BBEST Conference 2011 – Tutorials

Tutorial 5 – Biorefineries

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1. Biorefineries Concepts, raw material and Potentials, Biorefineries Technologies; Sugar and ethanol-based biorefineries

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This part of the tutorial will deal with Biorefineries covering in a broader perspective the main concepts, the raw materials, some applicable technologies and finally the biorefineries based on the sugar cane as raw material.

Nowadays there exist a large perspective and even incentive to obtain biofuels taking into several aspects including environmental concern, strategic safety and the relatively high costs of the available oil. A glance at the oil industry makes clear that not only the fuel (in the case of oil based fuel gasoline, diesel and kerosene) but rather several products such as chemicals and solvents add value to entire oil refining operation. If a parallel with the oil industry is considered a natural approach when biofuel is took into account is to use all the available material as feedstock to produce valuable products as chemicals and energy. This is in fact what already happens, in the bioethanol production from sugar cane, but it still may be improved in terms of a broader range of products.

According to the Biomass Research and Development Technical Advisory Committee (2002) of the U.S. Departments of Energy and Agriculture1 defines a biorefinery as:

“A processing and conversion facility that (1) efficiently separates its biomass raw material into individual components and (2) converts these components into marketplace products, including biofuels, bioelectricity, and conventional and new bioproducts.”

Basically, when lignocellulosic crops are considered is expected that after fractioned cellulose, hemicellulose, lignin, and other compounds are available to be converted in other products, whereas grains will generate starch, oils, proteins and fibers. Some crops already produce a fermentable sugar just after simple smashing, that is the case of sugar cane. Another possible via is to break plant into small building blocks as carbon monoxide (CO) and hydrogen (H2), from which the desired chemical products are synthesized through chemical routes. The concept of biorefinery is general and broad so that it may consist of some few units as paper or sugar mill which may generate bioelectricity by burning residues or may be very complex, having a large set of unit operation and conversion sectors making use of the available raw material. Depending upon the possible routes the biorefinery may potentially make use of a broader range of raw material as feedstock and generate a large set of products when compared to biofuel plants.

The success and viability of the biorefinery will depend of many factors and among them the extent of biomass availability at relative low price, the conversion process and its performance, including efficient use of the energy, and the value and marked of the products to be produced. Biomass availability may be region dependent and logistic will pay an important role. When biomass is a byproduct a much better scenario is foreseen.

Bearing all these in mind the sugar cane appears to be a quite suitable and competitive raw material to embrace the biorefinery concept. The first generation process, that means to produce bioethanol through the fermentation of glucose from the molasses originated from sugar cane smashing, is very well established running commercially for several years, producing bioethanol as biofuel, bioelectricity and sugar. The process is environmentally safe and approved with a very high productivity. Even so many improvements are expected to be placed in the first generation process and in fact there exist many possibilities, covering since fermentation as proposed by Rivera et al (2010a) and many possible advances in separation processes (Junqueira, 2010). In this scenario, processes based on second and third generation making use of sugar cane bagasse as feedstock appear to have significant advantage compared to other possible approaches. Dias et al (2011) shown how the second generation is fitted when bioelectricity is also a valuable product. As mentioned by Rivera et al (2010), bagasse, the by-product of bioethanol manufacture from sugarcane fermentation, is a very promising raw material for bioethanol production in the large scale process perspective. It is already available on the ethanol plant site, since it is produced in the mills where sugar is extracted from sugarcane, and better technologies of cogeneration are already being use in some units, showing a significant increase in surplus of bagasse at the plant site. Bioethanol and other products from sugarcane bagasse may share the infrastructure where conventional bioethanol is produced, such as fermentation and distillation units, which diminishes equipment costs. The product obtained after hydrolysis may be diluted in the sugarcane juice, thus decreasing the impacts of potential fermentation inhibitors, such as furfural and its derivatives formed during cellulose hydrolysis. Recent works by Mariano et all (2011a, 2011b) have shown the potential to produce biobutanol trough glucose fermentation and Lunelli et al. (2008, 2010, 2011) and Lasprilla et al (2011) have shown the potential for acrylic and lactic acid production, also, from molasses fermentation. These are some few examples of the sugar cane based biorefinery potential.

In this tutorial the biorefinery concepts and technologies will be presented and discussed. It is shown how a first generation plant is organized and how second and third generation may be coupled with the existing industrial facilities. The steps for second generation implementation will be depicted and especial concern for the pre-treatment methods will be given since they are fundamental for the hydrolysis and consequent fermentable sugar release. Alternatively, will be discussed the possibility to generate syngas from sugar cane bagasse and other possible residues (Peres, 2009), which may be used through chemical route for chemical production (Calais, 2010). The use of bioethanol as feedstock for chemicals is also addressed which enlarge the range of options for biorefinery establishment (Morais et al., 2011, Rho 1984).

The whole contents make in this tutorial allow to have a flavor of the potential of biorefineries that are not only contributing as possible alternative but rather as a potential tool to couple with environmental problems and possible draining of oils reserves or too high prices. A comprehensive list if references covering the several topics related to biorefineries will be provided.

Selected References

General Biorefinery Technologies and Concepts

APEC Bio-refinery Technology Review, 2009

www.biorefinery.nl/fileadmin/biorefinery/docs/Brochure_Totaal_definitief_HR_opt.pdf

Biorefineries- Industrial Processes and Products. Vol 1 and 2. Edited by Birgit Kamm, Patrick R. Gruber, Michael Kamm, Wiley-VCH, 2006

Specific Papers on Sugar Cane as raw material for Sugar, Bioethanol and Chemicals

Calais M. L. Master Science State University of Campinas, School of Chemical Engineering- 2011.

Dias, M.O.S. Master Science Dissertation. State University of Campinas, Campinas, SP, Brazil, 2008

Dias, M.O.S., Cunha, M.P., Jesus, C.D.F., Rocha, G.J.M., Pradella, J.C., Rossell, C.E.V., Filho, R.M., Bonomi, A., Second generation ethanol in Brazil: can it compete with electricity production?, Bioresource Technology, doi: 10.1016/j.biortech.2011.06.098, 2011

Elmer Ccopa Rivera, Daniel I.P. Atala, Francisco Maugeri Filho, Aline Carvalho da Costa, Rubens Maciel Filho. Development of real-time state estimators for reaction–separation processes: A continuous flash fermentation as a study case. Chemical Engineering and Processing 49,402–409, 2010.

Elmer Ccopa Rivera, Sarita Cândida Rabelo, Daniella dos Reis Garcia, Rubens Maciel Filho and Aline Carvalho da Costa. Enzymatic hydrolysis of sugarcane bagasse for bioethanol production: determining optimal enzyme loading using neural networks. J Chem Technol Biotechnol.(www.interscience.wiley.com) DOI 10.1002/jctb.2391, 2010.

Junqueira Lopes Tassia. Master Science Dissertation. School of Chemical Egineering- Stat University of Campinas, 2010.
LASPRILLA, A. J. R.; MARTINEZ, G. A. R. ; LUNELLI, B. H.; JARDINI, A. L.; MACIEL FILHO, R. Poly-lactic acid synthesis for application in biomedical devices — A review. *Biotechnology Advances*, DOI 10.1016/j.biotechadv.2011.06.019, 2011

LUNELLI, B. H.; MELO, D. N. C.; MORAIS, E. R.; VICTORINO, I. R. S.; VASCO DE TOLEDO, E. C.; WOLF MACIEL, M. R. MACIEL FILHO,R. Real-time optimization for lactic acid production from sucrose fermentation by Lactobacillus plantarum. *21st European Symposium on Computer Aided Process Engineering,Elsevier, v. 29, p. 1396-1400, 2011.

LUNELLI, B. H.; ANDRADE, R. R.; ATALA, D. I. P.; WOLF MACIEL, M. R; MAUGERI FILHO, F.; MACIEL FILHO, R. Production of Lactic Acid from Sucrose: Strain Selection, Fermentation, and Kinetic Modeling. Applied Biochemistry and Biotechnology, v. 161, p. 227-237, 2010.

LUNELLI, B. H.; RIVERA, E. C.; VASCO DE TOLEDO, E. C.; WOLF MACIEL, M. R.;
MACIEL FILHO, R. Analysis of kinetic and operational parameters in a structured model for acrylic acid production through experimental design.Applied Biochemistry and Biotechnology*, v. 148, p. 175-187, 2008.

MORAIS, Edvaldo Rodrigo de, LUNELLI, Betânia Hoss, JAIMEZ, Rubén R., VICTORINO, Igor Ricardo de Souza, WOLF MACIEL,Maria Regina, MACIEL FILHO, Rubens
Development of an Industrial Multitubular Fixed Bed Catalytic Reactor as CAPE-OPEN Unit Operation Model Applied to Ethene Production by Ethanol Dehydration Process. Chemical Engineering Transactions. , v.24, p.403 - 408, 2011.

Mariano AP, Keshtkar MJ, Atala, DIP, Maugeri Filho F, Wolf Maciel MR, Maciel Filho R. Energy requirements for butanol recovery using the flash fermentation technology. Energy & Fuels doi:10.1021/ef200279v,2011a

Mariano AP, Qureshi N, Maciel Filho R, Ezeji T. C. Bioproduction of butanol in bioreactors: New insights from simultaneous in situ butanol recovery to eliminate product toxicity. Biotechnology & Bioengineering, 108:1757-1765., 2011b

PERES. A. P.G. Master Science. State University of Campinas- Unicamp. School of Chemical Engineering-2009

RHO, S. B.; RYU, K. G.; LEE, W. K. Conversion of Ethanol to Ethylene Using a Gas-Phase Catalytic Reaction, Including the Effects of Cyclic Operation. *International Chemical Engineering*, 24, v. 3, p. 567-578. 1984.

2. The Biorenewables Opportunity – Towards Next Generation Process and Product Systems

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Different scenarios have been published recently which predict the depletion of fossil carbon resources for the production of fuels and chemicals in face of the increasing demand of a growing world population. Despite the uncertainty of such predictions, the switch from fossil to biorenewable carbon feedstock seems to be inevitable, if we aim at equilibrating global CO_2 binding and release to stop the increasing trend of the average surface temperature on our planet. This switch of feedstock provides a unique opportunity to redesign the value chain from raw materials to new molecular and functional products if we are willing to exploit the rich molecular structure of biomass to the extent possible.

Rather than breaking the molecular structure of the biomass into C_1 building blocks either by gasification to synthesis gas (CO and H_2) or by anaerobic fermentation to a methane-rich gas (CH_4, CO_2 and H_2), the synthesis power of nature should be preserved by refunctionalizing the existing molecular structures in biorenewable feedstock into new chemicals, materials and fuels. Such future products should differ from current products by their oxygen content. Current molecular products contain little oxygen because the processing effort to oxygenate fossil carbon feedstock is avoided if possible. In contrast, future bio-based products will contain higher oxygen content. Surplus oxygen has to be released in biorenewables processing. Reduction of the highly oxygenated raw material can be either reached by releasing CO_2 or H_2O. While the former reduces the carbon efficiency and contributes to the climate problem, the latter requires large amounts of hydrogen, which has to be produced sustainably, e.g. by means of solar water splitting.

Such future perspective calls for a radical change in chemical and biochemical catalysis, in the associated process technologies, and in the strategies towards novel molecular and functional products. The presentation will concentrate on evolving process systems engineering problems in this context. We will argue that a holistic systems approach orchestrating experimental and model-based methods and tools in a complementary manner offers an enormous potential for sustainable, first-time-right solutions.

In particular, we will touch in the first part of the tutorial on the whole value chain from raw materials to target products in a future bioeconomy from the perspective of process systems engineering. In particular, we look at the production of carefully selected or even specifically tailored raw materials, on novel methods for biomass pretreatment based on green solvents, on the design of novel reaction pathways to promising candidate fuels, on processes, equipment and supply chains, as well as on an integration of process design with product design. These research issues will be put into the context of both, a large collaborative research project aiming at the development of 3rd generation biofuels, and the strategic reorientation of chemical engineering research at RWTH Aachen University.

In the second part of the tutorial, a more detailed exposition will be given for selected areas emphasizing our current research interest in the field.

First, recent results on the pretreatment of woody biomass with ionic liquids and subsequent fractionation into major biomass constituents will be presented. In particular, we will look at the mechanisms of disintegration and dissolution kinetics of wood in the presence of ionic liquids. Major emphasis is on the mesoscopic phenomena which can be observed by high resolution measurement devices. It is shown that swelling, disintegration and dissolution processes are executed in a sequence of steps. Such understanding is a prerequisite for the design of sophisticated production processes using wood as a starting material.

The design of sustainable processes producing next-generation chemicals and fuels from biorenewable resources constitutes a complex systems problem. The decisions to be taken include the selection of feedstock, the decision on target products which satisfy the functional requirements of an application, suitable reactions pathways linking the starting materials with the target products and most economical process designs for the individual catalytic transformations.

To this end we will present a novel methodology for the screening of promising reaction pathways to a list of candidate bio-based products. This methodology aims at an assessment of the major process performance characteristics of the complete value chain in the very early phases of the design.

This methodology assumes that the target products are known. However, this is not the case if we hypothesize that future bio-based products will be of a different molecular nature than fossile-based products. In particular, these products will be richer in oxygene but still fulfil the requirements of an application. This perspective leads to model-based product design problems which aim at identifying molecular structures which fulfil certain requirements of an application. A very prominent example is a biofuel which has to fulfil a full set of thermodynamic and combustion kinetic properties. We present recent work on model-based fuel design using targeted QSPR and related approaches. We will show how this product design problem can be linked with the reaction pathway design problem. Obviously, the choice of a certain molecular structure should not only be guided by the functional requirements of the product but also the effort of its production. This combined process and product design problem will be formulated and solved. First results will be presented to demonstrate the validity of the concept.

Last but not least, novel processes need to be designed for all the steps in future bio-based value chains. These processes have to meet sustainability requirements in general, but also have to be competitive now to facilitate the migration from value chains based on fossil carbon to those using biorenewables. We will present a generic process synthesis framework which involves the creation of alternative process structures, their evaluation by means of thermodynamically sound short-cut methods and rigorous mixed-integer optimization. Various examples in the context of biofuels production will be presented.

Selected References

Perspective and review papers

W. Marquardt, A. Harwardt, M. Hechinger, K. Krämer, J. Viell, A. Voll: The biorenewables opportunity - towards next generation process and product systems. AIChE Journal, 2010, 56(9), 2228-2235

S. Fayyaz, P. Frenzel, M. Köster, B. Kollmeier, J. McIntyre, K. Meier, M. Müller, J. Schmidt, P. Schmidt, I. Somoza, N. Weber, T. Weinert, J. Ayesterán, N. Kopriwa, A. Pfennig: Wie können wir zukünftig ausreichend Energie nachhaltig bereitstellen?. Chemie in Labor und Biotechnik, 2009, 60, 32-39

A. Corma, S. Iborra, A. Velty: Chemical Routes for the Transformation of Biomass into Chemicals. Chem Rev, 2007, 107, 2411-2502

J. Sanders, E. Scott, R. Weusthuis, H. Mooibroek: Bio-refinery as the bio-inspired process to bulk chemicals. Macromolecular Bioscience, 2007, 7, 105-117

M. Poliakoff, P. Licence: Green chemistry. Nature, 2007, 450, 810-812

T. Wimmer: Tailor-Made Fuels from Biomass – Excellence RWTH Aachen University establishes a Fuel Design Center. NatureJobs, 2007, 502-502

G. Huber, S. Iborra, A. Corma: Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysis, and Engineering. Chem Rev, 2006, 106, 4044-4098

B. Kamm, P. Gruber, M. Kamm: Biorefineries - Industrial Processes and Products. Vol. 1 and 2. Weinheim, Germany: Wiley-VCH, 2005.

Novel biomass pretreatment and depolymerization processes

J. Viell, W. Marquardt: Disintegration and dissolution kinetics of wood chips in ionic liquids. Holzforschung, 2011, 65(4), 519-525

R. Rinaldi: Instantaneous dissolution of cellulose in organic electrolyte solutions. Chemical Communications, 2011, "Emerging Investigators"

R. Rinaldi, P. Engel, J. Büchs, A. Spieß, F. Schüth: An integrated catalytic approach to fermentable sugars from cellulose. ChemSusChem, 2010, 3(10), 1151-1153

G. Jäger, H. Wulfhorst, E. Zeithammel, E. Elinidou, A. Spieß, J. Büchs: Screening of cellulases for biofuel production: Online monitoring of the enzymatic hydrolysis of insoluble cellulose using high-throughput scattered light detection. Biotechnology Journal, 2011, 6(1), 74-85

P. Engel, R. Mladenov, H. Wulfhorst, G. Jäger, A. Spieß: Point by Point Analysis: How Ionic liquids effect the enzymatic hydrolysis of native and modified cellulose. Green Chemistry, 2010, 12, 1959–1966

Model-based process synthesis for biorenewables processing

A. Harwardt, K. Krämer, B. Rüngeler, W. Marquardt: Conceptual Design of a Butyl-levulinate Reactive Distillation Process by Incremental Refinement. Chinese Journal of Chemical Engineering, 2011, 19(3), 371-379

K. Krämer, A. Harwardt, R. Bronneberg, W. Marquardt: Separation of butanol from acetone-butanol-ethanol fermentation by a hybrid extraction-distillation process. Computers & Chemical Engineering, 2011, 35, 949-963

Frank Lipnitzki: Membrane process opportunities and challenges in the bioethanol industry, Desalination, 2010, 1067-1069

A. Bardow, K. Steur, J. Gross: A Continuous targeting approach for integrated solvent and process design based on molecular thermodynamic models, Ind. Eng. Chem. Res., 2009, 49, 2834.

F. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner: Selective and flexible transformation of biomass-derived platform chemicals by a multifunctional catalytic system. Angewandte Chemie International Edition, 2010, 49(32), 5510-5514

Y. Román-Leshkov, C. Barrett, Z. Liu, J. Dumesic: Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. Nature, 2007, 447, 982-986

A. Voll, W. Marquardt: Reaction Network Flux Analysis: Optimization-based evaluation of reaction pathways for biorenewables processing. Accepted for: AIChE Journal

A. Voll, W. Marquardt: Multi-objective screening of biorefining processes in the early design stage by reaction network flux analysis. ECOS 2011, Novi Sad, Serbien, 04.-07.07.2011

Fuel Design

M. Hechinger, M. Dahmen, W. Marquardt: Towards a Rigorous Heat Loss Model of a Rapid Compression Machine for the Screening of Auto-Ignition Properties of Biofuels. In: ECOS 2011, Novi Sad, Serbia, 04-07.07.2011

M. Hechinger, A. Voll, W. Marquardt: Towards an integrated design of biofuels and their production pathways. Computers and Chemical Engineering, 2010, 34, 1909-1918

M. Hechinger, W. Marquardt: Targeted QSPR for the prediction of the laminar burning velocity of biofuels. Computers and Chemical Engineering, 2010, 34, 1507-1514

O. Kahrs, N. Brauner, G. Cholakov, R. Stateva, W. Marquardt, M. Shacham: Analysis and refinement of the targeted QSPR method. Computers & Chemical Engineering, 2008, 32, 1397-1410

F. Eljack, M. Eden, V. Kazantzi, X, Qin, M. El-Halwagi: Simultaneous Process and Molecular Design – A Property Based Approach, AIChE J., 2007, 53, 1232

M. Shacham, N. Brauner, G. Cholakov, R. Stateva: Property Prediction by Correlations Based on Similarity of Molecular Structures, AIChE J., 2004, 50, 2481

R. Gani, L. Achenie, V. Venkatsubramanian: Introduction to CAMD. In Computer Aided Molecular Design: Theory and Practice. Elsevier, Amsterdam, 2003

M. Karelson, V. Lobanov, A. Katritzky: Quantum-Chemical Descriptors in QSAR/QSPR Studies, Chemical Reviews, 1996, 96, 1027