithms; undergo numerical simulations for different possible scenarios of biological pest control in sugarcane based on the mathematical models.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The main objective of the biological pest control is to maintain the pest population in an equilibrium state below the economic injury level. Thus, parasitoids and predators are commonly reared in laboratories and periodically liberated in high-density populations (inundative biological control) when the pest population reaches a control level.

For the modeling of first possible scenario, the ecosystem sugarcane borer – its parasitoid was described by two differential equations. For numerical simulations of interactions between the sugarcane borer (*Diatraea saccharalis*) and its parasitoid (*Cotesia flavipes*) were identified the values of model coefficients based on data from literature. *Figure 1* presents the population oscillations without control according to the mathematical model.

The numerical simulations show that the inundative control, applied in initial moment by introduction 20000 parasitoids/ha, maintain the pest population below the economic injury level (2500 pests/ha) only 35 days. After this period, it is necessary to apply the control again.

In order to determine algorithms of the optimal strategy of introduction of the natural enemy species, the biological pest control in sugarcane was formulated and solved as optimal control problem. The linear feedback control is designed to drive the ecosystem sugarcane borer – its parasitoid to the equilibrium state below the economic injury level, as shown in *Figure 2*. Numerical simulations showed that the great amount of parasitoid have to be introduced in initial instance. This fact suggests that the proposed feedback control strategy can be integrated into existing biological control technologies, applying the feedback control after the traditional inundative pest control. This control strategy directs the ecosystem to the stable equilibrium point. It is not necessary to apply the periodic releases or a seasonal introduction of a small population of natural enemies after this control application.

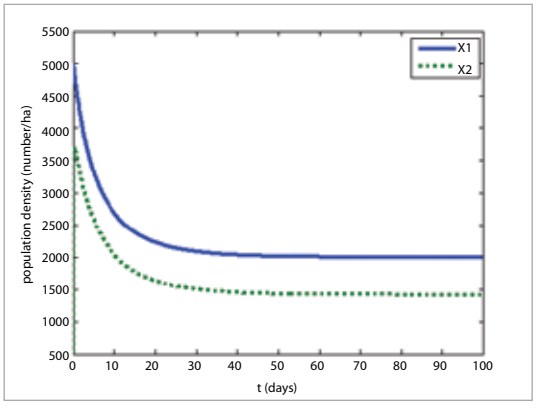

Figure 2. Evolution of sugarcane borer and parasitoid populations with optimal control (Rafikov, Angeleli, 2009)

The next steps of this project will study scenarios which consider age structures of populations and interactions between the sugarcane borer and two parasitoid species.

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Marat Rafikov

Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas / Universidade Federal do ABC (UFABC)
Rua Catequese, 242, 3º andar – Jardim
CEP 09090-400 – Santo André, SP – Brasil

+55-11-4996-0124
marat.rafikov@ufabc.edu.br

PROCESSING OF SUGARCANE CELLULOSE EMPLOYING ATMOSPHERIC-PRESSURE PLASMAS

Marco Aurélio Pinheiro Lima
Brazilian Bioethanol Science and Technology Laboratory (CTBE) / National Center for Research in Energy and Materials
FAPESP Process 2008/58034-0 | Term: Aug 2009 to Feb 2013 | Thematic Project
co-PI: Jayr de Amorim Filho

Figure1. Illustration of an atmospheric-pressure plasma jet of Ar/H2 generated by a radio-frequency wave at 50W. In this case, the microplasma jet glow length is about 15.0 mm, considering a gas flux of 700 sccm

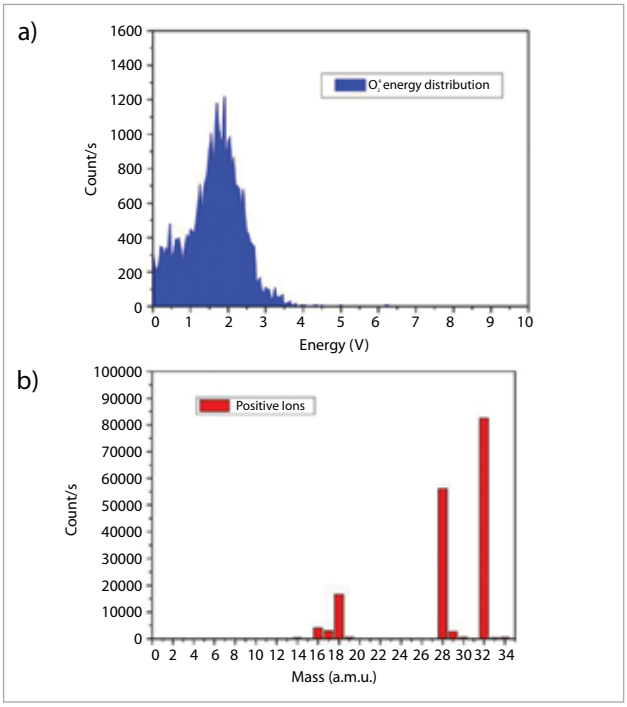

Figure 2. Specimens yielded by He DBD plasma at atmospheric pressure: (a) Energy distribution for O_2^+; (b) Mass concentration of positive ions inside the discharge

In this project we propose the implementation of a new method for selective treatment of lignocellulosic material based on atmospheric-pressure plasmas (*Figure 1*), which may become an important step towards the industrial production of second generation ethanol from sugarcane. The experiments in laboratory scale and the development of the equipment to produce the plasmas will be carried out at Brazilian Bioethanol Science and Technology Laboratory (CTBE). The experiment will be scaled-up in order to be implemented in the Pilot Plant, which is now under construction at CTBE.

From the theoretical point of view, the interaction of the plasma electrons with lignocellulosic material should be better understood. A study on this complex matter will be carried out in three different parts: (1) low-energy electron scattering from α-glucose and β-glucose monomers and dimmers. We expect these results to elucidate the differences in resonant processes responsible for the breakage of the respective (α1→4) and (β1→4) linkages. This study will be carried out at CTBE and the resonance energies should provide invaluable information for optimizing the plasma-based pretreatment of lignocellulosic raw materials. (2) Once the resonance states are identified, we plan to study dissociation mechanisms by electron impact with the help of nuclear dynamics simulations, at Federal University of ABC. (3) Lignocellulosic material contains a large amount of water. We also propose to investigate micro- and macrosolvation effects through some standard approaches coded in quantum chemistry computational packages. This study will be done at University of São Paulo.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

By applying the so-called atmospheric-pressure plasma (APP), low gas and power consumption could be achieved as well as a non-expensive operation [1]. The APP allows creating a convenient environment of chemical specimens, such as ozone and singlet oxygen, which have an important role in the deconstruction of a biomass lignocellulosic matrix, particularly degrading lignin with good efficiency [2, 3, 4, 5]. In this sense, it is necessary to apply diagnostic tools in order to investigate the chemical composition and physical properties of these plasmas. By using Optical Emission Spectroscopy, we are able to determine, for example, the electron density and the temperature of the plasmas [6,7]. Moreover, through Mass Spectrometry Analyzes (MSA), the concentration and energy of neutral specimens as well as of negative and positive ions in the APP can be determined. So far, we have applied MSA to study a helium APP created by a Dielectric Barrier Discharge (DBD). This DBD is going to treat the sugarcane bagasse in a reactor. Some chemical radicals existing in this kind of APP are shown in *Figure 2*.

The first theoretical results are related to the study of elastic collisions of low-energy electrons with the CH_2O-H_2O complex [8]. Previous studies reported a shape resonance for CH_2O at around 1eV. In the presence of water, the resonance appears at lower energies due to mutual polarization between the two molecules. This indicates that the presence of water may favor dissociation by electron impact.

Another interesting theoretical study is the low-energy electron collision with α-D-glucose and β-D-glucose monomers [9]. Our results show a strong isomeric effect for electron impact energies below 15eV. The integral cross sections for both monomers present shape resonances located at different positions. As a consequence, low-energy electrons may dissociate these two monomers at different energies, suggesting a specific bond-selective behavior. The next step is to study electron scattering by the D-glucopyranose dimmers, in order to investigate possible influence of electron capture in the rupture of the ($\alpha 1 \rightarrow 4$) and ($\beta 1 \rightarrow 4$) linkages.

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Marco Aurélio Pinheiro Lima

Laboratório Nacional de Ciência e Tecnologia do Bioetanol
Rua Giuseppe Maximo Scolfaro, 10.000
Caixa Postal 6170
CEP 13083-970 – Campinas, SP – Brasil

+55-19-3518-3112
maplima@bioetanol.org.br

SOLID-LIQUID EQUILIBRIUM OF FATTY COMPOUNDS AND BIODIESEL FLASH POINT

Mariana Conceição da Costa
School of Applied Sciences / University of Campinas (Unicamp)
FAPESP Process 2012/05027-1 | Term: Aug 2013 to Jul 2017 | Young Investigator

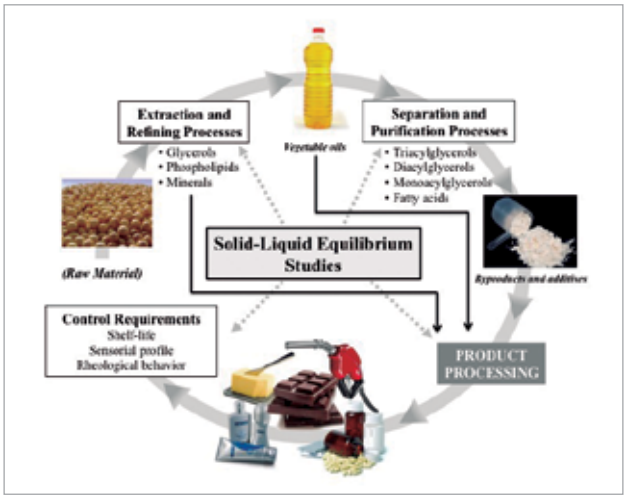

Figure 1. Action fields of solid–liquid equilibrium studies in the vegetable oil processing industry (Maximo et al., 2014)

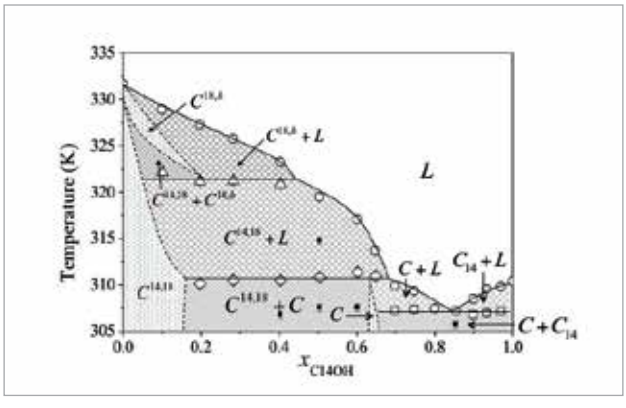

Figure 2. Solid–liquid phase diagram of the C14OH + C18OH system based on step- scan DSC. (○) Melting temperature; (□) eutectic reaction; (◊) peritectic reaction; (Δ) metatectic reaction; (■) solid-solid transition. (- - -) and (—) are guides to the eyes. L: liquid phase; C_{14}: C14OH on solid state, $C^{14,18}$: solid solution rich in C18OH; C: peritectic compound; and $C^{18,h}$: metatectic compound (Carareto et al., 2014)

The growing worldwide demand for new renewable energy sources puts the Brazil in a privileged position in the world due to our large experience in the ethanol production from sugar cane and also due to the large portion of farmland in our territory. In this way Brazil is one of the most capable country in the world to development the biorefineries. To realize this favorable situation it is necessary the development of new technologies related to the biocompounds, especially fatty compounds. It is important to study and understand all equilibrium conditions that can be observed during the processing of vegetable oils, since its extraction, processing refine until biodiesel production. The purpose of this research project is to construct solid-liquid equilibrium (SLE) phase diagrams of fatty compounds and investigate the different solid-solid (SSE) and solid-liquid (SLE) equilibrium regions. Besides the phase diagram, the flash point of ethylic and methylic biodiesel is going to be determined. SLE experimental data could be used to improve the separation processes and to propose new separation methods. Flash point data is an important property that must be observed in storage, transportation and production of biodiesel. Furthermore, in the near future, there is an intention of use these data to formulate products that should attend market requirements and physicochemical properties necessary for their distribution and use.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

It has been determined over than 30 solid-liquid equilibrium (SLE) phase diagrams of fatty compounds. The results have been found for binary mixtures formed by two fatty alcohols and mixtures of one fatty alcohol plus one fatty acid and such results are showed mostly very complex due to the occurrence of eutectic, peritectic and metatectic reactions and also by the solid solution formation. The systems formed by one triacylglycerol plus a fatty alcohol or fatty acids are simple ones in which they have been presenting just only the eutectic reaction and/or solid solution formation.

The SLE phase diagrams of fatty acid ethyl esters (FAEEs) of three binary mixtures were measured using high pressure microscopy in the range of 0.1–80 MPa. It was showed a linear dependence of pure FAEE from the pressure and that the binary phase diagrams are only slightly affected by the pressure, even at 80 MPa.

In terms of thermodynamic models, it was successfully purposed a new procedure, namely "Crystal-T algorithm" to describe some binary mixtures of triacylglycerols plus fatty alcohols that have been presenting a solid solution formation considering the non idealities of the solid and liquid phases. Moreover, the traditional Margules 3-suffix and NRTL equations may also be used to describe the liquidus line of such a systems. The FAEE high pressure data was also modeled employing a model previously applied to alkanes using the Soave-Redlich-Kwong equation to liquid phase fugacity coefficient with the LCVM mixing rule.

The Flash point (FP) is one of the most important physicochemical properties for establishing the potential for fire and explosion of a hazardous material such as a fuel and also for ensuring safe storage and transportation. FP data has been determined for binary and ternary mixtures formed by ethylic esters and for some ethylic biodiesel.

The path forward is related to the ongoing determination of the binary SLE phase diagrams consisted by triacylglycerols plus fatty alcohols or fatty acids and the determination of ternary SLE phase diagrams of such a substances along with the challenge of describing the determined systems through thermodynamic equations. Furthermore, the FP studies will be continued using methyl esters associated with the thermodynamic modeling of the experimental data. In order to have a complement of experimental work, it will be determined the heat capacity of some triacylglycerol compounds which are very important and critical for modeling as well as for computational simulation of such systems during processing and even for the new products formulation.

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Mariana Conceição da Costa

Faculdade de Ciências Aplicadas
Universidade Estadual de Campinas
R. Pedro Zaccaria, 1300 - Caixa Postal 1068
CEP 13484-350 – Limeira, SP – Brasil

+55-19-3701-6673
mariana.costa@fca.unicamp.br

METABOLIC ENGINEERING APPLIED TO BIOPOLYMER PRODUCTION

Marilda Keico Taciro
Institute of Biomedical Sciences / University of São Paulo (ICB/USP)
FAPESP Process 2010/51692-1 | Term: Mar 2011 to Feb 2016 | Young Investigator

Figure 1. Bioreactor bacterial cultivation collecting data in the project

Metabolic flux analysis (MFA) and other tools of metabolic and biochemical engineering are currently being applied for the improvement of the production of biodegradable polymers belonging to the polyhydroxyalkanoates family (PHA), particularly poly-3-hydroxybutyrate-co-3-hydroxyalkanoate of medium-chain-length [P(3HB-co-HAmcl)]. Using steady-state data generate in bioreactor experiments, flux analysis is performed through a freely available software. Bacterial cultures in a continuous mode operation, employing the technique of multiple nutrient limitation to induce polymer accumulation is another strategy to study the role of such nutrients and to generate data to MFA. Metabolic models will be proposed, simulated and validated utilizing the experimental data from bioreactor cultivations. The analysis of the metabolic models will provide information to propose genetic modifications and process strategies, to obtain higher yields and productivities. It is expected that, by the end of this project, the metabolic engineering approach emphasizing the integration of different methodologies and procedures has been established. As a result, a Metabolic Engineering Group is being created in the Microbiology Department at ICB USP, in such a way that, processes involving other bioproducts could be approached in a similar manner.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Analysis of the tracing pattern on C-labelled PHA has been performed, evidencing for the first time the extreme effectiveness of this approach to determine fluxes distribution in the central metabolism involved on PHA production. Associated with elementary mode analysis of the metabolism, this procedure allowed the identification of biochemical engineering and/or genetic approaches to improve production of these polymers and to characterize bacterial strains for the production of other compounds. Different strains were characterized with respect to PHA production. Those genes that showed promising performance and interest have been cloned. Thereby strains producing copolymers of P(3HB-co-HAmcl) in a controlled manner were successfully obtained. This group of copolymers has properties that have attracted great interest as they permit to obtain plastic films.

Bioreactor experiments were done to validate metabolic models and to propose possible strategies to improve polymer process production. Chemostat cultures exploring the regions of multiple nutrient limitations were done. The resulting steady states enable the study of different physiological situations and result on a snapshot representing each situation.

The genome sequencing performed in the studied bacteria (*Pseudomonas LFM 046*) enabled the construction of the model in genomic scale improving the metabolic modeling studies.

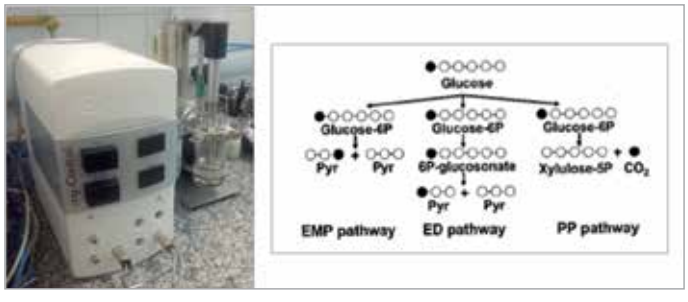

Figure 2. Minibioreactor (100 ml working volume) utilized on experiments with labeled carbon source. Illustration of how measurement of the ^{13}C enrichment patterns can be used to identify active pathways. EMP (Embden-Meyerhof-Parnas), ED (Entner-Doudoroff), PP (Pentose phosphate)

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Marilda Keico Taciro

Instituto de Ciências Biomédicas
Universidade de São Paulo (USP)
Av. Prof. Lineu Prestes, 1374
ICB 2 – 1º andar – Lab. 148
CEP 05508-900 – São Paulo, SP – Brasil

+55-12-3091-7730
mktaciro@usp.br

MOLECULAR DIVERSITY AMONG BASAL ANGIOSPERMS

Massuo Jorge Kato
Chemistry Institute / University of São Paulo (IQ/USP)
FAPESP Process 2009/51850-9 | Term: May 2010 to Feb 2015 | Thematic Project
co-PI: Eny Iochevet Segal Floh

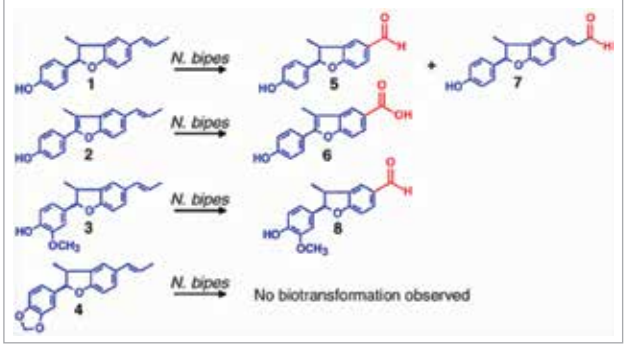

Figure 1. Biotransformation of neolignans 1-4 from Piper regnellii *(leaves and roots) by* N. bipes *beetle (larvae and adult). [Ramos CS, Kato MJ. 2013. Metabolism of neolignans from* P. regnellii *(Piperaceae) in the beetle* Naupactus bipes *(Coleoptera: Curculionidae).* Chemoecology. **23**: *143-148.]*

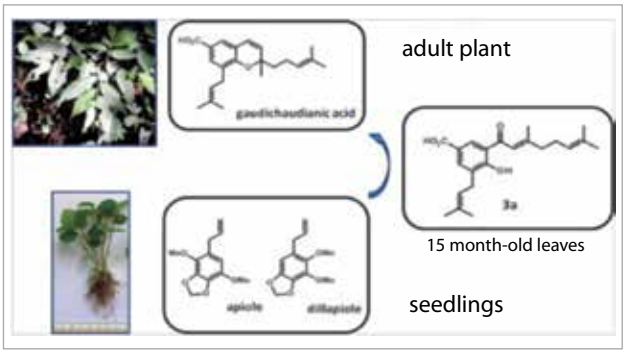

Figure 2. Biosynthetic pathway leading to major secondary metabolites through development of Piper gaudichaudianum. *[Gaia AM, Yamaguchi LF, Jeffrey CS, Kato MJ. 2014. Age-dependent changes from allylphenol to prenylated benzoic acid production in* Piper gaudichaudianum *kunth.* Phytochemistry. **106**, *86-93.]*

The Piperaceae was the model plant to study the evolution of secondary metabolism. The molecular phylogeny of *Piper* (200 species) and *Peperomia* (50 species) based on ITS (nuclear), matK (plastid) + ITS (nuclear), respectively, was compared to the chemical profiling based on ^{1}H NMR, ESI^{+} and HPLC data, using multivariate analysis (PCA and HCA). The major classes of compounds were amides, prenylated benzoic acids, chromenes, polyketides and phenylpropanoid derivatives with some specific occurrence in various clades. Detailed characterization of chemical composition was still a valuable tool to complement the chemical profiling. The bioactivity of amides from Piper and 2-acyl-1,3-cyclohexanediones from Peperomia species had their structure-activity relationship investigated. The synthesis of large number of analogues and cytotoxicity against twelve leukemia cell lines and herbicide against the enzyme HPPD (4-hydroxyphenylpyruvate dioxygenase) revealed structural requirements for activities. The ontogeny of Piper species, i.e. development of seedling until adult plants showed three different patterns: A (*P. tuberculatum*, *P. amalago, P. scutifolium* and *P. reticulatum*), with amides occurring throughout the stages; B (*P. regnellii*, *P. solmsianum*, *P. gaudichaudianum* e *P. caldense*) with phenylpropanoids (dillapiol-apiol or isoasarone) in seedlings while adult plants contained dihydrobenzofuran neolignans, tetrahydrofuran lignans or prenylated benzoic acid derivatives, respectively; C (*P. richardiaefolium*, *P. truncatum* and P. kelleyi) with the amide piplartine in seedlings and furofuran and dibenzylbutyrolactone lignans and prenylated benzoic acids, respectively.

In summary, the variability of Piperaceae species is highly associated with chemical variability, including complex pattern of differentiation during ontogeny with unpredictable consequences against specific or generalist herbivores that has been found predating the species.

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Massuo Jorge Kato

Instituto de Química
Universidade de São Paulo (USP)
Av. Prof. Lineu Prestes 748, B 11-T
CEP 05508-900 – São Paulo, SP – Brasil

+55-11-3091-1886
majokato@iq.usp.br

STUDY ON SELECTIVITY OF HYDROGENOLYSIS/REDUCTIVE HYDROGENATION PROCESSES OF SUGARCANE BAGASSE UNDER SUPERCRITICAL STATE CATALYZED BY STRUCTURED METAL OXIDES

Mauricio Boscolo
Institute of Biosciences, Literature and Exact Sciences / São Paulo State University (UNESP)
FAPESP Process 2013/23886-4 | Term: Apr 2014 to Mar 2016

The development of strategies for selective catalytic depolymerization and deoxygenation of lignocellulosic biomass is a challenge due to its complex structure, especially due to the recalcitrant behavior of lignin in relation to the hydrolysis of its phenolic ethers. The proposed research focuses on the synthesis and characterization of solid structured metal oxides catalysts derived from hydrotalcites with a formula of $Mg_6Al_2(CO_3)(OH)_{16}.4(H_2O)$ and doped with different transition elements (Cu, Zn, Fe, Nb, Ni, Zn, Mo, Ti, Zr), and lanthanides (La and Lu) for the deconstruction of lignocellulosic material by means of conventional catalytic hydrogenation and hydrogenolysis using as hydrogen source (methanol or ethanol) through their respective reforms in their supercritical state (250 to 300ºC and pressures above 62 atm). Using sugarcane bagasse as a substrate, we expect obtain lignin phenolic monomer units as well as their derivatives with different levels of saturation, including alcohols derived from cellulose and hemicellulose for use as fuel or for chemical intermediates.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Among the metals to be incorporated into the hydrotalcite structure, copper is what stands out most in catalyzing the reform of methanol and ethanol for hydrogen production. The incorporation of secondary metals as modifiers (Zn, Fe, Nb, Ni, Zn, Mo, Ti, Zr) is being investigated. An example of the synergistic effect obtained with hydrotalcites changes is that these modified material only with Ni in partial replacement of Mg does not reform the alcohols at the experimental conditions, but its incorporation in combination with Cu increases by 10% the volume of hydrogen produced. In parallel, we are studying the hydrogenation process of various phenolic compounds similar to the possible lignin fragments to understanding the effects on the hydrogenolysis process of this class of organic compounds.

Maurício Boscolo

Instituto de Biociências, Letras e Ciências Exatas
Universidade Estadual Paulista (Unesp)
Departamento de Química e Ciências Naturais
Av. Cristóvão Colombo, 2265
CEP 15054-000 – São José do Rio Preto, SP – Brasil

+55-17-3221-2477
boscolo@ibilce.unesp.br

DEVELOPMENT OF NEW METHODS FOR DETERMINATION OF SUGARS, FURANIC ALDEHYDES AND URONIC ACIDS FROM LIGNOCELLULOSIC MATERIALS DERIVATIVES OF CANE SUGAR

Nelson Ramos Stradiotto
Araraquara Institute of Chemistry / São Paulo State University (UNESP)
FAPESP Process 2012/00258-5 | Term: Jun 2012 to May 2014

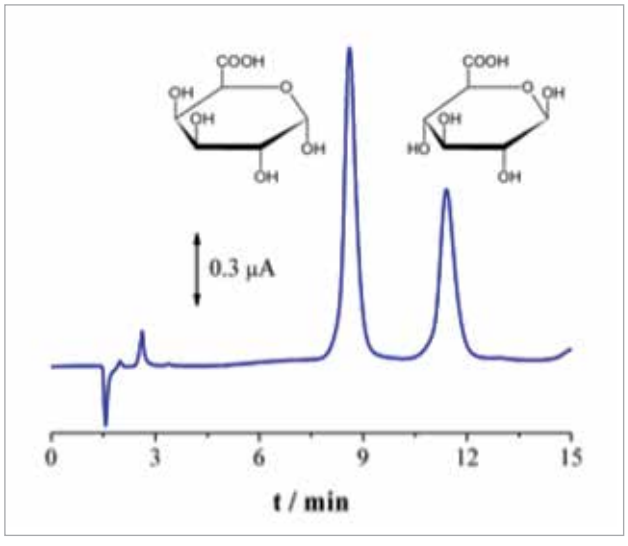

Figure 1. Isocratic separation chromatogram of standard solution D-galacturonic acid, and D-glucuronic acid in the CuNP detector. Mobile phase 0.1 mol L^{-1} NaOH plus 280 mmol L^{-1} CH_3COONa, detection potential of 0.45 V vs. Pd and flow rate of 1.0 ml min^{-1}

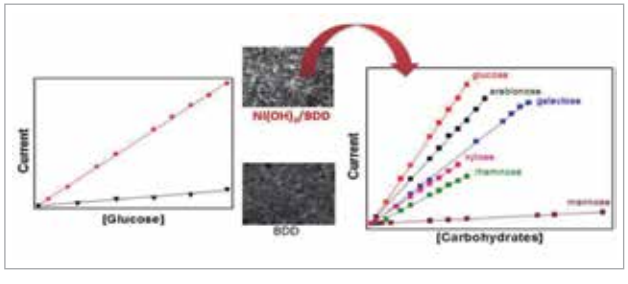

Figure 2. Detection of several carbohydrates using boron-doped diamond electrodes modified with nickel hydroxide n anoparticles

The energy needs of modern society are based primarily on the use of fossil fuels, which besides being finite cause numerous environmental problems. Due to this situation, the search for alternative renewable energy sources has intensified exponentially in order to meet the rising demand of energy. In this scenario, the lignocellulosic materials are presented as one of the viable alternatives in relation to fossil fuels, because it is a material rich in carbon and renewed availability. Among these materials, sugar cane bagasse, a residue of sugar mills, is a promising source for generating biofuels. The process of conversion of biomass to ethanol involves several steps such as pretreatment, hydrolysis, fermentation and distillation. During these steps is very important to know the composition of the different compounds participants to assess the efficiency and optimization of the steps involved in this process. The development of new methods of determination that are fast, sensitive and selective for specific compounds is highly essential in order to perform this conversion with yields economically competitive. Among these new methods of determination, one that uses the technique of liquid chromatography (HPLC) with electrochemical detection is presented as one of the most promising, since this technique stands out for being sensitive and selective, small display limits detection and a wide applicability to different substances. Therefore, this project aims to develop new methods for the determination of sugars, uronic acids and furanic aldehydes using HPLC with electrochemical detection technique aimed at producing lignocellulosic ethanol. The development project includes the preparation and characterization of modified electrodes, as well as the methodology for determining these compounds and their application in the determination of lignocellulosic materials derived from sugar cane.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The glassy carbon electrode modified with carbon nanotubes decorated with nickel oxy-hydroxide (GC/MWCNT/NiOOH) was used to studied electro-oxidation of glucose, galactose, xylose, arabinose and mannose in alkaline medium. Kinetic parameters such as, charge-transfer coefficient, electrocatalytic rate constant and diffusion coefficient were determined for sugars. Galactose exhibited a higher charge-transfer coefficient (0.37) with a diffusion coefficient of $1.3x10^{-6}$ cm^2 s^{-1} and showed the higher electrocatalytic rate constant of $2.1x10^4$ L $mol^{-1}s^{-1}$. The modified electrode exhibited a linear response to sugars concentration in the range around of $2.5x10^{-4}$ mol L^{-1} to $5.6x10^{-3}$ mol L^{-1} and limits of detection around of $1.9x10^{-4}$ mol L^{-1}-$4.3x10^{-4}$ mol L^{-1}.

In a similar study, the electrooxidation of glucose, galactose, mannose, rhamnose, xylose and arabinose was studied at of nickel hydroxide nanoparticle modified boron-doped diamond electrode and compared to unmodified electrode. Limits of detection were $5.3x10^{-5}$, $6.8x10^{-5}$, $2.7x10^{-4}$, $6.9x10^{-5}$, $8.8x10^{-5}$ and $2.6x10^{-5}$ $molL^{-1}$ for glucose, galactose, mannose, rhamnose, arabinose, xylose, respectively.

In another study an analytical method was development for iron and copper determination in ethanol fuel. This method was developed using stripping voltammetry with a glassy carbon electrode modified with Nafion/Carbon-nanotubes. With linear sweep stripping voltammetry was achieved a limit of detection of $7.1x10^{-7}$ mol L^{-1} for Fe^{3+} and $5.1x10^{-8}$ mol L^{-1} for Cu^{2+}. The amperometric sensitivities were $2.0 x10^6$ mA mol^{-1} L for Fe^{3+} and $2.8 x 10^7$ mA mol^{-1} L for Cu^{2+}.

A detector was modified with copper nanoparticles electrodeposited on the surface of the glassy carbon for determination of uronic acids in chromatography with pulsed amperometric detection in wall-jet cell. The separation of the acids was complete within 15 min. The method was applied to real samples of hydrolyzate bagasse and the value found in this sample was 15.8±0.5 g/kg of D-galacturonic acid and 12.5±0.5 g/kg of D-glucuronic acid. The results demonstrate that the proposed method can be used to detect these acids without the need for derivatization with the advantage of having fewer interfering, considerable accuracy.

For determination of furanic aldehydes a glassy carbon electrode chemically modified with nickel nanoparticles coupled to reverse phase chromatography with pulsed amperometric detection was used for the quantitative analysis in a real sample of sugarcane bagasse hydrolyzate. The values obtained in this sample by the standard addition method were 1.54 ± 0.02 g kg^{-1} for HMF and 11.5 ± 0.2 g kg^{-1} for furfural. The results demonstrate that the new proposed method can be used to quickly detect furanic aldehydes without the interference of other electroactive species, besides having excellent peak resolution, analytical reproducibility, sensitivity and accuracy.

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Nelson Ramos Stradiotto

Instituto de Química de Araraquara
Universidade Estadual Paulista (Unesp)
Departamento de Química Analítica
Rua Francisco Degni, s/n – Caixa Postal 355
CEP 14800-060 – Araraquara, SP – Brasil

+55-16-3301-9621
nrstradi@iq.unesp.br

NEW METHODS FOR DETERMINATION OF CARBOXYLIC ACIDS, AMINO ACIDS AND POLYOLS IN VINASSE OF THE MANUFACTURING PROCESS OF ETANOL

Nelson Ramos Stradiotto
Araraquara Institute of Chemistry / São Paulo State University (UNESP)
FAPESP Process 2014/23846-5 | Term: Mar 2015 to Feb 2017

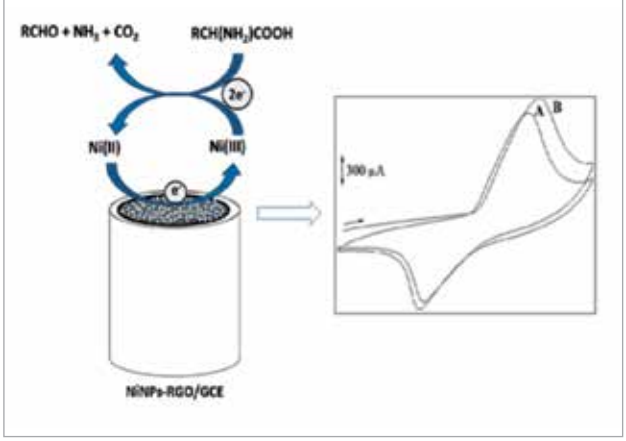

Figure 1. Modified electrode with graphene oxide containing nickel nanoparticles for determination of amino acids. Cyclic voltammograms at NiNPs-RGO/GCE in 0.1 mol L^{-1} NaOH solutions (A) in the presence of 1.0 mmol L^{-1} Alanine (B)

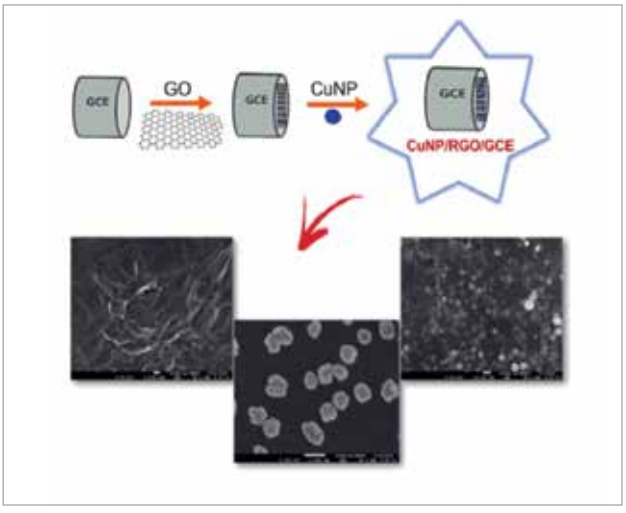

Figure 2. Modified electrode with graphene oxide containing copper nanoparticles for determination of polyols

The full energy utilization of sugar cane should be linked with the current biorefinery concept, which allows the conversion of biomass, besides the production of sugar and ethanol in various chemical products with high added value. Sugar and ethanol plants have on their plants, two residues (bagasse and vinasse) that can generate products with high added value. These wastes, bagasse has been used in the production of electricity and recent research shows its viability in the production of second generation ethanol. However, vinasse until now, has been used only as fertilizers in their own plantations cane sugar. Vinasse is a product of the distillation of ethanol being produced in a proportion which may range 11 to 18 liters per liter of distilled alcohol. This residue, consisting mainly of polyols, carboxylic acids and amino acids in significant concentrations, has attracted little attention as meaning transform vinasse as a significant industrial importance. The development of new methods for the determination of compounds with high added value is essential for the sugarcane mills can reclaim what is now considered waste. Among these new methods of determination, those using electrochemical sensors and electrochemical detectors coupled with separation techniques has distinguished itself by presenting high sensitivity, great selectivity, speed of analysis, which is very attractive options for the analysis of these compounds. For this reason, the aim of this project is to develop new methods for determination of compounds of high value added originating from vinasse of cane sugar. Thus, the project has the following objectives: a) development of new electrochemical sensors based on molecularly imprinted polymers anchored on graphene for determination of polyols in vinasse and b) development of new electrochemical sensors based on metallic nanoparticles anchored on graphene, coupled the chromatographic technique for determining carboxylic acids and amino acids vinasse.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

A modified glassy carbon electrode was developed to analysis of amino acids in sugarcane vinasse by ion chromatographic using pulsed electrochemical detection. The modification of glassy carbon electrode (GCE) with graphene oxide and nickel nanoparticles (NiNPs-RGO/GCE). Chromatographic separations were performed by using an anion-exchange column and isocratic elution. The separation of the amino acids was complete within 15 min. The value found in the sample was $1.5\times10^{-3} \pm 2.4\times10^{-5}$ mol L^{-1} (Alanine), $1.4\times10^{-2} \pm 4.0\times10^{-4}$ mol L^{-1} (Glycine) and $2.3\times10^{-2} \pm 4.5\times10^{-4}$ mol L^{-1} (Leucine) of sugarcane vinasse sample. The results demonstrate that the developed detector can be used to detect amino acids coupled with an anion-exchange column in quantitative analysis of amino acids, free of interferents and good accuracy in sample of sugarcane vinasse.

In another work we studied the electrochemical behavior of polyols in electrode modified with graphene containing copper oxide nanoparticles (CuNP/RGO/GCE) to be used as a sensor because these compounds do not exhibit electrochemical behavior in GCE unmodified. The voltammetric techniques used were cyclic voltammetry (CV) to characterize, the square wave electrode and voltammetry (SWV) and differential pulse (DPV) in order to search the most sensitive technique to operate the sensor. The electrode was characterized by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The CuNP/RGO/GCE showed lower charge transfer resistance (Rct), indicating that the electrode process is facilitated. From the SEM images it was observed that the nanoparticles are less than 100 nm and were distributed evenly on the graphene sheets. The polyols were analyzed separately and showed oxidation potential of 0.48 to 0.90 V, leading to the formation of formate ions and presenting irreversible behavior. The DPV was the best technique for quantification performance of these polyols, which is chosen for these studies on the construction of the sensor will be applied to the electrochemical determination of these compounds in vinasse sugarcane.

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Nelson Ramos Stradiotto

Instituto de Química de Araraquara
Universidade Estadual Paulista (Unesp)
Departamento de Química Analítica
Rua Francisco Degni, s/n – Caixa Postal 355
CEP 14800-060 – Araraquara, SP – Brasil

+55-16-3301-9621
nrstradi@iq.unesp.br

ENVIRONMENTAL IMPACT ASSESSMENT OF DIFFERENT SUGARCANE BIOREFINERIES CONFIGURATIONS WITH INTEGRAL USE OF BIOMASS

Otávio Cavalett
Brazilian Bioethanol Science and Technology Laboratory (CTBE) / National Center for Research in Energy and Materials
FAPESP Process 2010/17139-3 | Term: Sep 2011 to Aug 2016 | Young Investigator

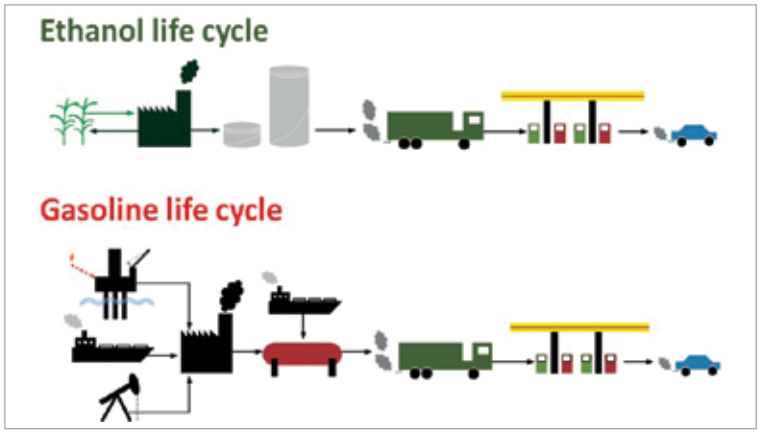

Figure 1. Simplified representation of ethanol and gasoline life cycle stages

Replacement of fossil fuels by biofuels has been considered an important alternative in the transition process to a economy based in higher proportion of renewable resources in several countries. It is recognized that large-scale production of ethanol, sugar and electricity from sugarcane in Brazil presents some environmental, economic, social and energy security benefits. However, new production routes for sugarcane biorefinery considering also the integral use of sugarcane biomass will be more and more important for the strategic plans of bioenergy production expansion in Brazil. Comprehensive studies of the environmental impacts of these novel biorefineries are important as the different routes/alternatives for use of lignocellulosic material contained in the sugarcane lignocellulosic material (bagasse and straw) are still not consolidated. These studies will require internationally competitive research, development and innovation to ensure sustainable production of the various products that may be obtained from sugarcane biorefinery. This research project will contribute to this scientific and technological demand evaluating the environmental impacts of different alternatives/routes for ethanol, co-products and derivatives production in a sugarcane biorefinery including processes for better integral use of available biomass. This assessment is based on the integration of Life Cycle Assessment with computer simulation platforms and will contribute to the constructions of a tool so called "Virtual Sugarcane Biorefinery".

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Various sugarcane biorefinery pathways were evaluated including agricultural, transportation and industrial conversion stages. Significant advances were achieved in the environmental assessment of current and novel sugarcane agricultural production systems; straw recovery alternatives; different technological scenarios for first and second generation ethanol production; different products using green chemistry and thermochemistry routes integrated to a sugarcane biorefinery ; and different technological options for second generation ethanol production. Other project results include application of different environmental impact assessment methods and methodological concepts involved in the life cycle assessment of sugarcane ethanol in Brazil. The main findings highlight the importance of comprehensive and reliable tools and methods for environmental impacts assessment applied to all the life cycle stages of different products can be obtained in a sugarcane biorefinery.

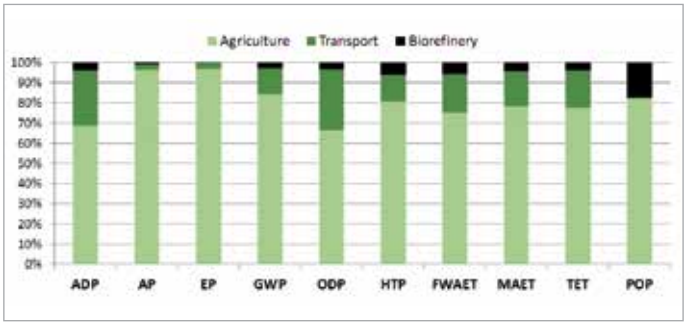

Figure 2. Environmental impacts breakdown for ethanol production stages (environmental impacts: ADP: abiotic depletion, AP: acidification, EP: eutrophication, GWP: global warming, ODP: ozone layer depletion, HTTP: human toxicity, FWAET: fresh water aquatic ecotoxicity, MAET: marine aquatic ecotoxicity, TET: terrestrial ecotoxicity, POP: photochemical oxidation) (CAVALETT et al., 2012)

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Otávio Cavalett

Laboratório Nacional de Ciência e Tecnologia do Bioetanol (CTBE), Centro Nacional de Pesquisa em Energia e Materiais (CNPEM)
Rua Guisepe Máximo Scolfaro 10000
CEP 13083-970 – Campinas, SP – Brasil

+55-19-3518-3197
otavio.cavalett@bioetanol.org.br

CONTINUOUS SEMI-SOLID STATE BIOREACTOR OPTIMIZATION THROUGH MODELING THE INTERNAL MULTIPHASE FLOW

Paulo Seleghim Júnior
São Carlos School of Engineering / University of São Paulo (USP)
FAPESP Process 2010/00442-5 | Term: May 2010 to Apr 2012

The increase in the use of biofuels raised new challenges to engineering problems. In this context, the optimization of chemical reactors, particularly bioreactors and photobioreactors, is crucial to improve the production of biofuels in a sustainable manner. This research work reports the development of an optimization method and its application to the design of a continuous flow bioreactor envisaged to be used in industrial fermentation processes. Mass and momentum conservation equations are simulated via CFD and specific a posteriori performance parameters, determined from the flow solution, are fed into a multiobjective evolutionary algorithm to obtain corrections to the parameters of the geometrical configuration of the reactor. This heuristics is iterated to obtain an optimized configuration vis-à-vis the flow aspects portrayed by the performance parameters, such as the shear stress and the residence time variations. An open source computer package (PyCFD-O) was developed to perform CFD simulations and the optimization processes automatically. First, it calls the preprocessor to generate the computational geometry and the mesh. Then it performs the simulation susing OpenFOAM, calculates the output parameters and iterates the procedure. ThePyCFD-O package has proved reliable and robust in attest case, a ~1m^3 continuous fermentation reactor. The multiobjective optimization procedure actually corresponds to search for the Pareto frontier in the solution space characterized by its geometric parameters and the associated performance parameters (dispersion of residence times and shear stresses). Optimal design configurations were obtained representing the best tradeoff between antagonistic objectives, i.e. the so-called non-dominant solutions.

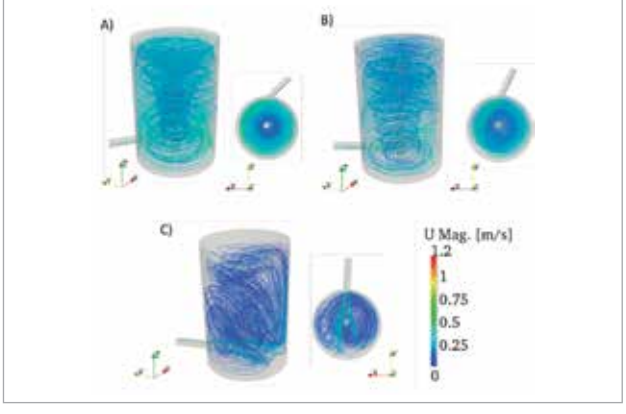

Figure 1. Example of the optimized geometries with streamlines for 3 individuals belonging to the non-dominated front: A) $\alpha = 43.5°$, $H_{out} = 1.15$ m; B) $\alpha = 62.7°$, $H_{out} = 1.28$ m; C) $\alpha = 87.3°$, $H_{out} = 1.28$ m

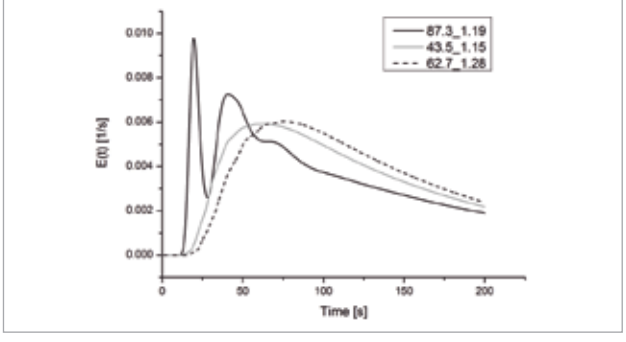

Figure 2. Example of reduction of the RTD dispersion during the optimization procedure

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Test cases were simulated using PyCFD-O package. The characteristic Pareto frontier associated with the problem was determined and the corresponding optimal configurations were identified. Performance was, thus, optimized with respect to minimum residence time distribution (RTD) and shear stress (SST). Results concerning the photobioreactor lead to the development of a new photobioreactor configuration which prevents performance degradation, permitting to upscale the geometry to thousands of cubic meters and more. This development resulted in two utility patents submitted to INPI, Brazil.

- Open source code (PyCFD-O) for optimal bioreactor design through CFD simulation and evolutionary multiobjective algorithms, as depicted below.

- Test case 1: optimization of a 1m3 continuous fermenter; optimal injection angle (α) and output pipe height (H_{out}) with respect to the residence time distribution and shear stress.

- Test case 2: optimization of a 1m3 airlift photobioreactor; optimal internal recirculation plate positioning with respect to the residence time distribution and shear stress.

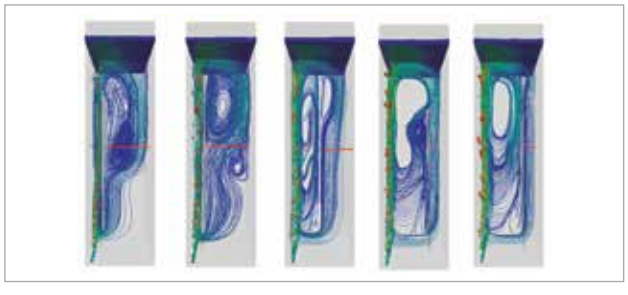

Figure 3. Influence of the horizontal position of the recirculation plate on the stream lines

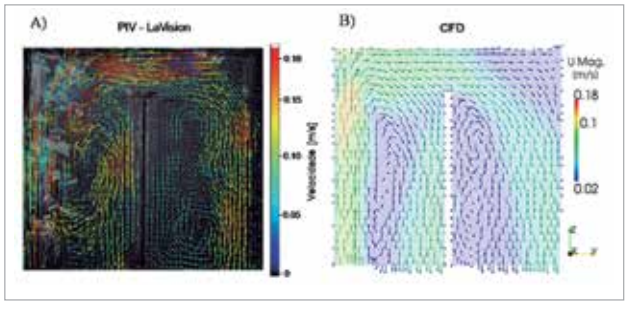

Figure 4. Detail of the flow field around the top of the recirculation plate for an optimal configuration

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Paulo Seleghim Júnior

Escola de Engenharia de São Carlos
Universidade de São Paulo (USP)
Departamento de Engenharia Mecânica
Av. Trabalhador Sãocarlense, 400
CEP 13566-590 – São Carlos, SP – Brasil

+55-16-3372-9416
seleghim@sc.usp.br

VAPOR LIQUID EQUILIBRIA AND LIQUID LIQUID EQUILIBRIA IN THE OIL/FAT AND BIODIESEL INDUSTRIES: EXPERIMENTAL DATA, MODELLING AND SIMULATION

Roberta Ceriani
Faculty of Chemical Engineering / University of Campinas
FAPESP Process 2013/12735-5 | Term: Oct 2013 to Sep 2015

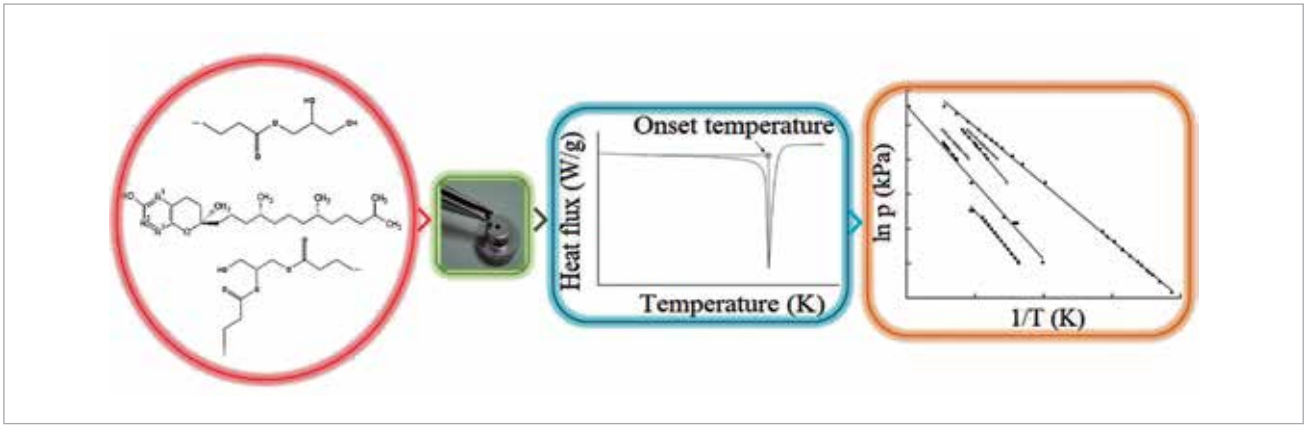

Figure 1. DSC tecnique applied for vapor pressure measurements. Toc graphic from article: Damaceno DS, Matricarde Falleiro RM, Krähenbühl MA, Meirelles AJA. 2014. Boiling Points of short-chain partial acylglycerols and tocopherols at low pressures by the differential scanning calorimetry technique. J. Chem.Eng. Data. **59**: *1515-1520*

Separation processes of the edible/oil and biodiesel involve multicomponent mixtures that consist of fatty acids, esters and alcohols, acylglycerols, glycerol, and also some minor compounds (nutraceuticals). In the case of edible oil/fat processing, the unit operations that are related to this project, include: steam stripping of fatty acids/odors for steam deacidification/ deodorization, with recovery of impurities as valuable side products, and solvent extraction as a new alternative for the deodorization process. In biodiesel production, the purification steps involve the separation of acylglycerols and glycerol from the methyl/ethyl esters. In these unit operations, some combination of phase equilibria between vapor-liquid and liquid-liquid phases takes place. Due to the inherent complexity of the mixtures involved, accurate and reliable predictive tools of phase equilibria and physical properties are very important for process design. With an increasing trend in the demand of edible oils/fats and biodiesel, correct prediction of the necessary properties (pure component and mixture) has become a concern. However, there is a lack of measured data in this research area that must be fulfilled in order to get suitable predictive models. The scope of this project can be divided as follows: Determination of novel vapor pressure data for partial acylglycerols by Differential Scanning Calorimetry; Determination of novel vapor liquid equilibrium data involving different classes of fatty compounds by Differential Scanning Calorimetry; Improvements in the Differential Scanning Calorimetry technique for the determination of vapor pressure and vapor liquid equilibrium data involving fatty compounds; Study of the viability of applying the solvent extraction process as an alternative for the deodorization step of edible oils. All experimental data will be used for testing and validating of modeling and simulation tools developed in the research group, and also for improving them when suitable.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The scope of this project is within vapor-liquid and liquid-liquid equilibria. In relation to vapor-liquid equilibria, the main efforts have been towards measurements of experimental data for physical properties and phase equilibria of pure fatty compounds and their mixtures using the Differential Scanning Calorimetry (DSC) technique, besides the improvement (optimization) of the technique itself. Up to data, novel boiling temperatures of pure short-chain mono- and diacylglycerols in the low-pressure range have been obtained, and these data were modeled using Antoine, Clapeyron and DIPPR equations. Also, the predictive group contribution equation of Ceriani et al. (2013) had its predictive capability checked by using these databank. DSC technique has been optimized for measuring vapor pressure of pure compounds in terms of its main variables, i.e., sample mass and heating rate. Further improvements will be achieved towards other variables that appear to be relevant in terms of accuracy of the DSC technique for measuring vapor-liquid equilibria of binary mixtures. Novel vapor-liquid equilibria have been obtained for mixtures involving vegetable oils by using other techniques. In relation to liquid-liquid equilibria, the work has focused in gathering experimental data for pseudoternary model systems composed by refined edible oil, odor compound and green solvent (ethyl lactate or ethanol). Odor compounds already investigated are aldehydes. Other classes of compounds will be evaluated. The main goal is to develop an alternative process for the industrial deodorization process used nowadays. Modelling and simulation tools applied in lipid technology have been updated and improved.

MAIN PUBLICATIONS

Belting PC, Gmehling J, Bölts R, Rarey J, Ceriani R, Chiavone-Filho O, Meirelles AJA. 2015. Measurement, correlation and prediction of isothermal vapor-liquid equilibria of different systems containing vegetable oils. *Fluid Phase Equilib.* **395**: 15-25.

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Roberta Ceriani

Faculdade de Engenharia Química
Universidade Estadual de Campinas (UNICAMP)
Rua Albert Einstein, 500 – Sala 226A
CEP 13083-852 – Campinas, SP – Brasil

+55-19-3521-3961
rceriani@feq.unicamp.br

PRODUCTION OF ETHANOL FROM BAGASSE SUGARCANE PRETREATED WITH OZONE: STUDY OF INHIBITORS, FERMENTATION AND INDUSTRIAL YEASTS

Roberto da Silva
Institute of Biosciences, Literature and Exact Sciences / São Paulo State University (UNESP)
FAPESP Process 2014/02080-4 | Term: Aug 2014 to Jul 2016

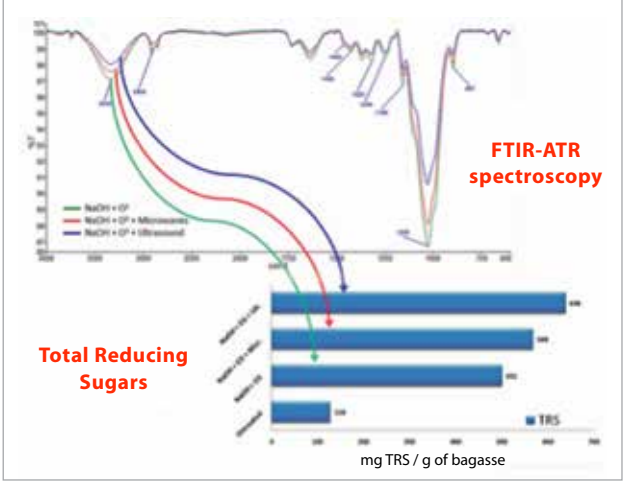

Figure 1. FTIR-ATR spectra of bagasse under ozone, microwave and ultrasound treatments and their respective reducing sugars released. (Perrone, 2015)

This project focuses on the bioenergy production from renewable raw materials. In Brazil, the hydrolysis of bagasse and straw from sugarcane, has been widely investigated by biochemical pathway toward bioethanol production. The goal of the research project is fully evaluate a second-generation ethanol production process, since the sugarcane bagasse until the ethanol obtained. To accomplish this the following steps are been taken: (1) pretreatment of bagasse using ozone for the delignification and increased permeability in the cellulose fiber; (2) enzymatic saccharification of biomass using commercial (or house made) enzymatic formulations; (3) fermentation using different industrial strains of the *Saccharomyces cerevisiae* (Cat1, Pedra2, JP1). After the execution of the fermentation step, it will be possible to close the whole process circle to the final product and, thus, information in integrated way of the three major steps required for the production of second generation ethanol.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

This project is a continuation of pretreatment and enzymatic hydrolysis studies that have been developed by our group. In previous work, it was developed a reactor for pretreatment with ozone (Travaini et al. 2013) it was found that this pretreatment generates minimal amounts of inhibitors that do not significantly interfere with the enzymatic saccharification. In this project, other pre-treatments such as acid, alkali, glycerol, microwave, ultrasound, associated or not with ozone, will also be evaluated (Perrone, 2015). Until now it was possible to isolate microorganisms producing cellulases with adequate characteristics for saccharification of biomass (De Cassia Pereira et al, 2014, 2015; Egea et al 2014; Moretti et al 2014). Also, we found that pretreatment using microwave shown significant effects for delignification of biomass (Moretti et al 2014; Diaz, et al 2015). In addition, further analysis will be made of the amount and types of inhibitors present after pretreatment. Also we will perform fermentation studies in the pretreated and saccharified material using commercial yeast strains used in ethanol plants, seeking to evaluate the whole process in an overview.

MAIN PUBLICATIONS

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Roberto da Silva

Instituto de Biociências, Letras e Ciências Exatas
de São José do Rio Preto – Univ. Estadual Paulista (Unesp)
Departamento de Química e Ciências Ambientais
Rua Cristóvão Colombo, 2265
CEP 15054-000 – São José do Rio Preto, SP – Brasil

+55-17-3221-2354
dasilva@ibilce.unesp.br

BIOPROCESS SYSTEMS ENGINEERING (BSE) APPLIED TO THE PRODUCTION OF BIOETHANOL FROM SUGARCANE BAGASSE

Roberto de Campos Giordano
Center for Exact Sciences and Technology / Federal University of São Carlos (UFSCar)
FAPESP Process 2008/56246-0 | Term: Jun 2009 to Oct 2013 | Thematic Project
co-PIs: Raquel de Lima Camargo Giordano, Antonio José Golçalves da Cruz

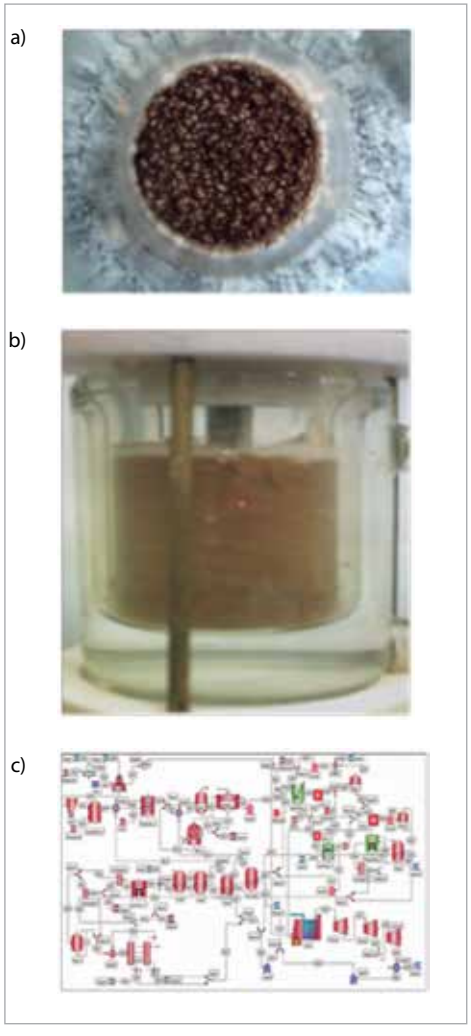


Figure 1. From micro scale to plant-wide optimization: (a) Cellulase-production fungus culture on bagasse substrate. (b) Lab scale bioreactor operating with immobilized pool of cellulolitic enzymes. (c) Biorefinery flowsheet: EMSO graphical user interface.

The consolidation of the industrial production of 2G bioethanol will depend on a combination of economical criteria, process robustness and compliance to environmental and sustainability restrictions. In this scenario the optimization of this complex, interconnected process ideally must be pursued ever since its early stages of development, aiming at costs reduction, negative overall CO_2 balance, cutback of water usage and of effluent emissions and so forth. Fine-tuned processes, operating at (near-) optimum conditions will have a significant competitive advantage.

This project focused on the rational application of (Bio-)Process Systems Engineering (BSE) techniques to the process for production of 2G bioethanol from an important lignocellulosic material in the Brazilian scenario, sugarcane bagasse (and leaves). In other words, the same approach that allowed oil refineries to achieve a high productivity is herein applied to biorefineries.

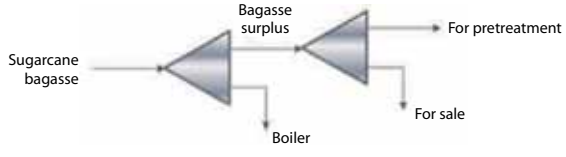
The validation of BSE tools for assessing different routes for bioethanol, however, must be based on real data. With this purpose, this project joined efforts of a group of researchers from the Chemical Engineering Department of UFSCar and from EMBRAPA. A biochemical route for production of ethanol from sugarcane bagasse was our selected case study, encompassing different technologies: *in-situ* production of cellulases in triphasic reactors; feedstock pre-treatment; intensification of the processing of the C5 fraction (from xylooligosaccharides to ethanol, within a nonconventional bioreactor); application of advanced control techniques for optimization of the C6 enzymatic hydrolysis reactor were some of the topics of the project.

A global view is necessary to integrate these processes from the early stage of development, including the analysis of their techno-economic feasibility. Particularly, the competition for the use of sugarcane bagasse and leaves, between bioelectricity (cogeneration) and 2G ethanol, was thoroughly addressed. The free software EMSO (http://vrtech.com.br/rps/emso.html) was the computational environment for the simulations.

Therefore, this project aimed simultaneously at providing the necessary software and at researching new feasible routes for bioethanol which, in addition to their intrinsic value, were employed for validation of the methodology.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

This project included the Laboratory for Development and Automation of Bioprocesses (LaDABio), the Laboratory of Enzymatic Process Engineering (LabEnz) and the Biochemical Engineering Group, all from the Department of Chemical Engineering of the Federal University of São Carlos (DEQ/UFSCar) and the Bioprocess Group of the EMBRAPA Agriculture Instrumentation unit, in São Carlos. Cooperation with other groups was also promoted, from Brazil: PEQ/COPPE/UFRJ, DEQ/UFRGS; and from abroad: Purdue University (USA), DTU and KU (Denmark), UMinho (Portugal), ICP-CSIC (Spain). The results are available through research papers, and one filed patent. With respect to transfer of technology for industry, this project induced a partnership of UFSCar with Petrobras (CENPES), which is presently supporting the continuation of the studies, using EMSO as the computational environment for simulation and optimization of a 1G-2G ethanol biorefinery.



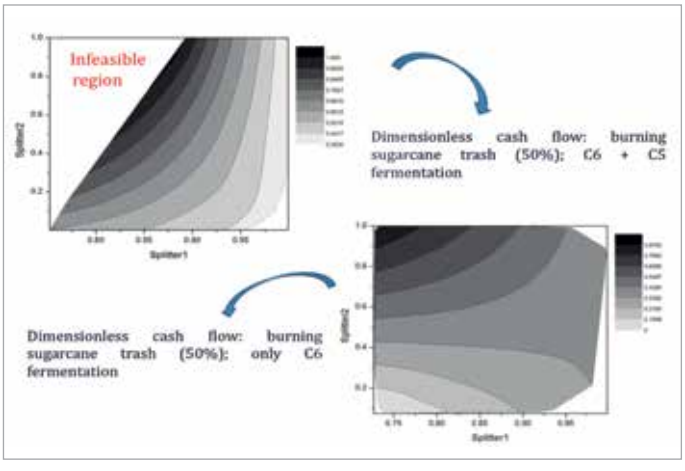


Figure 2. Furlan et al. Assessing the production of first and second generation bioethanol from sugarcane through the integration of global optimization and process detailed modeling. Computers & Chemical Engineering, 2012.

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Roberto de Campos Giordano

Universidade Federal de São Carlos (UFSCar)
Departamento de Engenharia Química
Via Washington Luis, km 235 – Monjolinho
Caixa Postal 676
CEP 13564-210 – São Carlos, SP – Brasil

+55-16-3351-8708
roberto@ufscar.br

HYBRID POLYMERS FOR NUTRIENTS RELEASE: PREPARATION, CHARACTERIZATION AND *IN SITU* EVALUATION OF NUTRIENTS RELEASE IN THE SOIL

Roselena Faez
Center for Agrarian Sciences / Federal University of São Carlos (UFSCar – campus Araras)
FAPESP Process 2014/06566-9 | Term: Oct 2014 to Sep 2016

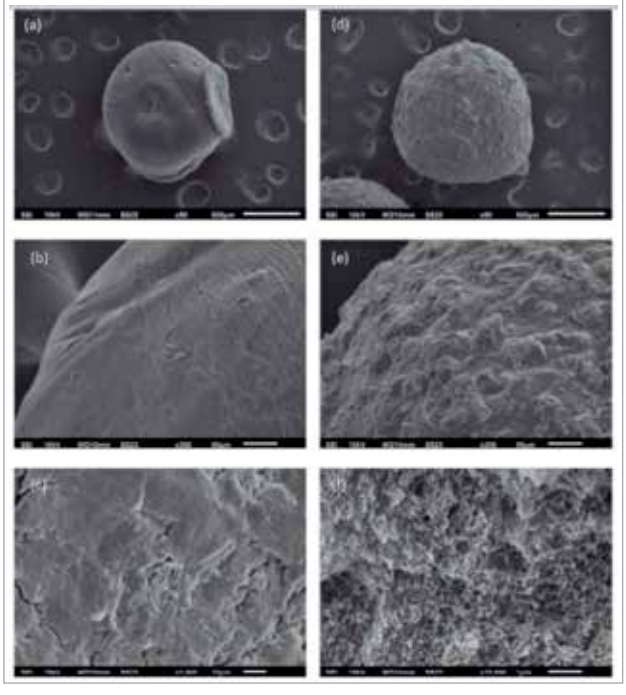

Figure 1. FEG-SEM images of (a-b) Ch and (d-e) ChMMt33 microspheres and (c) Ch and (d) ChMMt33 fracture region

The main goal of this project is the preparation, characterization and application of hybrid polymeric materials for nutrients release in soil and plant. The project comprises three main targets: 1) Preparation and characterization of hybrids polymeric materials as microspheres and with macronutrients (nitrogen and potassium), 2) Evaluation of the mechanism and kinetics of the release of the nutrient in the water, 3) Evaluation of the release in soil (laboratory and field) by TDR (time Domain Reflectometry) technique. The motivation is to prepare microspheres from natural materials (chitosan, montmorillonite clay and sugar cane bagasse) and nutrients. Also,the nutrients delivered in soil will be in situ evaluated by an electromagnetic technique which evaluates the ion motion in particulate systems such as soil. The increase of the fertilizer efficiency, reduction in soil toxicity and the decrease in adverse effects associated with overdosage are a few of advantages of the controlled release material. Chitosan is a natural biopolymer and has the ability to form films, fibers, gels and microspheres, responsible for its various applications. It is a multifunctional polymer containing amine groups (NH2) and hydroxyl (OH-) able to interact with different molecules and ions. The addition of layered silicates such as natural clays is a highly promising alternative to improve the mechanical properties and increase the sorption capacity of both water and chemical compounds. The sugar cane bagasse is a biomass with high water and chemicals sorption capacity and its mixture with chitosan can provides stiffness to the material to use it directly in the soil in a suitable proportions. It is noteworthy that the synergy of the properties of chitosan / clay materials and chitosan/ bagasse combines the properties of biopolymer and natural fillers for the sustainability of its use in soil as a function of the biodegradable properties of chitosan. Importantly, the use of TDR technique for monitoring the in situ release of the nutrient in the soil is innovative in the area of materials applied to agriculture and it is believed that it will provide quickly information about the effectiveness of the material in the soil and plant from short to long term.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Microspheres of chitosan and chitosan/clay composites prepared by inversion phase present the ability to deliver the fertilizer in the soil in a controlled and slow mode. The initial results show the perspective to modulate the material depending on the plant and soil. Additionally, the use of biopolymer and biomass guarantee the sustainability of the process in the role cycle, i.e., to prepare and to use the material. The biopolymer with biodegradability properties is an important factor since after the release of the fertilizer no residue must be in the soil. The first prepared material shows a rough and porous surface which provides better sorption of fertilizer, as demonstrate by the sorption-desorption results. Finally, TDR shows the profile of KNO_3 release and the relationship with the material structure could be described. The TDR technique used to determine the fertilizer release will be useful for determining the real profile of nutrient release in soil and help in the design of the best fertilizer delivery formulations. Spray dryer methodology is being now used to prepare microsphere and microcapsules and as perspectives we are evaluating this methodology in the release mechanism in the soil and plant system.

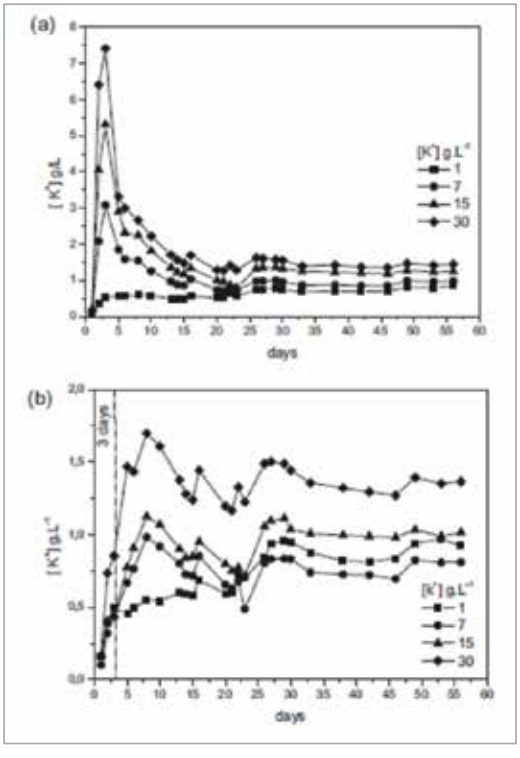

Figure 2. Determination of the potassium concentration release in the soil using TDR (a) central and (b) lateral probes

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Roselena Faez

Centro de Ciências Agrárias
Universidade Federal de São Carlos
Rod. Anhanguera, km 174
CEP 13600-940 – Araras, SP – Brasil

+55-19-3543-2946
faez@cca.ufscar.br

UNDERSTANDING THE EMULSION BEHAVIOUR OF FERMENTATION MIXTURES IN THE MICROBIAL PRODUCTION OF DIESEL AND JETFUEL-LIKE BIOFUELS

Rosiane Lopes da Cunha
Food Engineering Faculty / University of Campinas (UNICAMP)
FAPESP Process 2011/51707-1 | Term: Jul 2012 to Jun 2014

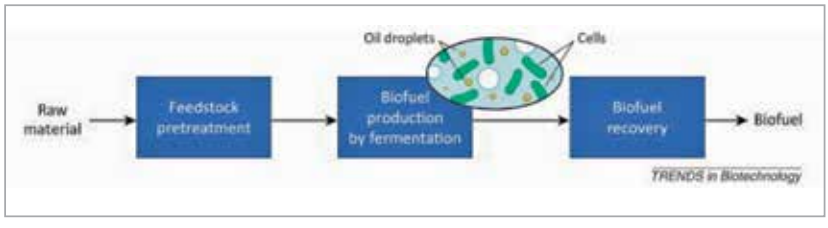

Figure 1. A simplified block diagram of the production of advanced biofuels

Within the many possible renewable energy resources, biofuels dominate the current market. Compared to the well-established alcohol biofuels (e.g. ethanol), the microbial extracellular production of diesel and jetfuel-like biofuels promises advantages in terms of product separation from the fermentation broth. However, the microbial production of diesel and jetfuel-like biofuels results in a four-phase (S-L-L-G) mixture in the reactor (microbial cells, aqueous medium, lipid product and fermentation gas), which shows emulsion characteristics. Although there have been studies on the emulsion behaviour of similar mixtures, little emphasis has been given to a systematic study of factors relevant for cost-efficient large scale operation. In this context, understanding the mechanisms behind emulsion formation is key for a rationale feedstock (and the pre-treatment associated to it) selection, for defining process (fermentation and product recovery) conditions and for identifying targets for synthetic biology of producing microorganisms (e.g. robustness at low pH, high salt concentration). Thus, this project aims at cooperation between two research groups able to contribute to the consolidation of processes for the large scale production of biofuels. The group of Delft University of Technology is expert in integrated bioprocesses, while the group at the University of Campinas has experience in emulsions and protein-based emulsifiers. As a result, it is expected to understand the mechanisms that lead to the formation of emulsion in the fermentation process to develop an efficient and cost-competitive integrated fermentation/recovery process, while at the same time preserving the microbial cell viability.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The project was divided into three steps in which the first one was the characterization of the process over time, determining the composition and properties of each phase obtained during the industrial process. Subsequently, a bottom-up study was performed with the building of model emulsions that showed increased complexity in order to understand the mechanisms involved in the emulsification process. Finally, a top-down study was proposed in which demulsification strategies were proposed.

In general, the evaluation of the stability mechanisms of model emulsions allowed understanding the phase behavior of these emulsions, as well as the interface thereof. Such information was used to evaluate the various strategies for demulsification aiming a greater separation of oil, making easier the downstream processes of biofuels production.

The strategies used in the demulsification process were based on the application of mechanical forces, changes in charge density of the droplets and reducing the viscosity of the dispersed phase.

Use of ultracentrifugation was the only process that caused total separation of the components of the cream phase. Temperature increase (up to 60 °C) could only partially recover the oil since viscosity decreasing was not enough to promote total phase separation. The use of alcohols caused a reduction of phases viscosity and greater affinity for the hydrophobic portion, leading to higher separation rates. However an additional step to recover the solvent would be required after the demulsification process. The use of salts, polymers, acids and bases was not efficient to destabilize the cream phase only by the action of gravitational forces. The combination of the strategies adopted with a later centrifugation step resulted in a more efficient separation.

The destabilization of the cream phase, almost entirely, it was possible through the use of magnetic nanoparticles by applying a magnetic field. This process is interesting because no additional steps of separation are needed.

Thus, it was possible to understand and evaluate the stability mechanism of the model emulsions, allowing study and examine various strategies demulsification aiming greater separation of oil.

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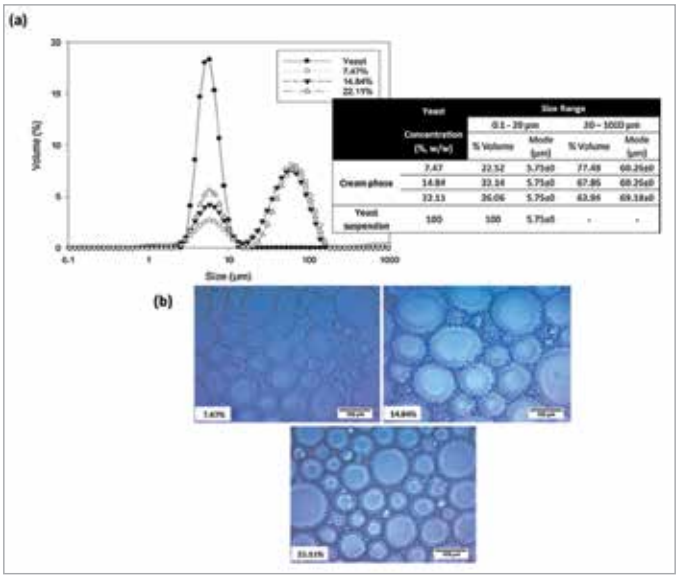

Figure 2. Particle size distribution by volume and particle size ranges (a) and micrographs (b) of the yeast suspension and cream phase of the emulsions prepared at varied yeast concentration (%, w/w)

Rosiane Lopes da Cunha

Faculdade de Engenharia de Alimentos
Universidade Estadual de Campinas - UNICAMP
Rua Monteiro Lobato 80
CEP 13083862 – Campinas, SP – Brasil

+55-19-3521-4047
rosiane@unicamp.br

AN INTEGRATED PROCESS FOR TOTAL BIOETHANOL PRODUCTION AND ZERO CO_2 EMISSION

Rubens Maciel Filho
Faculty of Chemical Engineering / University of Campinas (UNICAMP)
FAPESP Process 2008/57873-8 | Term: Jan 2010 to Sep 2014 | Thematic Project
co-PIs: Aline Carvalho da Costa, Carlos Eduardo Vaz Rossell, Dejanira de Franceschi de Angelis, Francisco Maugeri Filho, Maria Isabel Rodrigues, Maria Regina Wolf Maciel

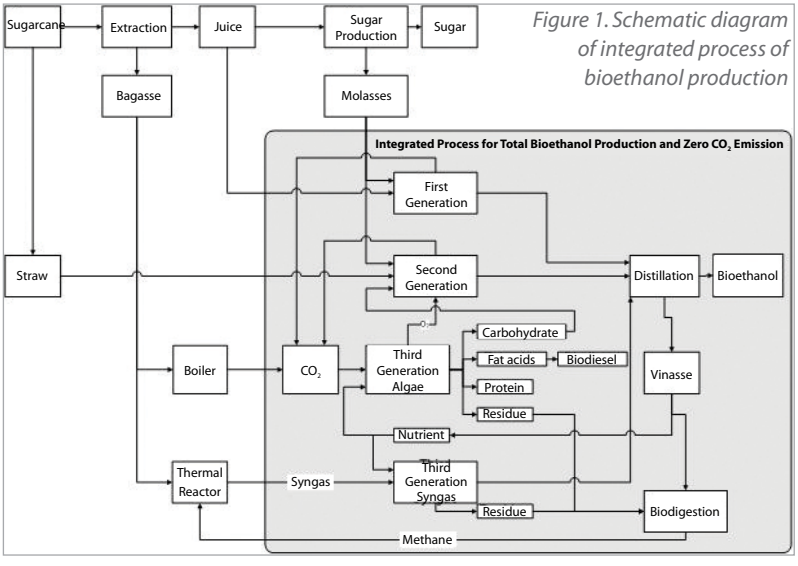

Figure 1. Schematic diagram of integrated process of bioethanol production

Increasing oil prices and global concern about climate change motivate the investigation of more efficient means of bioethanol production. An integrated process is proposed in this Thematic Project, aiming to maximize the productivity of bioethanol from sugarcane molasses, bagasse and straw, which give rise to, respectively, first and second generation bioethanol. The Greenhouse Gas carbon dioxide, produced in this two ethanol generations processes, is proposed to be used in the production of a third generation of ethanol, which comes both from algal/bagass biomass and catalytic transformation or biological fermentation of synthesis gas. This challenging integrated process has the major appeal of not emitting carbon dioxide and makes the best of the carbon-containing material for producing ethanol, turning it, when technically and economically feasible, a milestone for improving Brazilian bioethanol competitiveness.

The specific objectives of this project look for ways of turning this integrated process into a technically and economically feasible one, investigating new technologies for each part of processes, covering first, second and third generation aiming anhydrous low bioethanol production. In this way, it will be studied alternative fermentation processes (extractive units), eco-efficient pretreatments as a part of an integrated bioethanol from sugarcane bagasse and straw, development of high-performing enzyme formulations and process techniques of both enzymatic hydrolysis and fermentation, coupled with the development of suitable yeast to ferment sugarcane biomass carbohydrates. In addition, the possibility of microalgae consuming CO_2 from alcoholic fermentation, constituting energy generation cycle with environment protection and production of bioethanol through the synthesis gas, which is obtained from biomass will be investigated. Besides that, multiple effect operation of the distillation columns of the process will be studied in order to reduce steam consumption on reboilers and compared to alternative strategies, including the hybrid ones. The study of alternative entrainers (ionic liquids and hyperbranched polymers) for the extractive distillation process for anhydrous bioethanol production will be carried out. Process modeling and simulation, either of single units or for the large scale plant will be used as a tool for process evaluation and decision taking. Process optimization will be considered to extract the best yield of each routes so that quantitative discrimination will be possible. In any case, methodologies that may be necessary whenever a re-estimation of parameters is required and among other tools software sensors based on Artificial Neural Network will be developed to infer concentrations of biomass, bioethanol and substrate from secondary measurements, such as pH, turbidity and CO_2 flow rate. The global processes evaluation will make use of the experimental data collected in the experiments, industrial data and information and together with process simulation trough commercial simulators and tailor made softwares. All the routes will be evaluated in the optimal conditions achieved by a set of suitable optimization algorithms including the deterministic and stochastic based ones.

The project proposed concept

This research project aims a totally integrated bioethanol production process, in order to improve the productivity of existing ethanol generation (sugar cane molasse fermentation), the so-called First Generation Bioethanol, to develop suitable processes for improving the Second Generation Bioethanol (from biomasses) and to investigate the viability of the Third Generation Bioethanol, which is produced from algal/bagasse biomass or from catalytical or biological fermentation of synthesis gas. The Third Generation Bioethanol has a major appeal of consuming carbon dioxide produced in the First and Second Generation processes, causing the great impact of almost zero CO_2 emission within the whole integrated process. The improvement of the energy intensive processes that constitute the distillation units are also objective of study in the present project and the proposal of alternatives procedures will be evaluated, including the hybrid configurations. *Figure 1* depicts a schematic diagram of the integrated process for bioethanol production.

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Rubens Maciel Filho

Faculdade de Engenharia Química
Universidade Estadual de Campinas (UNICAMP)
Departamento de Desenvolvimento de Processos e Produtos
Av. Albert Einstein, 500 - Cidade Universitária Zeferino Vaz
CEP 13083-852 - Campinas, SP - Brasil

+55-19-3521-3958
maciel@feq.unicamp.br

BIOFUEL PRODUCTION BY PHOTOCHEMICAL CRACKING OF VEGETABLE OILS EMPLOYING AROMATIC IMIDES SUPPORTED ON MESOPOROUS SILICATES AS SENSITIZERS

Sergio Brochsztain
Center for Engineering, Modelling and Applied Social Sciences / Federal University of the ABC (UFABC)
FAPESP Process 2008/57940-7 | Term: May 2009 to Apr 2011

Catalytic cracking is a key reaction in the petrochemical industry, allowing the conversion of high molecular weight hydrocarbons into low molecular weight fuel. Up to the years 1930, the cracking reaction was performed by thermal methods, but since then, with the introduction of the zeolites, which are microporous heterogeneous catalysts, catalytic cracking has become the most widely used method. More recently, it has been recognized that catalytic cracking of vegetable oils could be used to obtain biofuel, as an alternative to the transesterification reaction. The use of photochemistry in cracking reactions, however, has remained largely unexplored. In the present proposal, the development of photochemical catalysis as a method for the cracking of vegetable oils will be pursued, using principles of nanotechnology to design nanostructured photocatalytic systems (*Figure 1*). For this goal, aromatic imides, such phthalimides, 1,8-naphthalimides, 1,4,5,8-naphthalenediimides and 3,4,9,10-perylenediimides, will be employed as photosensitizers. Our group has great expertise in the photochemistry of these compounds. When excited by light, these compounds generate a variety of free radicals, which are expected to stimulate the cracking reaction, which is a radical chain reaction. The imides will be immobilized by covalent grafting onto the surface of silicates MCM-41 and SBA-15 (*Figure 1*), which are mesoporous nanostructured materials synthesized in the presence of surfactant micelles. The modified particles will be irradiated with a UV lamp and with natural sun light, in the presence of different vegetable oils. Mesoporous materials with different loads of the organic dye will be tested, containing either a single imide or a mixture of different imides.

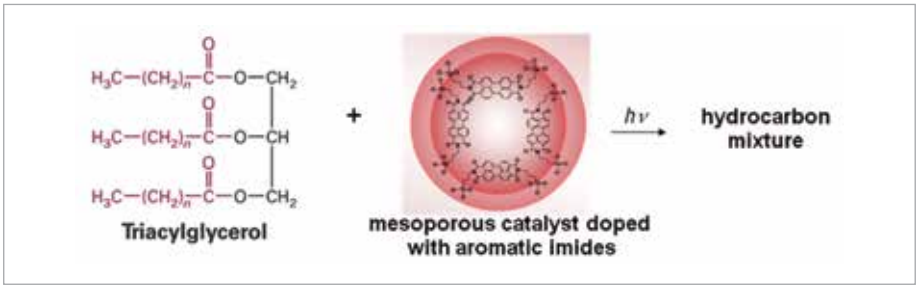

Figure 1. The concept of photochemical cracking of vegetable oils, showing a mesoporous catalyst with a perylenediimide sensitizer grafted into the inner pore walls

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The mesoporous heterogeneous catalysts doped with the photosensitizers were prepared by covalent grafting of the aromatic imides onto the walls of molecular sieves MCM-41 and SBA-15. Details of the synthesis and characterization of these materials are given in references 1-3. Cracking of a commercially available brand of soy oil in the presence of the new catalysts was first tested in the dark, in a thermogravimetric analyser (TGA) furnace, using 3 mg of soy oil and 0.1 mg of the mesoporous catalyst (*Figure 2A*). It can be observed that the soy oil, in the absence of catalyst, was cracked within the temperature range 400 - 500 ºC. In the presence of the catalysts, on the other hand, the thermal degradation range was decreased to 350 - 450 ºC, showing that the catalysts were active in the thermal cracking of the soy oil. In order to test the photochemical activity of the catalysts, however, it is necessary to drive the light beam inside the TGA oven. A system is being presently built that will allow irradiation of the samples inside the TGA oven.

Meanwhile, the performance of the heterogeneous photocatalysts under irradiation was evaluated using a standard system, namely the photodegradation of methylene blue (MB), a blue dye present in the effluents of the textile industry. When MB solutions were irradiated at room temperature with a 100 W Hg lamp (bandpass = 320 - 480 nm) in the presence of the heterogeneous photocatalysts, total mineralization of MB was observed after 5 h irradiation (*Figure 2B*). These results, which are presently submitted for publication, show the potential of the new catalysts in photodegradation reactions. The mesoporous catalysts were also effective in the photodegradation of asphaltenes isolated from petroleum.

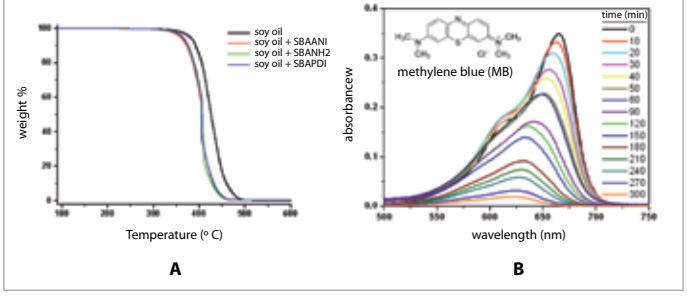

Figure 2. (A) Thermogravimetric analyses showing the cracking of soy oil in the presence and in the absence of the new catalysts. (B) Time-dependent absorption spectra for the irradiation of a MB solution in the presence of SBA-15 modified with 1,8-naphthalimide

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Sérgio Brochsztain

Centro de Engenharia, Modelagem
e Ciências Sociais Aplicadas
Universidade Federal do ABC (UFABC)
Av. dos Estados, 5001
CEP 09210-580 – Santo André, SP – Brasil

+55-11-4996-7940
sergio.brochsztain@ufabc.edu.br

AISE – THE SWEET AND BITTER SIDES OF THE SUGARCANE. AN INTEGRATED SUSTAINABILITY ASSESSMENT FOR THE BRAZILIAN ETHANOL CONTEXT

Tadeu Fabrício Malheiros
São Carlos School of Engineering / University of São Paulo (USP)
FAPESP Process 2008/58033-3 | Term: May 2009 to Apr 2012

Photo by Joviniano Pereira da Silva Netto

The recent global movement to encourage bioenergy as an alternative to excessive consumption of fossil fuels has triggered policy actions to promote the energy use generated from biomass in line with sustainable development. In this context, sustainability management modus operandi has to be able to bring the social, cultural, and environmental dimensions to the same priority level of the economic dimension. The current modus operandi of public policy formulation and implementation, based on punctual and setorized socio environmental impact assessment, limits and hides complex productive system functioning essential factors, as observed for the sugarcane ethanol context, enlarging ethanol production sustainability compromising risks. Therefore, with the Brazilian fast growing participation in the global economic scenario, it means that decision makers must be aware of the implications for the transition to an economy driven by biofuels. In this context, tools for evaluating sustainability of ethanol become a need in order to integrate values and principles of sustainable development. However, their effectiveness depends not only on building tools that allow the insertion and integration of large amounts of data. It is essential that the products generated are understood and accepted by the stakeholders, whether under the collective government, business or individual. It is fundamental that these tools have credibility among decision makers. In this context, this research focus at carrying out a strategic analysis of the socio-technical network of sugarcane ethanol for supporting the design, development and implementation of sustainability assessment tools, with a focus at the ethanol policy context at the State of São Paulo. Also efforts will put in developing and applying ISA - Integrated Sustainability Assessment frameworks for sugarcane ethanol context.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The main results of this ongoing applied research are: (i) sustainability assessment applied research network implemented; (ii) several case studies were conducted discussing Sustainability Assessment - SA applied to sugarcane ethanol context; concepts and methodology available for use by the governmental and nongovernmental institutions related to the bioenergy context and also for institutions engaged within the BIOEN Program; (iv) scientific events were organized; (v) courses at graduate level on sustainability assessment implemented; (vi) research team consolidation; (vii) several scientific papers are under analysis for publication in per-reviewed journals.

Figure 2. Research project developed with the engagement of the Brotas Municipality Environmental Council. The goal was to improve strategic planning process capacity through participatory scenario design for the ethanol context (Photo by Ana Paula Regra)

The concluded dissertations and thesis are:

- Environmental Management System and sugarcane ethanol production in São Paulo State: case studies in the municipalities of Araraquara and Brotas
- Instruments for government intervention and corporate environmental behavior: an analysis of the sugarcane industry in São Paulo State.
- Environmental indicators in the discussion of sustainability: a proposal for strategic analysis in the context of sugarcane ethanol in São Paulo – SP.
- Use of sugarcane biomass to generate electricity: energetic, exergetic and environmental analysis of cogeneration systems in sugarcane plants in the State of São Paulo
- Biofuel integrated production: a proposal for fossil fuel reduction in sugarcane ethanol life cycle
- Environmental Marketing and socio-environmental certifications: an analysis of Brazilian ethanol context
- Indicators System for Water Resources Sustainability Assessment in the context of sugarcane sector: methodological contribution for planning and management
- Analysis of environmental vulnerability in the planning space for growing sugarcane in the State of São Paulo

The ongoing dissertations and thesis research are

- Sustainability Assessment Methodologies: potentialities for applying to sugarcane ethanol context
- Environmental Cumulative Impacts of the ethanol production system
- Scenarios Design as tool for local environmental management systems- case study for Brotas, SP
- Sugarcane Ethanol Socio-technical Network Actors: a social-representations study on sustainability

Tadeu Fabrício Malheiros

Escola de Engenharia de São Carlos
Universidade de São Paulo (USP)
Departamento de Hidráulica e Saneamento
Av. São Carlense, 400 – Centro – Caixa Postal 359
CEP 13566-590 – São Carlos, SP – Brasil

+55-16-3373-9534
tmalheiros@usp.br

BIOREFINERY IN AGRICULTURAL AND FOOD INDUSTRY: RECYCLING WASTE FOR NEW CHEMICALS AND BIOHYDROGEN

Tânia Forster Carneiro
Faculty of Food Engineering / University of Campinas (UNICAMP)
FAPESP Process 2011/19817-1 | Term: Jun 2012 to May 2016 | Young Investigator

Figure 1

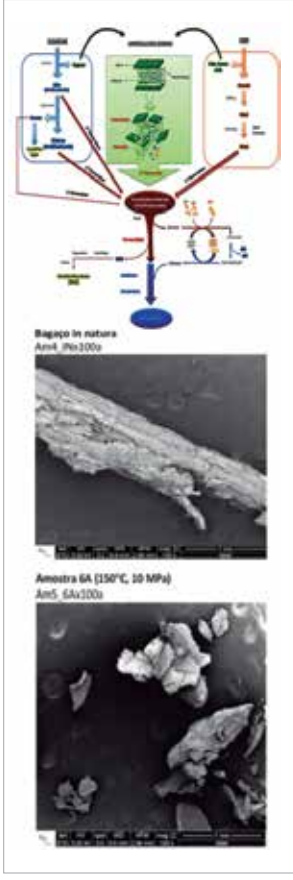

Figure 2

Figure 1. The operating diagram of the operational unit hydrolysis and gasification sub-supercritical water in detail hydrolysis reactor [from: Perez DL, Berni MD, Forster-Carneiro T, Meireles MAA. Pilot plant for residues of food industry in supercritical gasification process and hydrogen production. In: SLACA - Latin American Symposium of Food Science, 2013, CAMPINAS. Acta of Latin American Symposium of Food Science. Campinas: Galoá - Academic events, 2013. p. 1.]

Figure 2. Overview of the process for the production of 1st and 2nd generation bioethanol and images of scanning electron microscopy (FESEM) for samples of bagasse initial sugar cane and hydrolyzed with an average particle diameter with an increase of x100 micron scale bar [from: Rostagno MA, Prado JM, Mudhoo A, Santos DT, Forster Carneiro T, Meireles, MAA. Subcritical and supercritical technology for the production of second generation bioethanol. Critical Reviews in Biotechnology. *1-11, 2014].*

Waste recycling technologies to produce new products with energy recovery are emerging as an efficient and economically viable alternative with a great potential in terms of production and market value. Sub/supercritical hydrolysis and gasification are among these emerging technologies.
Recent research indicates that supercritical fluid technology is economically viable when compared with thermal gasification due to high solubility of the components of biomass in supercritical water generating a gas cleaner (no tar and pitch) and the highest concentration of bio-hydrogen. The challenge of this technology is the optimization of operating parameters involved in the process to maximize the effect of temperature and pressure. In this project, a new line of research is proposed to develop new products with high added value chemicals from the waste of food industry in the context of industrial units known as biomass biorefineries. This will be achieved by integrating two emerging technologies, hydrolysis and gasification with subcritical/supercritical water. Extensive tests with different operating parameters will be needed, as well as determination of gas composition and the performance of different wastes (soy, sugarcane, peanuts and tomatoes wastes). This project proposes the production of a clean gas with high bio-hydrogen concentration at lower temperatures (subcritical conditions, 200-374 °C) seeking the reduction of production costs of sub /supercritical gasification at large scale.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Biomass is an important renewable and sustainable source of energy. The rational utilization of biomass wastes is important not only for the prevention of environmental issues, but also for the effective utilization of natural resources. Reducing sugars obtained from sugarcane bagasse, as a waste biomass energy precursor, can be further transformed to fuel alcohol in a fermentation process. Subcritical water is an environmentally friendly solvent and attractive reaction medium. In this work, a subcritical water process was used for the hydrolysis of sugarcane bagasse with the aim of producing fermentable sugars. The present study evaluates the use of subcritical fluid technology, particularly subcritical water hydrolysis, to add value to residues from a sugarcane biorefinery that produces first and second generation ethanol. This paper is the first in a series examining the use of biomass as a fuel source via a two-step process consisting of hydrolysis (reactor 1) using subcritical water followed by gasification (reactor 2) in supercritical water. Hydrolysis in subcritical water performance was studied under semi-batch conditions in a 110 mL reactor (reactor 1). Hydrolysis was conducted for different sample loadings (3 and 5 g), flow-rates (9 and 12.5 mL/min), temperatures (100, 150, 200 and 250 °C) and pressures (2.5, 5, 10, 15 MPa). The experimental results show that the highest reducing sugar yields could be obtained at temperature above 200°C. Under these conditions, the reducing sugar yield reaches 13%. Scanning electron microscopy (FESEM) was used to analyze the sugarcane bagasse undergoing supercritical water hydrolysis and confirmed that high temperature (max 200-250 ºC) disrupts the cell walls, enhancing production of monosaccharides. Diffuse reflectance infrared spectroscopy (DRIFTS) was used to characterize the residual solids, with results consistent with the removal of hemicellulose during hydrolysis. In addition, further experiments were performed to study the conversion of other important organic waste (green coffee powder and coming green coffee residue of coffee oil extraction). The operating conditions were sub-critical temperature conditions (200-250 °C) and pressure (22.5 MPa). The study includes evaluating the physicochemical characterization of raw materials for moisture content, extractives, ash, carbohydrates and lignin in the standard method of the National Renewable Energy Laboratory. The liquid fraction or hydrolyzate was analyzed for total sugar content by a colorimetric technique. The experimental results show que the highest reducing sugar yields could be obtained at temperature above 150-175 °C. Finally, the results will compare the best production of hydrogen for each agri-food waste.

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Tânia Forster Carneiro

Faculdade de Engenharia de Alimentos
Universidade Estadual de Campinas (UNICAMP)
Rua Monteiro Lobato, 80
CEP 13083-862– Campinas, SP – Brasil

+55-19-3521-4041
taniafc@unicamp.br

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Grant applications s hould be presented to the FAPESP programs for Regular Projects Awards and Young Investigators Awards.
Applications for Regular Awards must be submitted by researchers from public or non-profit private higher education and research institutions in the State of São Paulo, Brazil.
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