4-CIAB

Proceedings of the 4th IBEROAMERICAN CONGRESS ON BIOREFINERIES

UNIVERSIDAD DE JAÉN
JAÉN (SPAIN)
24 TO 26 OCTOBER 2018

CO-ORGANIZED BY

Centre for Advanced Studies in Energy and Environment (CEAEMA), Universidad de Jaén
Iberoamerican Society for the Development of Biorefineries (SIADEB)
Spanish Network on Sustainable Biorefineries

Universidad de Jaén

COLECCIÓN actas

2018

ISBN
978-84-9159-144-3

Depósito Legal
J-617-2018

COLECCIÓN
Actas, 48

Edita
Publicaciones de la Universidad de Jaén
Vicerrectorado de Proyección de la Cultura y Deportes
Campus Las Lagunillas, Edificio Biblioteca
23071 Jaén (España)
Teléfono 953 212 355
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Plenary and keynote talks

Gregg Beckham
National Renewable Energy Laboratory, USA

Catalytic valorization of lignin in the biorefinery

Lignin valorization is critical to the economic viability of lignocellulosic biorefineries. Most lignin depolymerization and upgrading approaches today yield a highly heterogeneous slate of reaction products, making downstream separations and valorization challenging when attempting to produce chemicals where purity is often a key cost driver. Reductive Catalytic Fractionation (RCF) has recently emerged as an exciting and potentially viable approach to selectively solubilize lignin from whole biomass and cleave aryl-ether linkages to produce a narrow slate of aromatic monomers along with C-C linked dimers and oligomers.

This talk will highlight recent progress in transitioning the RCF process to flow-through systems and discuss scientific and engineering challenges and opportunities to develop a holistic, integrated process to valorize both lignin and polysaccharides starting with RCF as the initial step.

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Recent Advances on the Surface Functionalisation of Cellulose Fibres: Fundamentals, Techniques of Characterisation and Concrete Applications

SUMMARY

The present lecture is focused on the recent advances on surface chemical modification of polysaccharides. It will be divided into four parts:

1. The first part will be devoted to the basic consideration on surface phenomena with a special care about the difficulties associated with surface contamination, the surface energy characterization, the surface properties determinations, etc.

2. The second part will be focused on the relevant characterization techniques, including classical low-resolution ones and more efficient tools such as: X-ray photoelectron (XPS) and more recently Time of Flight Secondary Ion Mass Spectrometry (ToF SIMS). This presentation assesses the merits and the drawbacks of these techniques [1, 2].

3. The third part points out the interest in using polysaccharides (cellulose mainly starch) in several functional materials. These two raw materials could be subjected to several surface modification strategies, namely (i) physical treatments (ii) chemical grafting by direct condensation, “grafting from” and “grafting onto” approaches [1, 2]. In this context, recent works investigating green solvent-based or solvent-less systems will be reported [3, 4].

4. All these treatments aim at providing these substrates specific functions, such as hydrophobic character, anti-microbial properties, etc. [5, 6]. Typical examples of achievements in this field will be given and discussed.

Finally, some relevant concluding remarks and perspectives will be given.

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Status on Biorefineries Development for Bioenergy and Biofuels in World – a review of conversion technologies and flagship plants

Emerging new biofuels obtained from sustainable biomass either from biochemical-based pathways or thermochemical-based pathways are at advanced stage of development and new investments in Europe will be boosted by the new legislative EU framework for the next decade after the agreement on the next Renewable Energy Sources Directive to be implemented from 2021 to 2030 (1).

Both thermochemical and biochemical conversion routes will be deployed in the coming decade to produce biofuels directly such as ethanol, methanol and FT-diesel. Cellulosic ethanol flagships plants are a reality despite some setbacks. Other biochemical conversion technologies focused on higher alcohols (e.g., iso-butanol, n-butanol) and hydrocarbons (e.g., isobutene, farnesene) are paving their own road to commercialization. Also, thermochemically produced intermediates, bio-oils, will be produced by processes such as e.g. pyrolysis and, particularly for high-moisture content feedstocks, hydrothermal liquefaction. Such intermediates will predominantly be upgraded to drop-in biofuels by refinery-like processes, either as an integrated biofuel value chain or as a co-feed to a fossil refinery value chain.
Key innovations on bioenergy for the next 10-years are expected to occur both by evolution of technologies now being demonstrated or piloted and by development of new technologies that will in some years possibly also reach such a stage.
The main cost drivers in biofuel and bioenergy conversion systems are the feedstock cost and the capital related cost, while the main benefit is the GHG reduction. Since, overall, biomass resources are limited, optimization calls for allowing the use of a variety of feedstocks including low cost, low quality materials in cost-efficient plants. This becomes a trade-off between the cost of the installation and the biomass conversion efficiency together with the greenhouse-gas emissions.

But, in this context one should also acknowledge that there are also other and wider benefits such as and creating income for all the stakeholders of the entire value chain from field or forest to ready-for-use fuels.

Reference

Waldheim, L. & Gírio, F. (2018) Bioenergy and biofuels – innovation and technology progress. BE-Sustainable, issue 9. Published on May 13.
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Energy cane, second-generation technology and public policies: the three main axes for the bioeconomy establishment.

Containing the effects of anthropogenic climate change is one of the greatest challenges faced by society in all fields. Most countries have committed through global agreements to mitigate the greenhouse gases emissions (mainly CO_2), but fossil fuel consumption, mainly in the energy and transportation sectors, keeps increasing. Under such an alarming scenario, the major challenge is assuring energy supply for current and future generations while transitioning to less cleaner alternatives, that is, the establishment of bioeconomy, an economy based on renewable resources. Biofuels produced from vegetal biomass, a fully renewable resource, besides establishing a cyclical process for energy production can also result in the net capture of CO_2 from the atmosphere.

From vegetal biomass transformation, it is possible to develop entire value chains of high complexity. However, one of the critical processes in the transition from fossil to biofuels is increasing the production of vegetal biomass in an economical and sustainable way, besides augmenting the process of transforming the carbon chains into fuels and compounds usable for energy production. Therefore, in this talk, I will explore the science and technology that permeates the biofuels chain. In particular, I will address the productivity potential of sugarcane varieties, with a focus on the energy cane; the state of the art of the second-generation ethanol production; and the Brazilian National Biofuels Policy, the Renovabio, a program that provides incentives for the production of biofuels and for the development of new technologies, including those aimed at capturing and storing CO_2 from the atmosphere.

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Electric field-based technologies for valorization of bioresources

Renewable Energy Directive (2009/28/EC) has targeted for the EU to have 20% of its final energy consumption provided by renewable sources by 2020. Moreover, legislation establishes that biofuels must be produced by environmentally friendly processes. In this context, biorefinery development is considered an appropriated strategy for the suitable use of renewable sources. The biorefinery is based on the raw materials processing for bio-based products, chemicals, and fuels manufacturing as an alternative to the petroleum refinery.

Lignocellulosic biomass, the most abundant source of biomass, is composed of three major components namely cellulose, hemicellulose and lignin. However, several other sources of biomass and in particular agro-food and forestry wastes and surplus are key elements on the development of biorefineries. They represent a rich supply of valuable nutrients and functional biomolecules bringing together the potential needed to be used as raw material for the development of new food products, and being thus kept within the food supply chain for human nutrition, or to be incorporated in other value chains such as cosmetics, pharmaceuticals or bioplastics. This is of particular relevance as it is estimated that, in 2012, 12.5 % of the global population was undernourished this demanding for a rational use of land, energy, chemicals/fertilizers and water. Therefore, food security, climate changes, health, energy and sustainability issues jumped into the last decades' political agenda and public consciousness.

Although processing of the biomass has been receiving a great deal of attention in particular due to the interest on the production of 2nd generation biofuels, there are several issues that need to be optimized, in particular the development of more efficient technologies for their fractionation. This becomes more relevant as the use of agro-food and forestry wastes is considered. The high number of added value compounds existing in these materials, in some cases in low concentrations, demands the development and implementation of fractionation strategies that will allow for an efficient valorization of the available biomass. The successful re-utilization of these streams and extractable biomolecules will always require a judicious intervention of strategies and processing technologies for safety and functional enhancement. Moreover the fractionation strategies to be developed must be "green" and environmental friendly as well as economically feasible.

The achievement of the goals established for the development of a circular economy and a biorefinery demands not only the rethinking of existing production methods and strategies, but the development of new approaches and technological solutions is also a fundamental requirement.

Among the novel and emergent bioprocess technologies, electro-technologies, which are based on the application of electric current in biomaterials with technological purposes have been receiving an increasing interest.

The application of an EF on a biological or bio-based system will result on dissipation of heat, since the system will act as a semi-conductor. Often designated as Ohmic Heating (OH), this is explained by the Joule effect and provides a fast and homogeneous heating rate along with high energetic efficiencies. Other consequence of the EF presence is electroporation, as the exposure of cells to an external EF results on the formation of a transmembrane potential. Some advantages have been recognized on the use of electrotechnologies for bioresources valorization as they may promote stabilization of the biomaterials, endorse or enhance extraction and diffusion of compounds, assist in separation and fractioning, among others.

The application of an EF is classified according to type of electric flow (i.e. direct or alternating current), application in pulses or not, electric field strength (voltage applied by the section length), extension of heat deposition, among others. High voltage electrical discharges (HVED), Pulsed electric field (PEF) and Moderate electric fields (MEF), also known as Ohmic heating (OH) are the EF based technologies being currently developed for the fractionation of the biomass/extraction of bioactive compounds.

In the last years, MEF and the corresponding ohmic heating (OH) have been gaining an increasing interest for extraction processes. OH presents high heating rates with a precise temperature control allowing mild processing and preserving nutritional, functional and structural properties. Heat is generated inside the material to be heated (Joule effect), the heating process does not depend on heat transfer between phases and interfaces, allowing uniform heating and an extremely rapid heating rate. Furthermore, it also allows heating of large particulates and fluids at comparable rates, as long as their conductivities remain similar. Moreover, the process has high energy conversion efficiencies resulting in lower operational costs and in a more environmentally-friendly system.

Results describing application of OH on the extraction of bioactive compounds will be presented and challenges and perspectives on the future of the application of OH will be discussed aiming at the development of more sustainable biorefineries.

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Challenges in biomass pyrolysis and catalytic bio-oil upgrading for the production of advanced biofuels

Biomass pyrolysis is an attractive route for the production of biofuels and/or chemicals. It is particularly interesting when applied to lignocellulosic materials due to their high availability. Moreover, pyrolysis of biomass residues, such as those generated by agriculture and forestry activities, presents the advantage of removing wastes by their transformation into valuable products with commercial applications.

Biomass pyrolysis is a relatively simple process that takes place under inert conditions and usually at atmospheric pressure, leading to the formation of several fractions: gases, liquid (bio-oil) and a solid called char or bio-char. In recent years, a great research effort has been focused in the bio-oil fraction as it offers the possibility of producing liquid biofuels that could be used in the transportation sector. When bio-oil is the target product, the optimum conditions for biomass pyrolysis involve operating at intermediate temperatures (in the range 500 – 600 ºC) and high heating rates (fast pyrolysis) [1]. Depending on the reactor type, operation conditions and the properties of the raw biomass, bio-oil can be produced with relatively high yields, typically in the range 30 -70 wt% (Figure 1).

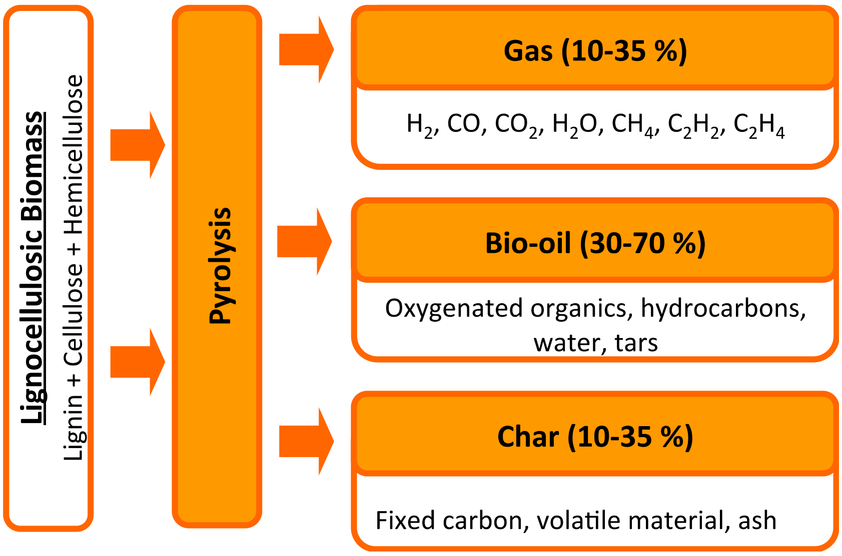

Figure 1. Product fractions obtained in biomass pyrolysis.

The bio-oil is a very complex mixture of oxygenated organic compounds, including carboxylic acids, alcohols, aldehydes, ketones, sugars, furans, guaiacols, syringols, phenolics, etc (Figure 2). Moreover, the bio-oil usually contains a significant amount of water and fine char particles. The water presence provokes that bio-oil is often separated into two phases: aqueous-rich and organic-rich ones. As a consequence of its complex composition, bio-oil presents a number of non-desired properties: high oxygen content (about 40 – 45 wt%), acid pH, low heating value, high viscosity and limited stability upon storage [2]. These properties are very different compared to those of the fossil fuels currently employed in the transportation sector. Therefore, the direct use of bio-oil as fuel is currently limited to just few applications.

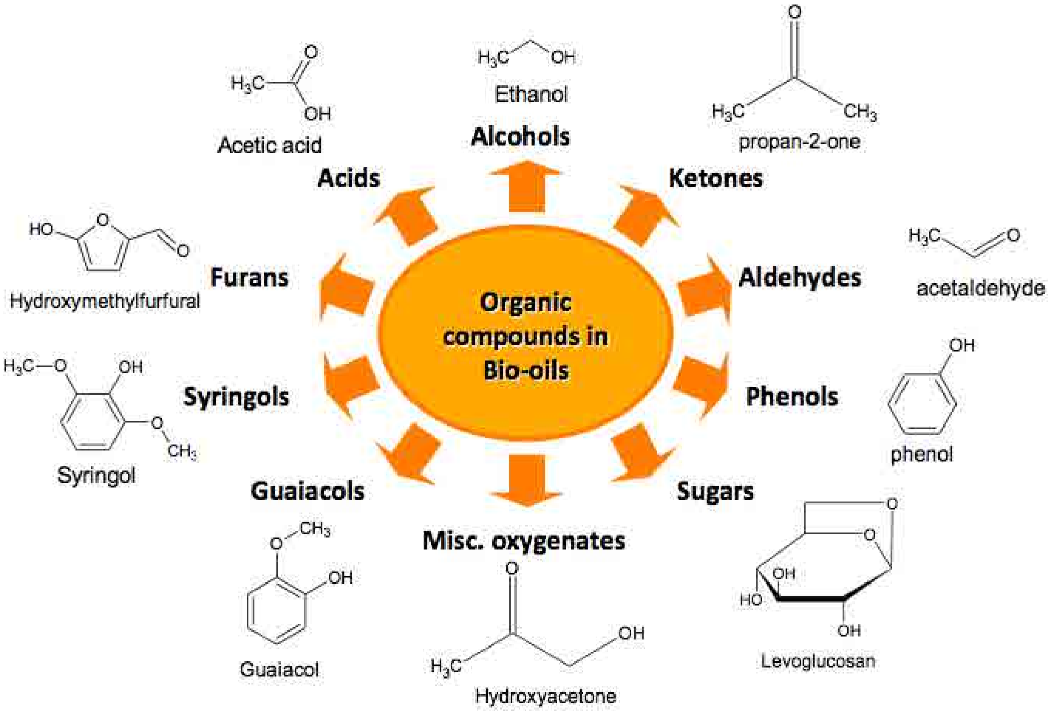

Figure 2. Types of organic compounds present in pyrolysis bio-oil.

During the last two decades, a high interest has emerged in the development of processes and treatments for bio-oil upgrading into advanced biofuels, being produced from non-edible biomass resources and possessing composition and properties very similar to those of the fossil-derived fuels. One of the major targets in these bio-oil upgrading strategies is to reduce in a large extent the oxygen content of the bio-oil while keeping as high as possible its mass and energy yield in respect to the raw biomass. These processes are based in most cases in catalytic transformations, such as catalytic pyrolysis and hydrodeoxygenation (Figure 3).

Catalytic pyrolysis proceeds by contacting the pyrolysis vapours with a catalyst prior to its condensation, which allows obtaining bio-oils with higher heating values, improved stability and lower corrosiveness [3,4]. The catalyst promotes the reduction of the oxygen content and the removal of acids, anhydrosugars and other reactive organic compounds. Deoxygenation of the bio-oil takes place by a complex combination of reactions, which in a simplified way can be classified into decarboxylation, decarbonylation and dehydration as they lead to the formation of CO_2, CO and H_2O, respectively. In this process, the bio-oil yield is strongly reduced in favour of the production of more gases and the deposition of coke over the catalyst. The latter represents an important limitation since, in addition to the loss of bio-oil, it provokes a fast deactivation of the catalyst. Zeolites have shown very promising properties as acid catalysts for bio-oil upgrading through catalytic pyrolysis. Thus, relatively high yields into aromatic hydrocarbons have been achieved over different zeolitic structures, mainly when using ZSM-5 based catalysts. Moreover, as it has been recently reported, adjusting the zeolite acidity is an essential factor to get an efficient bio-oil deoxygenation pathway [5].